

Reactions of I_2 and Cl_2 with In- and As-terminated InAs(001)

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(Received 29 September 1999)

The reactions of I_2 and Cl_2 with InAs(001) were investigated with synchrotron-based soft-x-ray photoelectron spectroscopy and low-energy electron diffraction. I_2 saturates the In-terminated InAs(001) surface, forming a well-ordered overlayer of InI, while As-terminated InAs(001) becomes disordered and forms both In and As iodides. Both the In- and As-terminated surfaces are disordered by Cl_2 adsorption, forming InCl, $InCl_2$, and As chlorides. The differences in the behavior of I_2 and Cl_2 are attributed primarily to the inability of InI_2 to form on the outermost surface.

I. INTRODUCTION

The reactions of halogens with III-V semiconductor surfaces can follow many different pathways. There are numerous reconstructions that can form on a given single-crystal face, such as the (001).¹ Each of these reconstructions is characterized by a slightly different stoichiometry in the outermost few atomic layers. When exposed to molecular halogens, a well-ordered overlayer forms on some of these reconstructions,²⁻⁷ while others become disordered.⁷⁻¹⁰ Although many of the details have been charted, a comprehensive understanding of the factors that determine the reaction pathway is still lacking.

A number of previous studies have demonstrated that the reaction pathway at room temperature depends on the initial surface structure. The authors of Ref. 7 used molecular-beam scattering to show that chlorine passivates Ga-terminated GaAs(001)- $c(8 \times 2)$ by forming a layer of GaCl, while it etches the As-terminated GaAs(001)- $c(2 \times 8)$ surface. Simpson and Yarmoff¹¹ showed that not only is the surface stoichiometry important, but the degree of ordering also plays a large role in determining the reaction pathway. Varekamp and co-workers¹²⁻¹⁴ investigated the reaction of I_2 with In-terminated InAs(001) and InSb(001) and As-terminated GaAs(001), and found that I_2 forms an ordered iodine overlayer on all of these surfaces. It was later shown that I_2 actually disorders As-terminated InAs(001).¹⁵ Murrell *et al.*⁵ studied the reaction of Cl_2 with InP(001)- 4×2 , and found that an ordered monolayer forms after small exposures, followed by a subsequent corrosion of the substrate. A two-stage adsorption of Cl_2 on InP(110), consisting of weakly bound chlorine at low exposures followed by the removal of phosphorus with large exposures, was proposed in Ref. 16.

Recently, we introduced a microscopic mechanism that explains the behavior of I_2 reactions with In- and As-terminated InAs(001).¹⁵ This mechanism is based on the idea that halogens initially adsorb at group-III, as opposed to group-V, surface sites. This is because the closed-shell halo-

gen molecular orbitals are attracted to empty dangling-bond orbitals, such as those associated with group-III surface atoms, and not to group-V surface atoms which have filled dangling-bond orbitals that repel halogen molecules.^{17,18} Thus, on the In-terminated surface, iodine simply bonds to the outermost surface atoms, forming an ordered structure. On the As-terminated surface, on the other hand, iodine initially bonds to a second-layer In atom that is exposed in one of the missing rows. When iodine attaches to this second-layer In atom, charge is transferred away from a surface As atom, making it reactive to additional incoming I_2 . When iodine has bonded to both In and As, the In-As bond breaks, which leads to surface disordering. Although this model is successful in explaining I_2 /InAs reactions, it does not account for observations that have been made for other III-V materials.

In order to further our understanding of this issue, we present a detailed investigation of I_2 and Cl_2 adsorption on In- and As-terminated InAs(001) using synchrotron-based surface-sensitive soft-x-ray photoelectron spectroscopy (SXPS) and low-energy electron diffraction (LEED). We confirm our earlier results for I_2 with a more in-depth analysis, and show that Cl_2 breaks In-As bonds disordering both In- and As-terminated surfaces. The differences between I_2 and Cl_2 reactions can be understood by a consideration of the ability to form higher halides on the surface.

