

Room-temperature chlorination of As-rich GaAs (110)

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As-rich GaAs (110) is prepared by ion bombardment and annealing, followed by chlorination and reannealing. The surface is then reacted at room temperature with Cl₂ gas and examined with soft x-ray photoelectron spectroscopy of the Ga and As 3*d* core levels. After low exposures ($<5 \times 10^4$ L), the surface appears to passivate with half a monolayer of Cl adsorbed, primarily as AsCl. Following sufficiently large ($>5 \times 10^4$ L) exposures, however, the surface begins to etch, as indicated by the continuous uptake of chlorine and the formation of As and Ga chlorides. After the largest exposures, the distribution of As chlorides still favors the monochloride, whereas the Ga chlorides favor GaCl₂. It is proposed that the heavily reacted surface is covered with –AsCl–GaCl₂ treelike structures. The addition of Cl to form GaCl₃ from GaCl₂ is identified as the rate-limiting step in the overall etching reaction. © 1996 American Vacuum Society.

I. INTRODUCTION

It is becoming increasingly important to understand the basic mechanisms involved in the chemical etching of semiconductor wafers as processing technology is applied to III–V substrates. The interactions of Cl₂ with GaAs are particularly significant, since chlorine is the primary chemical etchant involved in GaAs device fabrication. The study of Cl₂/GaAs reactions is complicated somewhat by the fact that many GaAs surface stoichiometries are stable and that the composition and crystallinity of the starting surface affect the path of the reaction.^{1,2}

For example, in the room-temperature reaction of Cl₂ with GaAs(110), there is a competition between passivation and etching, as well as between Ga–Cl and As–Cl bonding. Under certain conditions, GaAs(110) is observed to passivate against further reaction with Cl₂ at room temperature, presumably via the formation of an AsCl overlayer.² To explain this result, surface order was suggested to be the controlling factor in determining whether or not passivation occurs. On the other hand, soft x-ray photoelectron spectroscopy (SXPS) studies of the room-temperature reaction of Cl₂ with cleaved GaAs (110), which is highly crystalline, observed both Ga and As chloride formation accompanied by continuous chlorine uptake, which is suggestive of etching.^{3–5} Moreover, scanning tunneling microscopy (STM)⁶ and high-resolution electron energy loss studies (HREELS)⁷ of the etching reaction showed that there is a preference, at least initially, for Ga–Cl bonding over As–Cl bonding.

A possible means of reconciling these apparently contra-

dictory results lies in the sample preparation technique used in each study. In Refs. 3 and 5–7, clean starting surfaces were prepared by cleavage in vacuum, whereas in Ref. 4 they were prepared by ion bombardment and annealing (IBA). In contrast, GaAs(110) wafers were prepared in Ref. 2 by IBA followed by exposure to Cl₂ and reannealing to ~535 °C, which likely produced a starting surface different than those in Refs. 3–7.

In this investigation, it is shown that cleaning GaAs(110) with Cl₂ in this manner produces an As-rich surface. The subsequent room-temperature reaction of Cl₂ with such an As-rich surface is then followed with core-level SXPS. At low exposures, the reaction appears to passivate with a half-monolayer (ML) of AsCl formed, as reported in Ref. 2. After sufficiently large Cl₂ exposures, however, further reaction does occur, generating AsCl and GaCl₂ as the primary surface products.

II. EXPERIMENTAL PROCEDURE

The SXPS measurements were performed in a multichamber ultrahigh vacuum (UHV) system on beamline UV-8a at the National Synchrotron Light Source. Spectra were collected using a 3 m toroidal grating monochromator and an angle-integrating ellipsoidal mirror analyzer (EMA). Ga 3*d* and As 3*d* spectra were collected with photon energies of 57 and 79 eV, respectively, to generate core-level photoelectrons with kinetic energies of ~35 eV, which maximizes the surface sensitivity of the measurements. The combined resolution of the analyzer and monochromator at these photon energies is better than 150 meV.

Prior to being placed in the UHV system, GaAs(110) wafers (*n* type, Si doped, 10^{17} cm⁻³) were chemically etched in a dilute solution of HNO₃/H₂O₂/H₂O, rinsed in isopropyl al-

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cohol, and then dried with N_2 gas. The samples were degassed in UHV, then ion bombarded with 500 eV Ar^+ ions and annealed to $\sim 550^\circ C$ in order to remove any remaining oxides. As a final step, the wafers were exposed to a small (<100 L) dose of Cl_2 and reannealed to $\sim 550^\circ C$ for ~ 10 min (note: 1 L=1 Langmuir= 10^{-6} Torr s). Exposure to Cl_2 gas was carried out in a separate UHV dosing chamber (base pressure= 8×10^{-10} Torr). Following chlorination, the sample was transferred to the spectrometer chamber (base pressure= 2×10^{-10} Torr) for measurement. The sample remained in UHV throughout the cleaning, dosing, transferring, and measuring procedures.

