Role of surface stoichiometry in the Cl$_2$/GaAs(001) reaction

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The room-temperature reaction of Cl$_2$ with GaAs(001)-4×6, -$c(2\times8)$, and -$c(4\times4)$ surfaces is studied with synchrotron soft x-ray photoelectron spectroscopy. The chemical composition of the reacted surfaces is found to depend on the stoichiometry of the starting surface. In all cases, the reaction occurs stepwise, with Ga and As monochlorides formed prior to the dichlorides. The Ga-rich surface is initially more reactive than either of the As-rich surfaces and it forms more GaCl than the As-rich surfaces, which instead form more AsCl. The sticking coefficient for chlorine on GaAs(001) decays exponentially with coverage. A contribution from Cl atoms comprising the surface dichlorides is identified in the Cl 2p core-level spectra. © *1996 American Vacuum Society.*

I. INTRODUCTION

A critical step in the manufacture of microelectronic devices is the dry etching of semiconductor substrates, typically via reactive-ion etching, ion-beam assisted etching, or plasma etching. To refine these processes, the mechanisms responsible for etching must first be understood. Since the complexity of these "real-life" processes precludes their direct study, a simpler approach is often taken in which individual steps of the etching reaction are investigated using model systems under highly controlled conditions.

Since chlorine-based etchants are often used in the fabrication of GaAs devices, due primarily to the volatility of Ga and As chlorides, the Cl$_2$/GaAs reaction has received a lot of attention. The Cl$_2$/GaAs(001) reaction, in particular, has been the focus of a number of studies since this crystal face is the one most commonly used in device manufacturing. These studies have investigated both the volatile reaction products[1-7] and the surface products[4,5,8-10] and how, for example, these are affected by the substrate temperature.[1-3,7,11-13] Consequently, much has already been learned about the reaction.

Investigations of GaAs(001) are complicated, however, by the fact that it exhibits a range of clean-surface reconstructions that depend on the stoichiometry. For instance, the 4×6 reconstruction contains only $\sim\frac{1}{4}$ monolayer (ML) of surface As,[14-16] whereas the $c(2\times8)$ reconstruction has 0.6–0.8 ML of As[14-16] and the $c(4\times4)$ surface is terminated by between 0.9 and 1.7 ML of As.[14-18] Certain aspects of the Cl$_2$/GaAs reaction, particularly surface passivation, are already known to be affected by the stoichiometry and crystallinity of the starting surface,[5,13] indicating a need for more detailed investigations of such effects.

To that end, high-resolution soft x-ray photoelectron spectroscopy (SXPS) is used in this investigation to study how the initial surface stoichiometry and order affects the resulting chemical composition of GaAs(001) following small exposures to Cl$_2$ at room temperature (RT). Not too surprisingly, it is found that Ga monochlorides form preferentially on the Ga-rich surface, whereas As monochlorides form preferentially on the As-rich surface. Also, the Ga-rich 4×6 surface is found to have a higher initial reactivity than the As-rich $c(2\times8)$ and $c(4\times4)$ surfaces. Analysis of the adsorption kinetics indicates that, for all three surfaces, the sticking coefficient decays exponentially with Cl coverage.

II. EXPERIMENTAL PROCEDURE

The SXPS measurements of the Cl$_2$GaAs(001)-4×6 reaction were carried out at beamline UV-8b of the National

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Synchrotron Light Source, located at Brookhaven National Laboratory in Upton, NY. GaAs(001) wafers (*n* type, Si doped, 10^{18} cm^{-3}) were first etched in a 1:1:200 solution of HNO_3:H_2O_2:H_2O, then rinsed with de-ionized water and isopropanol before being placed in the ultrahigh vacuum (UHV) chamber. The samples were cleaned *in situ* by sputtering with 500 eV Ar$^+$ ions, followed by annealing to ∼825 K. SXPS spectra were collected at RT with an angle-integrating ellipsoidal mirror analyzer, which accepts photoelectrons emitted from the sample within an ∼85° cone centered about the surface normal. Photon energies were selected with a 10 m focal length grazing incidence toroidal grating monochromator that is optimized for collecting Cl 2*p* spectra, as well as Ga and As 3*d* spectra. The high-resolution SXPS spectra of the 4×6 surface were collected with a total energy resolution of ∼0.3 eV.