II. EXPERIMENTAL PROCEDURE

The experiments were carried out at beamline UV-8a of the National Synchrotron Light Source (Brookhaven National Laboratory, Upton, NY). The ultrahigh-vacuum (UHV) apparatus consists of three chambers connected via a UHV sample transfer system. The spectrometer chamber is used for the SXPS measurements. The sample preparation chamber is equipped with LEED optics (Omicron) and a

sputter gun (Perkin-Elmer), and was also used for the I₂ exposures. A small turbomolecular-pumped dosing chamber was used for the Cl₂ exposures.

Monochromatic photons were generated with a 3-m toroidal grating monochromator.¹⁹ The photoelectron spectra were collected with an ellipsoidal mirror analyzer operated in an angle-integrating mode to collect electrons within an 85° acceptance cone centered about the surface normal.²⁰ The combined resolution of the monochromator and spectrometer was better than 0.15 eV. All spectra were collected with the sample at room temperature.

Single-crystal InAs(001) wafers (*n* type, carrier concentration $3.0 \times 10^{16} \text{ cm}^{-3}$) were cleaned *in situ* by repeated cycles of Ar⁺-ion sputtering at 500 eV for 20 min, and annealing at about 420 °C for about 20 min. The sample temperature was measured with an IR pyrometer (IRCON). LEED patterns were collected from the clean and halogenated surfaces. For the halogenated surfaces, LEED was carried out following the collection of the SXPS spectra, so that electron-stimulated desorption of iodine or chlorine by the LEED electron gun did not affect the SXPS measurements.

Iodine and chlorine were generated from UHV-compatible solid-state electrochemical cells similar to those described in Refs. 12 and 21. The cells consist of a silver halide pellet with a Ag plate and a Pt mesh as the electrodes. The AgCl pellet was also doped with CdCl₂. The cells were operated at temperatures between 120 and 160 °C. The exposures are reported in $\mu\text{A min}$, which refers to the operating current integrated over time. It was verified, using a quadrupole mass spectrometer in a separate UHV chamber, that the exposure is linear in both current and exposure time. As an approximate calibration, a 1- $\mu\text{A min}$ exposure is equivalent to 1.8×10^{14} molecules emerging from the cell. This number is likely an upper limit to the actual I₂ or Cl₂ exposure, however, as not all of the molecules hit the sample surface. Also, some current may be drawn by the residual Ohmic conduction of the pellet, but this effect should be minimal. By consideration of the chamber geometry, it is estimated that a 10- $\mu\text{A min}$ exposure approximately corresponds to having each surface atom hit by one I₂ or Cl₂ molecule. Note that it is possible that some atomic iodine or chlorine may be emitted from these cells, but a small number of atomic reactants would not affect any of the conclusions concerning the surface reactions. All of the I₂ and Cl₂ exposures were carried out with the sample at room temperature.

In order to identify the chemical species on the surface, the high-resolution SXPS spectra were collected and numerically fit in the following manner. First, the secondary electron background was subtracted from the raw data by assuming that the number of secondaries at each point is proportional to the integrated intensity of the photoelectron peak above that point.²² The spectra were then numerically fit to a sum of Gaussian-broadened Lorentzian spin-orbit-split doublets using a least-squares optimization procedure. The binding-energy shifts, areas, and Gaussian contributions to the full width at half maximum (FWHM) of each component were determined for each spectrum. The Lorentzian FWHM and the spin-orbit splitting and branching ratio were first chosen from the literature^{12,13} and then optimized by an initial fitting of the entire data set. After these parameters were determined, they were kept constant in refitting the en-

TABLE I. Fitting parameters obtained for InAs(001).

	In 4 <i>d</i>	As 3 <i>d</i>
Lorentzian FWHM	0.14 eV	0.10 eV
Spin-orbit splitting	0.85 eV	0.69 eV
Spin-orbit branching ratio	0.68	0.62

tire set of spectra. The values found for the parameters are listed in Table I. The binding-energy shifts determined for each individual component are listed in Table II.