III. RESULTS

The Ga and As 3d core-level spectra were numerically fit, via the method outlined in Ref. 4, to a sum of spin-orbit split, Gaussian-broadened Lorentzian line shapes. A Lorentzian width of 0.15 eV was used, as were spin-orbit splittings and branching ratios of 0.45 eV and 0.65 for Ga 3d and 0.68 eV and 0.65 for As 3d, respectively. In addition to the signal arising from atoms in the bulk, the spectra collected from the clean surface have contributions from surface Ga and As atoms, which are in a tricoordinate geometry, and therefore have different core-level binding energies (BEs) than the bulk atoms. The magnitude and direction of shifts obtained for these surface-shifted core levels (SSCLs) are identical to those previously reported for cleaved GaAs.³

Examples of spectra from the reacted surfaces are shown in Figs. 1 and 2, which contain As 3d and Ga 3d spectra collected after exposures of 1.5×10^3 L and 1.2×10^6 L of Cl_2 . In both figures, the filled circles are the background-subtracted raw data, dashed lines are the individual contributions to the spectra from each chemical species, and the solid line is the sum of all these contributions. Except for the low-BE Ga peak, each spectral component is labeled by the chemical species with which it is associated.

In addition to the signal originating from bulk atoms, the spectra collected from the reacted surfaces have several other core-level components, which have been identified previously. The As 3d spectra contain features shifted ~ 0.45 and ~ 1.2 eV higher in BE than the bulk component, which are identified as arising from AsCl and AsCl₂, respectively.^{1,3-5,8} Additional Ga 3d components are also observed, shifted ~ 0.9 and ~ 1.7 eV higher in BE than the bulk component, and are identified as due to GaCl and GaCl₂, respectively.^{1,3-5}

There are also contributions in the spectra from tricoordinate Ga and As atoms, which have been observed previously in the reactions of Cl_2 and XeF_2 with GaAs.^{3,9-11} The production of subsurface tricoordinate Ga and As atoms has been shown to be a consequence of the etching reaction. Because of the valences of Ga and As, tricoordinate configurations are reasonably stable. Ga, with three valence electrons, prefers a tricoordinate bonding geometry, while As, with five valence electrons, has a stable lone pair of electrons remaining when the other three are involved in bonding.

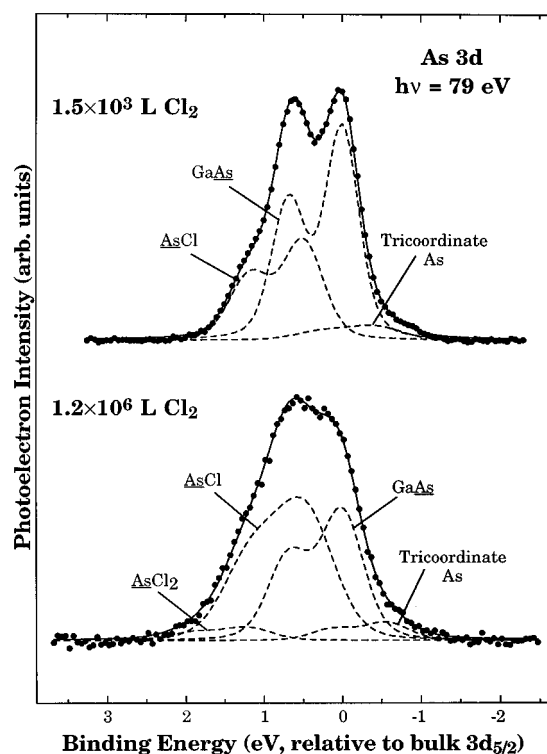


FIG. 1. High-resolution SXPS spectra of the As 3d core level collected from GaAs(110) exposed at room temperature to (a) 1.5×10^3 L of Cl_2 and (b) 1.2×10^6 L of Cl_2 . Dots are the background-subtracted raw data. The dashed lines are the individual fit components. The solid line is the sum of the fit components.