Low-energy electron diffraction (LEED) measurements were not carried out on these samples prior to chlorination. However, sputtering GaAs is known to result in the preferential removal of As to form a slightly Ga-rich surface,[19,20] and annealing GaAs(001) *in vacuo* has been shown to result in a surface which exhibits a 4×6 reconstruction.[14,21] Furthermore, in subsequent investigations carried out in two different UHV systems, sputtering and annealing a GaAs(001) wafer in the manner described above reproducibly generated surfaces exhibiting slightly streaky 4×6 LEED patterns. Thus, although the reconstruction of the sputter-annealed surface was not measured, it is assumed to be 4×6 and is labeled accordingly.

The SXPS measurements of the As-rich *c*(8×2) and *c*(4×4) surfaces were carried out at beamline 41 of MAX-Lab in Lund, Sweden. This beamline has a molecular beam epitaxy (MBE) system connected to the spectroscopy chamber, via an UHV transfer system, making it possible to study high quality, MBE-grown surfaces *in situ*.[21,22] Surface reconstructions were identified via reflection high-energy electron diffraction (RHEED) in the MBE chamber, and again via LEED in the spectroscopy chamber. The material grown in this MBE system has a typical background *p*-type doping of ∼3.5×10^{14} cm^{-3}.[21] In the measurements of the MBE-grown surfaces, angle-resolved SXPS spectra were collected at RT along the surface normal, using a goniometer-mounted hemispherical analyzer with an angular resolution of ∼2° and a total energy resolution of better than 0.2 eV, with the angle between the surface normal and the incident *p*-polarized light fixed at 45°.

In all cases, Cl₂ was delivered to the GaAs surfaces in an equivalent manner, using identically constructed solid-state electrochemical cells.[23] These cells, which have a heated AgCl pellet as their active element, are designed to emit a collimated beam of Cl₂ molecules. Cl₂ dosages are reported in terms of the time-integrated operating current, in units of μA min. The operating current results from ionic flow of Cl$^-$ through the pellet, and is thus proportional to the amount of Cl₂ produced. For comparison, running 1 μA through the cell for 1 min would ideally produce ∼10^{14} Cl₂ molecules, although this should be considered an upper limit to the actual
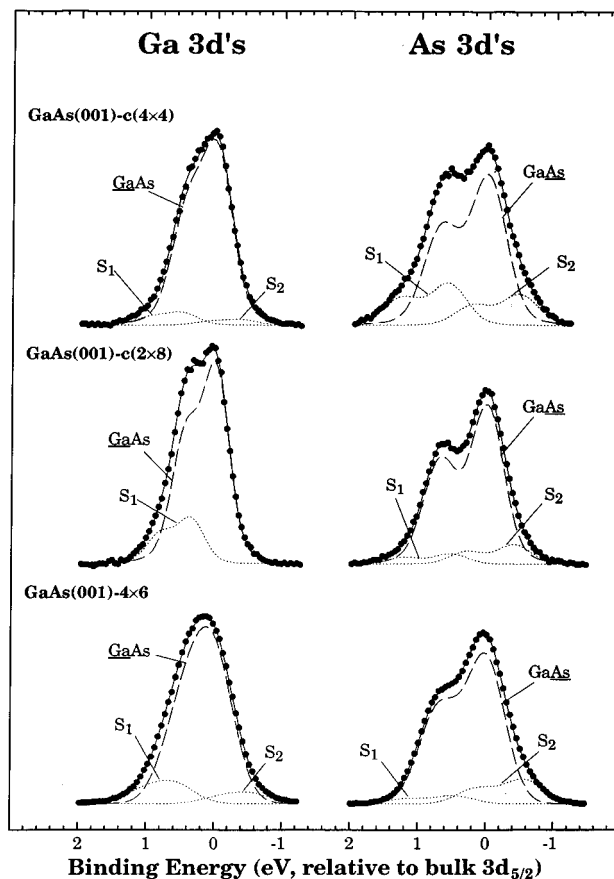