III. RESULTS AND DISCUSSION

A. Adsorption of I₂ on InAs(001)

LEED patterns provide a measure of the surface order. The LEED patterns collected at different stages of the reaction of I₂ with InAs(001) were shown in Ref. 15, so they are not repeated here. After several cycles of sputtering and annealing, a LEED pattern is observed that is consistent with the mixed (4×2)/c(8×2) structure reported in Ref. 23. This pattern is composed of sharp integral and fourth-order diffraction spots along the major axes in the *x* direction, with streaky half-order lines in between. In both the 4×2 and c(8×2) structures, the outermost atomic layer is composed of In dimers.^{12,23} When this In-terminated surface is first exposed to I₂, all of the LEED spots broaden. After an exposure of ~100 $\mu\text{A min}$, the higher-order spots disappear. At saturation (after ~600 $\mu\text{A min}$), a sharp 1×1 pattern is obtained, in which the spots are brighter than the first-order spots of the original clean surface. These observations are consistent with previous results.¹² After heating the sample to ~385 °C to remove the adsorbed iodine, the LEED pattern rotates by 90°, i.e., appears to result from a mixed (2×4)/c(2×8) structure. Such a pattern is characteristic of an As-terminated surface, as discussed in Ref. 12. Note that the quality of the rotated pattern is not quite as good as the original In-terminated surface pattern, as the half-order streaky lines were rather weak. The removal of the surface group-III element and the subsequent formation of a group-V-terminated surface have been discussed previously for halogen/III-V systems.^{3,12,24} When the As-terminated

TABLE II. Core-level binding-energy shifts (in eV), given with respect to the corresponding bulk InAs component, obtained from clean InAs(001) and from InAs(001) reacted with I₂ and Cl₂.

		In 4 <i>d</i>	As 3 <i>d</i>
SSCL	S ₁	-0.27--0.30	-0.25--0.27
	S ₂	0.30	0.31
I ₂ reacted	Monoiodide	0.52	0.53
	Di-iodide	1.2	1.1
	Tri-iodide		1.85
Cl ₂ reacted	Monochloride	0.54	0.51
	Dichloride	1.33	1.30
	Trichloride	1.93	

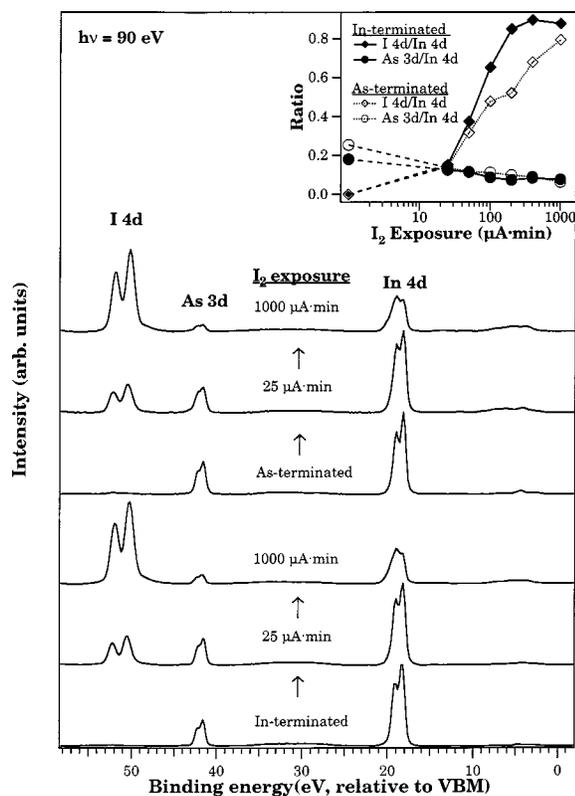


FIG. 1. Representative SXPS survey spectra collected from InAs(001)-(4×2)/c(8×2) and I₂-reacted surfaces. The spectra are scaled to the same maximum peak height, and are offset from each other for display purposes. The ratios of the total As 3d to In 4d and I 4d to In 4d intensities are shown in the inset as a function of I₂ exposure.

(2×4)/c(2×8) surface is exposed to 25-μA min of I₂, the higher-order spots quickly fade away. After the 200-μA min exposure, the first-order spots also disappear, indicating that the As-terminated surface is disordered by iodine adsorption.