Finally, for Cl_2 exposures above $\sim 5 \times 10^4$ L, an additional component shifted 0.5–0.6 eV lower in BE than the bulk component is present in the Ga 3d spectra (see Fig. 2). A similar shift, 0.5–0.6 eV to lower BE, is observed for Ga surface atoms on clean GaAs(001)- 4×6 , which persists with chlorination.¹ It is therefore proposed that this low-BE shift is due to Ga–Ga bonds and that Ga dimers, or possibly some other type of Ga cluster, may be responsible for this shift. The persistence of the low-BE shifted component with increasing chlorination may indicate that Ga atoms in such a configuration are reasonably inert to further reaction.

A simple calculation based on the areas of the core-level components provides a quantitative estimate of the coverage of each chemical species present on the surface following reaction. The coverage of each species is simply proportional to its relative contribution to the total core-level intensity, if attenuation within the overlayer and chemically induced variations in the photoionization cross sections are neglected. The proportionality constant is determined straightforwardly by comparing intensity ratios of the reacted surfaces to those of a surface with known composition. This is done by assuming that the ratio of the SSCL area to the total core-level area, in a spectrum collected with the same photon energy from a cleaved GaAs(110) surface, represents the signal from 0.5 ML of surface atoms. Coverages estimated in this manner, using the core-level intensities reported in Ref. 3 for cleaved GaAs(110), are given in Fig. 3.¹² The amount of Cl adsorbed

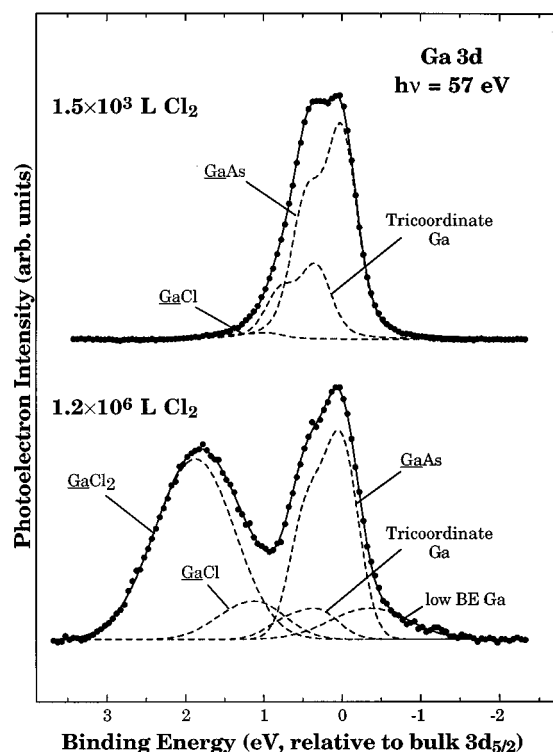


FIG. 2. High-resolution SXPS spectra of the Ga 3d core level collected from GaAs(110) exposed at room temperature to (a) 1.5×10^3 L of Cl_2 and (b) 1.2×10^6 L of Cl_2 . Dots are the background-subtracted raw data. The dashed lines are the individual fit components. The solid line is the sum of the fit components.

on the surface is found by summing the coverages of each of the Ga and As chlorides, appropriately weighted by the number of Cl atoms, and is given in Fig. 4.

IV. DISCUSSION

The starting surface, which was cleaned by Cl_2 adsorption and annealing, is slightly As-rich. This is apparent from the coverage estimates, described above, which indicate that there is ~ 0.65 ML of surface-shifted As and only ~ 0.35 ML of surface-shifted Ga on the clean surface. These data are shown at the left side of the top panel of Fig. 3 by the two points labeled "SSCL." The atoms that contribute to the SSCL components are all exposed at the surface, as their total coverage is not more than ~ 1 ML. Experimentally, it has been shown that up to 1 ML of As can be grown on GaAs(110), and that the excess As is stable on the surface for temperatures below ~ 575 K.¹³ The structure of As-rich GaAs(110) is unknown, but a theoretical investigation suggests that the excess As atoms form chains, bonding to both Ga and As atoms below.¹⁴ Presumably, the Cl_2 adsorption and annealing procedure generates an As-rich surface via the preferential formation and removal of Ga chlorides. Note that, in other systems, halogen adsorption followed by annealing also produces a group-V terminated surface via the preferential removal of group-III halides.^{15–20}