FIG. 1. Background-subtracted, high-resolution SXPS spectra of Ga and As 3*d* core levels, collected from clean GaAs(001) surfaces, are shown along with numerical fits to the data. Photon energies of 150 and 170 eV were used to collect the Ga and As 3*d* spectra from the 4×6 surfaces, respectively, whereas 60 and 81 eV photons were used in collecting the Ga and As 3*d* spectra from the *c*(4×4) and *c*(2×8) surfaces, respectively. Dotted lines show the SSCLs. The dashed line indicates the contribution from the bulk atoms. The solid line is the sum of the fit components. Spectra are scaled so that the bulk 3*d* components have equal areas.

Cl₂ exposure since not all of the current is due to ionic conduction and since the sample does not intersect the entire Cl₂ beam. Previous experiments with cells of this design have shown that doses are linear in both time and operating current and are typically reproducible to better than a factor of 2. All Cl₂ doses were carried out with the substrate at RT.

III. RESULTS

High-resolution Ga and As 3*d* core-level spectra are shown in Figs. 1 and 2. The spectra in Fig. 1 were collected from clean GaAs(001) surfaces. The spectra in Fig. 2 were collected from the same surfaces following exposure to between 300 and 500 μA min of Cl₂. In both Figs. 1 and 2 the data have been scaled so that the contributions from bulk atoms are of the same intensity, and each spectrum is labeled with the corresponding surface reconstruction.

The spectra were numerically fit, following background subtraction, to a sum of Gaussian-broadened Lorentzian spin-orbit split doublets, using a least-squares optimization routine.[24] A smooth background was determined by fitting a

third-order polynomial to each side of the peak. The fitting procedure was used to determine the binding energy (BE), area, and Gaussian contribution to the width of each core-level component. The Lorentzian full width at half-maximum was fixed at 0.10 eV in all of the fits. For the Ga 3d core level, the spin-orbit splitting and branching ratio were fixed at 0.45 and 0.65 eV, respectively. For As 3d, these parameters were fixed at 0.69 and 0.65 eV, respectively.

In order to establish a consistent fitting procedure, some additional constraints were imposed during fitting. The surface-shifted core-level (SSCL) components are generally difficult to resolve, primarily because their binding energies are not very different from those of the bulk atoms. Therefore, to obtain consistent results, the SSCL components were constrained to have the same widths as the bulk component. Also, to fit the Ga 3d spectra from the chlorinated surfaces, the separation between the SSCLs and the bulk component were held fixed at the values found for the clean surface. The fits to the data, obtained in this manner, are also shown in Figs. 1 and 2.

The magnitude and direction of the surface-induced shifts obtained from fitting the data are listed in Table I, along with values from the literature.[16–18,25] Several different values have been reported for surface-induced shifts on GaAs(001), resulting in sufficient uncertainty that it was deemed necessary to determine these shifts directly from the present data. Although values for the surface-induced shifts are reported here, no attempt is made to interpret their origin, given the complex nature of the reconstructions. The principal reason for determining values for these shifts is to ensure that unreacted surface atoms are adequately represented in the fits to spectra collected from surfaces exposed to very small amounts of chlorine. As is seen from Table I, although the surface-induced shifts obtained in this study differ slightly from some of the previously reported values, they are in general agreement. In any case, minor variations in the values used for the positions and widths of the SSCLs would not significantly affect the analysis of the chlorinated surfaces.