Representative SXPS survey spectra, consisting of the valence band and shallow core levels, are shown in Fig. 1. The binding energies were calibrated to the valence-band maximum by assigning 17.2 eV to the In 4d_{5/2} component.¹² The ratios of the integrated areas as a function of I₂ exposure are shown in the inset. The I 4d peak intensity increases with I₂ exposure as iodine builds up on the surface, and the signals arising from As 3d and In 4d photoelectrons are attenuated. The iodine 4d signal from the In-terminated surface saturates by approximately 200 μA min, while the iodine signal from the As-terminated surface has not yet reached a maximum after the largest exposure employed (1000 μA min). The ratio of As to In photoelectron intensity decreases by about a factor of 2 during the exposures, and there is no significant difference for the two terminations. This decrease may be due to a photoelectron diffraction effect as iodine builds up on the surface. As discussed below, most of the iodine is bonded to In in an on-top configuration, which could cause an increase in the intensity of In photoelectrons, relative to As, due to forward scattering.

High-resolution In 4d and As 3d core-level spectra were collected after I₂ exposures ranging from 10 to 1000 μA min. Photon energies of 79 and 102 eV were used to excite In 4d

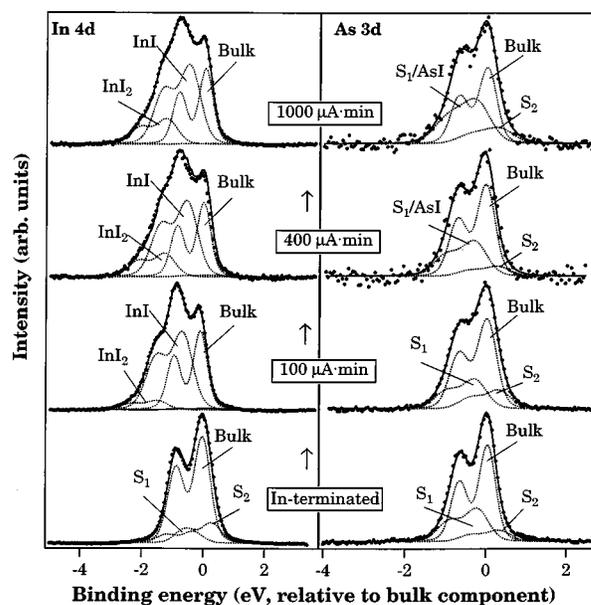


FIG. 2. High-resolution In 4d and As 3d SXPS spectra collected from the In-terminated InAs(001) surface after representative I₂ exposures. The raw data after background subtraction are shown as filled circles, the individual components of the numerical fits are shown as dashed lines, and the solid lines show the sum of the fit components.

and As 3d core-level electrons, respectively, so that the emitted electrons all have kinetic energies in the neighborhood of 50 eV. This corresponds to a probing depth of 6 Å and the maximum surface sensitivity.²⁵ Also, this insures that the measured In 4d and As 3d photoelectrons have roughly the same kinetic energies so that they provide information from the same portion of the near-surface region. Representative spectra collected from clean and I₂-reacted surfaces are shown along with the numerical fits in Fig. 2 for the In-terminated surface, and in Fig. 3 for the As-terminated surface.

Shifted-surface core-level (SSCL) components, labeled S₁ and S₂, are apparent in the clean surface In 4d and As 3d spectra. The SSCL components represent the outermost surface atoms, which are in different electronic environments than the atoms in the bulk. The magnitudes of the binding energy shifts of the SSCL components, as listed in Table II, are consistent with previous reports.^{12,13} Some of the SSCL components disappear following reaction with I₂, while others remain.

Chemically shifted components in the spectra collected from reacted surfaces arise from monoiodide, di-iodides, and tri-iodides, i.e., substrate atoms with one, two, or three iodine atoms attached. The binding energy shifts, as determined from the fitting procedure, are listed in Table II.