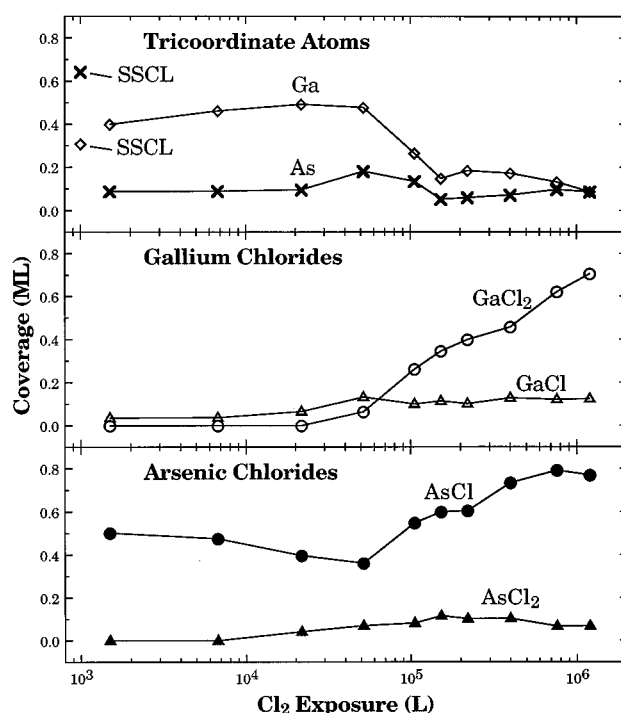


FIG. 3. Coverage of each surface species, in monolayers (ML), as a function of Cl_2 exposure.

From Figs. 3 and 4, it is seen that this As-rich surface is remarkably resistant to chlorine attack. That is, once ~ 0.5 ML of Cl is adsorbed (primarily as AsCl), there is minimal Cl uptake over an order-of-magnitude increase in Cl_2 exposure. As previously noted, this apparent passivation to chlorine attack is not observed for cleaved GaAs(110),^{3,5} nor for sputtered and annealed GaAs(110),⁴ but it is seen for sputtered and annealed GaAs(110) wafers that are further cleaned by exposure to Cl_2 and reannealing.² Since the cleaved surfaces, which are highly crystalline, show no sign of passivation, surface order does not appear to be the only factor

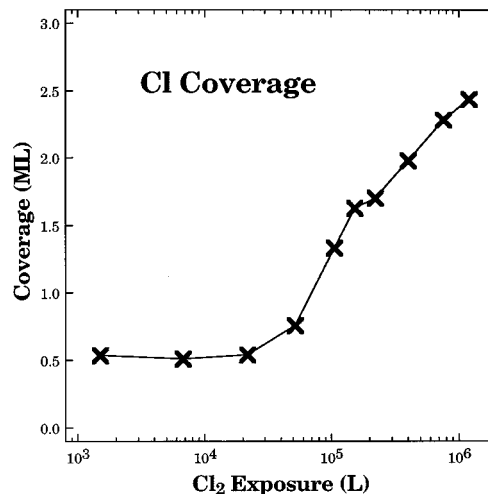


FIG. 4. Cl coverage, in monolayers (ML), as a function of Cl_2 exposure.

governing whether or not the surface passivates. Instead, it is suggested that excess surface As is also involved in impeding the reaction. How this occurs is unclear, however, especially since the surface is not entirely covered with As, but has only ~ 0.15 ML of excess As. A possibility is that As migrates to defects, thereby impeding the dissociation of Cl_2 by tying up the active sites.

It is unexpected for the principal chloride on the passivated surface to be AsCl, since photoemission^{3,5} and STM⁶ studies indicate that there is a clear preference for Ga-Cl bonding in the initial stages of the reaction on GaAs(110). It is possible that differences in the atomic structure or the morphology of As-rich GaAs(110), as compared to cleaved GaAs(110), are responsible for altering the distribution of surface reaction products. STM measurements of As-rich GaAs(110), both before and after reaction with Cl_2 , would be of great use for understanding this unexpected result.

This apparently passive surface is not absolutely unreactive, however, since the reaction does continue providing that the Cl_2 exposure is sufficiently large. That is, for exposures greater than $\sim 5 \times 10^4$ L, the amount of AsCl increases noticeably and a measurable amount of GaCl_2 forms. The chlorine uptake also begins to increase at this point (see Fig. 4), signaling the onset of etching. Once etching has begun, the Cl coverage increases linearly with the logarithm of the Cl_2 exposure, as is observed for the chlorination of GaAs(001).¹ This linear dependence of the coverage on the logarithm of the exposure implies that the sticking coefficient decays exponentially with coverage, i.e., $S(\Theta) = a \exp(-b\Theta)$. Thus, although excess surface As does slow the reaction significantly, once this As is removed the etching reaction continues normally.