The chlorine-induced Ga and As 3d chemical shifts found in this study are consistent with previously reported values. The inclusion of just two components, shifted 0.9 and 1.7 eV
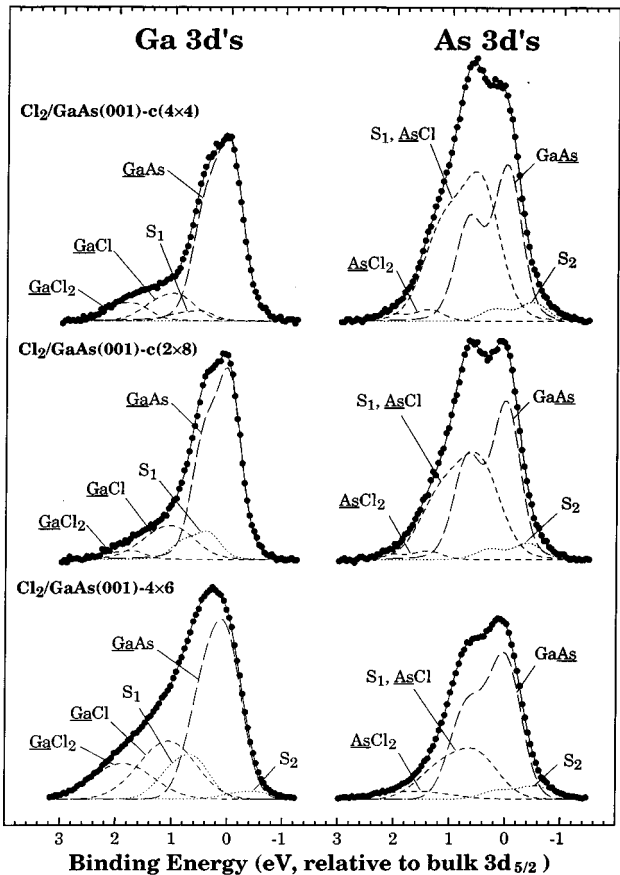

FIG. 2. Background-subtracted, high-resolution SXPS spectra of Ga and As 3d core levels, collected from the same surfaces as in Fig. 1 following a large (~300 μA min) dose of Cl$_2$, are shown along with numerical fits to the data. The photon energies used to collect these spectra are the same as in Fig. 1. Dotted lines show the SSCLs. The long-dashed lines indicate the contribution from the bulk atoms, whereas the short-dashed lines show the mono- and dichloride contributions to the core level. The solid line is the sum of the fit components. Spectra are scaled so that the bulk 3d components have equal areas.

to higher BE, is sufficient to fit all of the Ga 3d spectra from the reacted surfaces. These additional core-level components have been previously identified as arising from Ga atoms comprising surface GaCl and GaCl$_2$ species,[26,27] and are la-

TABLE I. The magnitude and direction of the surface-induced shifts for the clean surfaces. Positive shifts are to higher binding energy.