On both InAs(001) surfaces, iodine is primarily attached to In as a monoiodide. A small amount of InI₂ is also formed after the 100-μA min exposure. The total amount of InI₂ that can be accommodated on the surface is limited, however, by repulsive interactions between I atoms on neighboring dimers (as discussed below). Thus the major surface product is InI, and the InI₂ that is present may have formed at defect sites. For example, a common defect observed on III-V (001) surfaces is a vacancy in which one of the dimer atoms

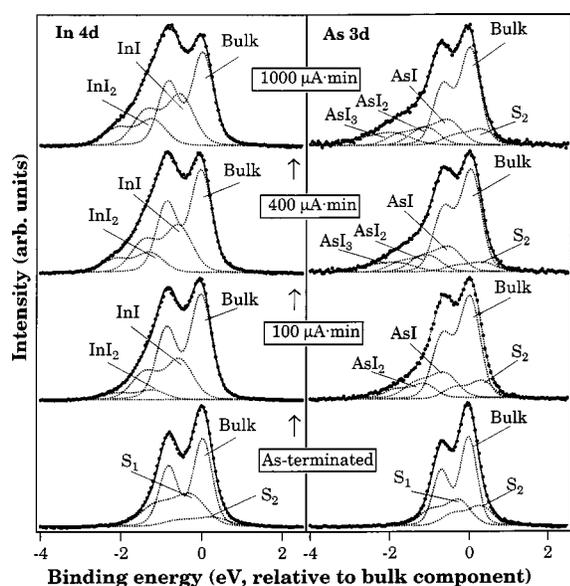


FIG. 3. High-resolution In 4*d* and As 3*d*SXPS spectra collected from the As-terminated surface after representative I₂ exposures. The raw data after background subtraction are shown as filled circles, the individual components of the numerical fits are shown as dashed lines, and the solid lines show the sum of the fit components.

is missing.²⁶ InI₂ can form if two I atoms bond to such a lone In surface atom. Note that two Br atoms attached to a Ga atom at a defect site have been observed for the adsorption of Br₂ on GaAs(001).¹⁸

Arsenic atoms are only slightly affected by iodine adsorption on the In-terminated surface, while As iodides clearly form on the initially As-terminated surface. The As 3*d* spectra in Fig. 2 show that the SSCL components persist throughout the range of I₂ exposures for the In-terminated surface. The binding energies are unchanged from the clean surface,¹² but the widths and areas of the SSCL components increase, particularly for S₁ after the largest exposure. This suggests that some iodine is bonded to As, since the shift for AsI is not resolvable from the S₁ component. In the As 3*d* spectra shown in Fig. 3 for the As-terminated surface, on the other hand, the peak shape is clearly modified by the reaction. The fitting procedure indicates that arsenic monoiodides, di-iodides, and tri-iodides have formed on the surface. The production of both In and As iodides implies that In-As bonds were broken by the reactions.

The fitting results further show that the S₂ SSCL component for the As-terminated surface does not completely disappear, as might be expected for a disordered surface. The residual S₂ intensity is likely due to a small number of tricoordinate As atoms in the near-surface region.¹⁵ Arsenic, which has five valence electrons, can form a stable tricoordinate species with the remaining two electrons pairing up. Arsenic atoms on the clean surface are actually in a similar tricoordinate configuration, and therefore the tricoordinate As atoms have a binding energy close to that of S₂. Such tricoordinate As atoms were previously identified in SXPS spectra collected following the reactions of Cl₂ (Refs. 9 and 10) and XeF₂ (Refs. 27 and 28) with GaAs. It is interesting to note that the SSCL components persist for As, but not for