By carrying out the reaction at a sufficiently low temperature, in this case room temperature, the lifetimes of the reaction intermediates are sufficiently long that a determination of the rate-limiting step can be made. It is seen from Fig. 3 that, following the largest Cl_2 exposures, the principal As surface reaction product continues to be AsCl, whereas GaCl_2 is the primary Ga product. The Cl_2/GaAs reaction occurs in a stepwise fashion,^{1,3} with the primary volatile etch products at or near room temperature being AsCl_3 and GaCl_3 .^{21,22} Because the crystal structure of GaAs constrains the availability of reaction sites, the etching reaction cannot be simply divided into discrete decoupled pathways. Hence, a build-up of AsCl and GaCl_2 on the surface suggests that the rate-limiting step in the overall etching reaction is either



or



The rate of one of these steps probably limits the other, which then results in the simultaneous build-up of both GaCl_2 and AsCl.

After the highest Cl_2 exposures, the coverages of AsCl and GaCl_2 are nearly identical (see Fig. 3). A likely reason for there being equal amounts of AsCl and GaCl_2 on the surface, and for the stability of one of them to limit the

removal of the other, is that they form a common moiety. If such an assumption is made, then the simplest and most reasonable arrangement having AsCl and GaCl_2 bound together, and to the surface, is $-\text{AsCl}-\text{GaCl}_2$. In this moiety, the Ga and As atoms are bound to each other, while the Ga atom is also bonded to two Cl atoms and the As atom is bonded to a single Cl atom and to the surface. This structure has three requisite properties: (1) it consists of an equal number of AsCl and a GaCl_2 moieties; (2) it can bind to the surface, in this case through the As atom; and (3) both Ga and As are tricoordinately bonded, which they prefer in the absence of a crystal field. Any other possible arrangement does not satisfy these criteria. In this configuration, it must be the terminal- GaCl_2 group that is the more stable of the two species, i.e., the one that limits the reaction rate. Otherwise, it would quickly form GaCl_3 and desorb. Furthermore, due to its stability, the terminal- GaCl_2 group prevents further chlorination of the AsCl moiety by tying up an otherwise available reaction site. Thus, it appears that the rate-limiting step in the reaction is that given by Eq. (1).

Note that the formation of an $-\text{AsCl}-\text{GaCl}_2$ structure in the Cl_2 etching of GaAs is analogous to the generation of fluorosilyl trees (e.g., $-\text{SiF}-\text{SiF}_3$ and $-\text{SiF}_2-\text{SiF}_3$) in the XeF_2/Si etching reaction.²³ An interesting experiment, which could confirm the existence of such a structure, would be to study heavily chlorinated GaAs(110) with molecular beam scattering or secondary ion mass spectrometry, and to look for desorbing species that contain both Ga and As atoms.

The Cl_2 exposure at which significant chlorine uptake begins on As-rich GaAs(110) ($\sim 5 \times 10^4$ L) is uncommonly large compared to the exposures that cause appreciable reaction on other GaAs surfaces.^{1,3-5} In addition, prior to the onset of reaction, the AsCl coverage dips slightly and the AsCl_2 and GaCl coverages begin to rise (see Fig. 3). The gradual transformation of the surface product distribution away from AsCl, combined with the very large exposures needed to produce appreciable reaction, suggests that the reaction nucleates at defects on an otherwise unreactive AsCl-stabilized surface. Thus, barring such defects, an AsCl-covered surface would be inert to further reaction.

V. SUMMARY

In summary, As-rich GaAs(110) was exposed at room temperature to large doses of Cl_2 and examined with SXPS. Following the initial Cl_2 exposures, the surface appears to passivate with half a monolayer of AsCl formed, in a manner similar to that observed previously.² The reaction continues, however, following much larger Cl_2 exposures, with both As and Ga chlorides formed on the surface. For the most heavily reacted surfaces, the distribution of chlorides favors AsCl and GaCl_2 . It is concluded that the chlorination of GaCl_2 to form GaCl_3 is the rate-limiting step in the reaction, and that GaCl_2 stabilizes AsCl on the surface, possibly through the formation of a treelike $-\text{AsCl}-\text{GaCl}_2$ structure.

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