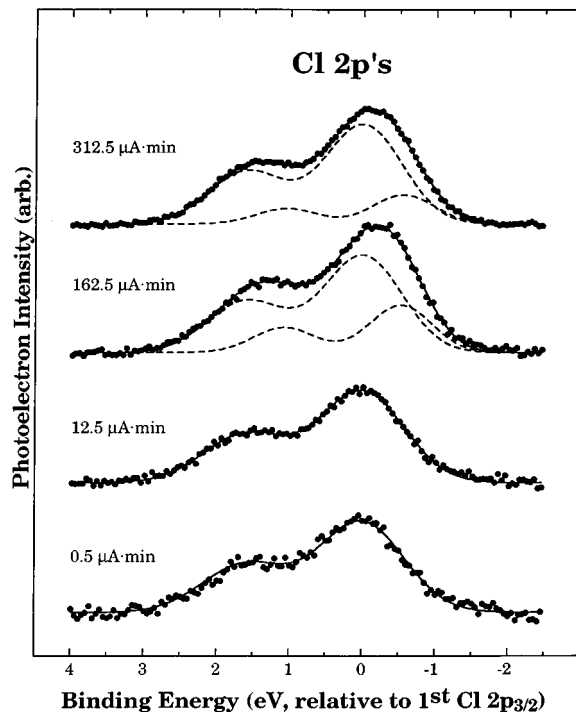|	GaAs(001)-4×6		GaAs(001)-c(2×8)		GaAs(001)-c(4×4)	
	Ga 3d	As 3d	Ga 3d	As 3d	Ga 3d	As 3d
This work	+0.57 eV	+0.45 eV	+0.36 eV	+0.53 eV	+0.51 eV	+0.58 eV
	−0.55 eV	−0.57 eV	···	−0.40 eV	−0.36 eV	−0.47 eV
Reference 16	+0.40 eV	···	+0.30 eV	+0.55 eV	+0.49 eV	+0.55 eV
	−0.21 eV	−0.61 eV	···	−0.25 eV	···	−0.28 eV
Reference 25	+0.34 eV		+0.38 eV	···	···	
	−0.40 eV		···	−0.35 eV	−0.41 eV	
Reference 17						+0.62 eV
						···
Reference 18						+0.50–0.60 eV
						−0.32–0.38 eV

FIG. 3. Background-subtracted, high-resolution SXPS spectra of Cl $2p$ core levels, collected from the chlorinated GaAs(001)-4×6 surface, are shown along with numerical fits to the data. A photon energy of 230 eV was used to collect these spectra. The dashed lines show the individual fit components and the solid line is the sum of individual components. Spectra are scaled so that the low BE components have equal areas.

FIG. 4. The relative contributions of GaCl, GaCl$_2$, AsCl, and AsCl$_2$ to the total Ga and As $3d$ core-level intensities plotted vs the logarithm of the Cl$_2$ dosage for all three surfaces. (▲), (■), and (✕): the 4×6, $c(2×8)$, and $c(4×4)$ surfaces, respectively.

beled as such in Fig. 2. Fitting the As $3d$ spectra is complicated by the fact that the chemical shift expected for surface AsCl on GaAs (~0.5 eV)[26–28] is nearly identical to the S$_1$ SSCL found for all three reconstructed surfaces. Consequently, no clear distinction can be made between contributions from AsCl and S$_1$, thereby forcing both to be combined into a single, slightly broader component that is shifted 0.5 ±0.1 eV to higher BE than the bulk component. The inclusion of one other component, shifted 1.4 eV to higher BE, was sufficient to obtain good fits to all of the As $3d$ spectra. This other component has been previously identified as arising from surface AsCl$_2$ species,[26–28] and is labeled as such in Fig. 2.