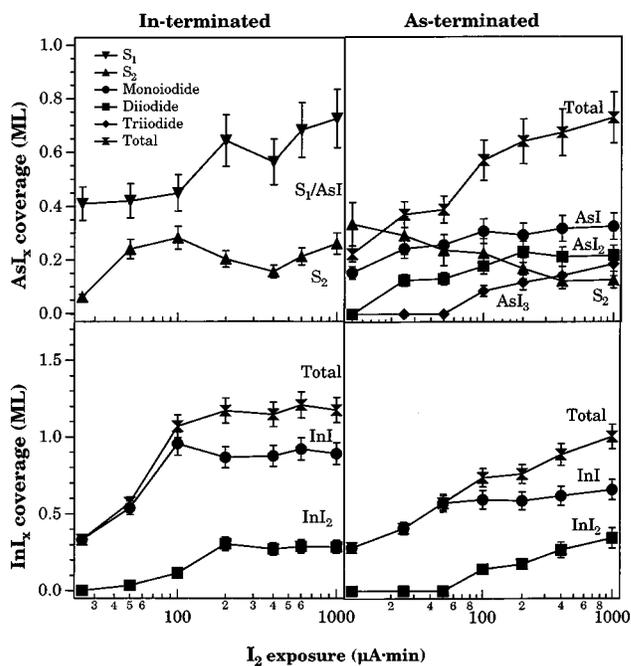


FIG. 4. Coverages of the various In and As iodides shown as a function of I₂ exposure. The panels on the left show the coverages on the initially In-terminated surface, while the panels on the right show the coverages on the initially As-terminated surface.

In. This is actually a corroboration of the higher reactivity of halogens with In, as compared to As. A tricoordinate In atom would be very reactive to incoming halogens, as it would have an empty orbital, while the tricoordinate As atoms are unreactive due to the filled orbital. Thus many In iodides are formed while many As atoms remain unreacted.

The iodide coverages as a function of I₂ exposure are shown in Fig. 4. To determine the coverages, chemically induced changes of photoionization cross section were assumed to be negligible, and the area of an individual component relative to the total core-level intensity was assumed to be proportional to its relative surface coverage.²⁹ This latter assumption is accurate for coverages up to 1 ML. In order to calibrate the calculation, the SSCL components in the clean surface spectra were presumed to arise solely from the outermost surface atoms. According to the surface reconstruction model for InAs(001),¹ there is 0.75 ML of dimerized surface In atoms. The total SSCL intensity measured from the clean surface was thus assigned to 0.75 ML, and the intensities of all the chemically shifted components were compared to this value in order to calculate their corresponding coverages. Note that this procedure produces the coverage of surface halides, such as InI and InI₂, and not the coverage of iodine itself. A similar method was used to calibrate the As iodide coverages. The error bars were calculated by individually varying the intensity of each component until the fit was clearly deteriorated from the optimum result. This enabled the determination of a minimum and maximum for each component area. Then these values were used to calculate the minimum and maximum possible coverages.

It is seen in Fig. 4 that monoiodide forms prior to the higher iodides on both the In- and As-terminated surfaces. The total iodide coverage on the In-terminated surface reaches saturation after 200- μ A min exposure, consistent

with the behavior of the $I\ 4d$ intensity (Fig. 1). The total coverage on the As-terminated surface, however, is still increasing even after 1000- μA min exposure.

To summarize the I_2 results, both LEED and SXPS show that there are clear differences in the adsorption behavior on the In- and As-terminated surfaces. LEED shows that the In-terminated surface becomes ordered, while the As-terminated surface becomes disordered. SXPS shows that the In-terminated surface forms primarily InI, while the As-terminated surface forms both In and As iodides. The In-terminated surface saturates when the ordered structure is formed, while the As-terminated surface continues to react. The differences in the behavior of the two surfaces were previously explained by a mechanism that begins with iodine initially bonding to the electron-deficient group-III In atoms.¹⁵

On the In-terminated surface, the outermost layer consists of In-In dimers and missing rows. The reactive empty dangling-bond orbitals associated with the In dimer atoms stick out from the surface. The filled unreactive dangling-bond orbitals of the second-layer As atoms are located in the missing rows. As this surface is exposed to I_2 , iodine attaches to the outermost In atoms, forming primarily InI. The extra electrons needed to form the In-I bonds presumably come from the breaking of In-In dimers. The surface reconstruction is lifted after sufficient iodine coverage, and a sharp 1×1 LEED pattern is observed. Note that the formation of a 1×1 LEED pattern also necessitates that some first-layer atoms diffuse laterally.¹² The surface passivates when all of the surface In atoms have attached to iodine.