Cl $2p$ spectra were also collected throughout the experiments on the 4×6 surface. Four representative spectra are shown in Fig. 3, along with fits to the data. For the Cl $2p$ level, a spin-orbit splitting of 1.6 eV and a branching ratio of 0.53, as determined from a high-resolution Cl $2p$ spectrum of chlorinated Si, were used to fit to the data. At low Cl coverages, a single Cl $2p$ spin-orbit doublet is sufficient to achieve a high quality fit to the data. In addition, the measured changes in the kinetic energy of the substrate $3d$ photoelectrons, arising from movement of the Fermi level pinning position at the surface, are accurately reproduced by the low-coverage Cl $2p$ spectra. At the highest Cl coverages, however, the use of a single Cl $2p$ doublet results in a lower quality fit to the data, and this doublet does not exhibit the
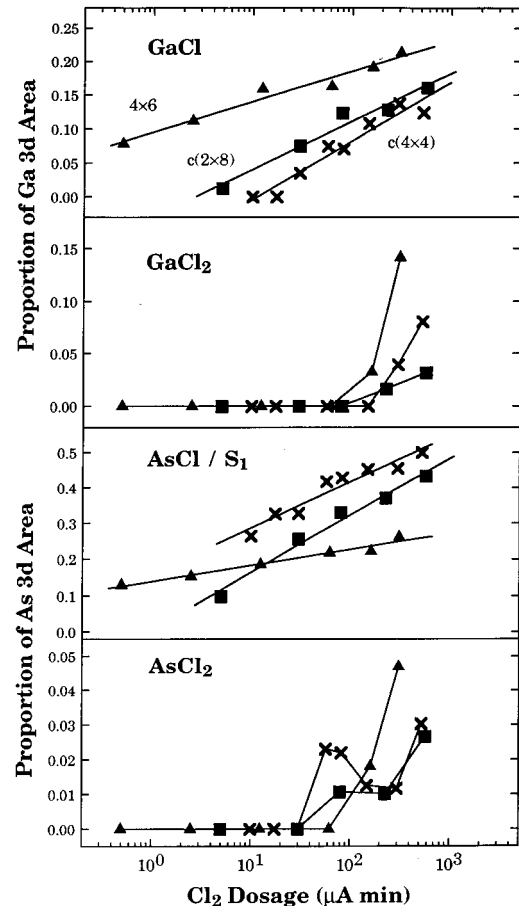
same kinetic energy changes as the substrate $3d$ core levels. Thus, two doublets are used to fit these spectra, with the position of one constrained to reproduce the kinetic energy changes observed in the substrate core levels. With this constraint, a typical value for the separation between the two doublets, which increases slightly with coverage, is ~0.55 eV. The source of the additional Cl $2p$ component is discussed below.

IV. DISCUSSION

The proportions that each mono- and dichloride core-level component contributes to the total $3d$ core-level intensities are shown in Fig. 4, plotted versus the logarithm of the Cl$_2$ dosage. For low coverages, chlorine simply chemisorbs on the outermost surface atoms.[27,29] The relative contribution to the overall core-level intensity for each surface species is then simply proportional to its coverage. Often, a proportionality constant can be determined by correlating the relative intensity of the SSCLs to a known coverage of surface atoms. In the present case, however, this approach introduces a large uncertainty, as the GaAs(001) reconstructions are sufficiently complex that it is not clear which surface atoms

contribute to S$_1$ and S$_2$. Therefore, Fig. 4 shows only the relative contribution of each core-level component.

The data from the three surfaces are plotted together in Fig. 4 to facilitate their comparison. It should be noted, however, that comparison can be made only under certain limitations. First, since different electrochemical cells were used and, since dosages vary somewhat from cell to cell, an accurate quantitative comparison of Cl$_2$ dosage cannot be made between samples. Second, the spectra of the 4×6 surface are angle integrated, whereas those from the $c(2 \times 8)$ and $c(4 \times 4)$ surfaces are angle resolved. Minor diffraction effects in the angle-resolved spectra, which may alter the relative contributions of core-level components slightly, must be taken into account when comparing them. Last, in order that a single grating could be used for the Ga 3d, As 3d, and Cl 2p levels, the 3d spectra of the 4×6 reconstructed surface were collected with a photon energy ~100 eV higher than that used for the MBE-grown surfaces. Thus, the photoelectron attenuation length for the spectra of the 4×6 surface is ~6.0 Å, but is only ~5.5 Å for the MBE-grown surfaces,[17] leading to a slight enhancement in surface sensitivity for the spectra collected from the MBE-grown surfaces. Despite these uncertainties, however, none of these effects, in and of themselves, is severe enough rule out a qualitative comparison and, in fact, certain conclusions can be drawn without the need for an accurate quantitative comparison.

The first, and most obvious, conclusion that can be made is that the monochloride species form before the dichlorides on all of the surfaces, indicating a stepwise chlorination process. Furthermore, the Cl$_2$ exposure at which an appreciable amount of monochlorides begins to form varies by more than a factor of 10 from one surface to another, indicating that the formation of monochlorides is sensitive to the initial surface stoichiometry. The dichlorides form at Cl$_2$ exposures ranging from 50 to 300 μA min, with AsCl$_2$ forming prior to or at the same point as GaCl$_2$ for all three surfaces, which may indicate that AsCl$_2$ is more easily formed than GaCl$_2$.

An unexpected result is that the monochloride coverage varies linearly with the logarithm of the Cl$_2$ exposure, as illustrated by the best-fit lines drawn through the data points in Fig. 4. Such a logarithmic dependence would not result from Langmuir adsorption kinetics, which would exhibit an exponential dependence. Instead, it corresponds to a sticking coefficient that decays exponentially with coverage, as described by the Elovich equation[30]

$$S(\Theta) = a \exp(-b\Theta).$$

The Elovich equation has been used to describe the oxidation of a number of metals, alloys, and semiconductors, but it is not supported by a unique microscopic model.[31] Coverage-dependent or reconstruction-dependent activation energies, or the weakening of backbonds due to chlorine adsorption can all account for this type of adsorption behavior. Further investigation is needed to determine which microscopic model best supports the adsorption kinetics observed for this system.

Both Ga and As monochloride formation on GaAs(001) depend on the initial surface reconstruction. The As-rich, MBE-grown surfaces exhibit similar behavior, with slopes and intercepts that are essentially the same, within the certainty of the measurements. The 4×6 surface, however, forms significantly more GaCl and AsCl following the smallest Cl$_2$ exposures, indicating that it is initially more reactive. Yet, the rate of Cl$_2$ uptake with increasing exposure, which can be inferred from the slope of the line drawn through the data, appears to be somewhat less for this surface. A lower reaction rate for the initially more reactive surface is not unexpected, since all three surfaces attain nearly identical compositions in the limit of large exposures.[5]

The initially high reactivity for the Ga-rich 4×6 surface has two possible origins—(1) preferential bonding of Cl to Ga over As, or (2) enhanced Cl$_2$ adsorption on the sputtered and annealed surface due to the presence of defects. Either possibility can equally well explain the present results, and it is likely that both are involved. Preferential bonding to Ga sites has been observed in the reaction of Cl$_2$ with GaAs(001)[5] and (110)[26] surfaces and may, in part, be due to slightly stronger Ga–Cl bonds (4.99 eV) compared to As–Cl bonds (4.64 eV). Sputtering a Ga-rich (001) surface does enhance its reactivity to Cl$_2$, suggesting that defects do play a role in chlorine adsorption.[5] Similar effects have also recently been observed by Sullivan *et al.* in a molecular beam scattering study of Cl$_2$/GaAs.[13]

One other observation is noted, although it is less conclusive due to the quantitative uncertainty of the data. From Fig. 4, it is seen that the amount of GaCl and AsCl present at a given dosage qualitatively tracks with the Ga:As ratio of the initial surface reconstruction. That is, the 4×6 reconstruction has the highest concentration of surface Ga and the lowest concentration of As of the three reconstructions investigated and, following reaction with Cl$_2$, it appears to have the most GaCl at all of the Cl$_2$ dosages studied, and the least amount of AsCl for dosages above ~10 μA min. The $c(4 \times 4)$ surface, on the other hand, has the highest concentration of surface As and essentially no exposed Ga. Following reaction with Cl$_2$, it appears to have the most AsCl and the least amount of GaCl at all of the dosages studied. The $c(2 \times 8)$ surface is intermediate to the 4×6 and $c(4 \times 4)$ surfaces in terms of surface stoichiometry, and this is reflected in the amount of each of the monochlorides formed.

Finally, in order to identify the source of the low binding energy Cl 2p component in Fig. 3, the relative contributions of the two Cl 2p components are plotted in Fig. 5 as a function of both Cl$_2$ dosing and annealing. Also plotted in Fig. 5 are the relative contributions of the Ga and As mono- and dichlorides, for comparison. The intensity of the second, lower-BE component qualitatively follows the intensities of the dichlorides. It shows up at the same exposure at which both GaCl$_2$ and AsCl$_2$ are first discernible. Furthermore, when the sample is annealed to remove chlorine, the second Cl 2p component vanishes at roughly the same point as the dichlorides (see caption for details of annealing treatment). Based on these observations, this second component is iden-
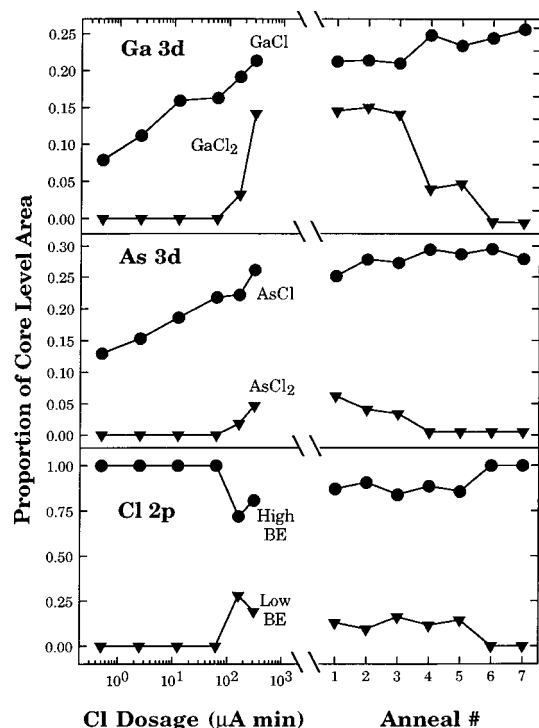
FIG. 5. The relative contributions of GaCl and GaCl$_2$ to the total Ga 3d core-level intensity, of AsCl and AsCl$_2$ to the total As 3d intensity, and of the low and high binding energy components to the total Cl 2p intensity plotted vs the logarithm of the Cl$_2$ dosage and vs annealing treatment. The anneals are numbered as follows: (1) 350 K for 20 s; (2) 425 K for 20 s; (3) 500 K for 20 s; (4) 825 K for 10 s; (5) 825 K for 20 s; (6) 825 K for 1 min, and (7) 825 K for 2 min.

tified as arising from the Cl atoms that comprise the GaCl$_2$ and AsCl$_2$ surface species. The additional Cl 2p component reported by Shuh *et al.*,[26] in the reaction of Cl$_2$ with GaAs(110), probably has the same origin. However, this appears to be a different phenomenon than the two Br 3d components seen for Br$_2$/GaAs(110) by Weaver *et al.*,[32] or the two I 4d components seen for I$_2$/GaAs(001) by Varekamp *et al.*[22] In both of those studies, no apparent correlation exists between the formation of dihalides and a second halogen core-level component.

V. CONCLUSIONS

The initial reaction of Cl$_2$ with GaAs(001) is found to be sensitive to the stoichiometry, and possibly the crystallinity, of the starting surface. The Ga-rich 4×6 surface is initially more reactive than either of the As-rich surfaces, possibly due to a higher density of defects in the sputter-annealed 4×6 surface. The Ga-rich surface also forms more GaCl than the As-rich surfaces, which form more AsCl. Hence, for reaction at room temperature, chlorine shows no strong preference for bonding to one element over the other, but instead bonds to whichever element is exposed at the surface, similar to I$_2$ adsorption on several III–V surfaces, including GaAs.[21] Thus, care must be taken when comparing results from dif-

ferent studies of the Cl$_2$/GaAs(001) reaction, because they are likely to depend greatly on the composition and quality of the starting surface.

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