On the As-terminated surface, the outermost layer consists of As-As dimers and missing rows. The surface As dimer atoms have unreactive filled dangling-bond orbitals, while the reactive empty orbitals associated with the second-layer In atoms are located in the missing rows. Thus iodine initially attaches to the second-layer In atoms that are exposed in the missing rows. Charge must be transferred in order to form an In-I bond, however, which presumably comes via depletion of charge from the filled orbital of a surface As atom. Iodine can now attach to this first-layer As atom since its surface orbital is no longer full. When iodine attaches to both a first-layer As atom and a second-layer In atom, the In-As bond must break in order to provide the electrons needed for bonding to iodine. This bond breaking starts the disordering process. This scenario shows how the I_2 reaction disorders the As-terminated surface, leaving iodine bonded to both In and As.

B. Adsorption of Cl_2 on InAs(001)

LEED shows that both the In- and As-terminated surfaces are disordered by Cl_2 reaction. The mixed $(4 \times 2)/c(8 \times 2)$ LEED pattern from the clean In-terminated surface reconstruction changes to a mixture of $c(8 \times 2)$ and (1×1) after a 25- μA min exposure, and then becomes a weak 1×1 as the exposure increases. No LEED pattern is observed after an 800- μA min exposure. On the As-terminated surface, the higher-order spots disappear after a 10- μA min exposure of Cl_2 , and only a weak 1×1 LEED pattern is present after 50 μA min. No LEED pattern remains after a 400- μA min exposure.

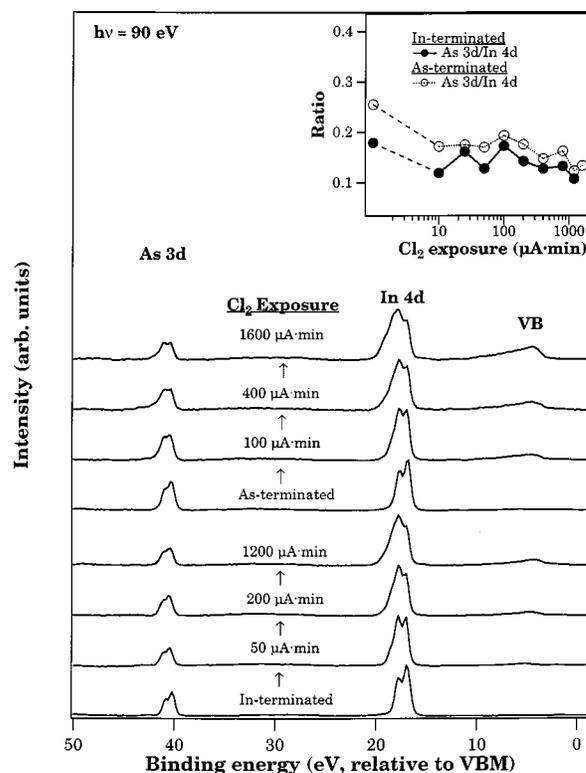


FIG. 5. Representative SXPS survey spectra collected from InAs(001)- $(4 \times 2)/c(8 \times 2)$ and Cl_2 -reacted surfaces. The spectra are scaled to the same maximum peak height, and are offset from each other for display purposes. The ratios of the total As 3d to In 4d intensities are shown in the inset as a function of Cl_2 exposure.

SXPS survey spectra collected after various Cl_2 exposures are shown in Fig. 5. As the surface is exposed to Cl_2 , there is an increase of the valence-band feature at ~ 4.5 -eV binding energy, similar to the observation reported in Ref. 9 for Cl_2 adsorption on GaAs. This feature is related to the Cl $3p$ band.² The increase of the valence-band intensity is larger on the As-terminated surface than on the In-terminated surface, indicating a larger chlorine uptake. The ratios of the integrated intensities of the As 3d to In 4d core levels as a function of Cl_2 exposure are shown in the inset. The As 3d to In 4d ratios both decrease by about a factor of two, similar to the reaction with I_2 .

Representative high-resolution In 4d and As 3d core-level spectra collected from clean and chlorinated surfaces are shown in Figs. 6 and 7 for In- and As-terminated surfaces, respectively, along with the results from curve fitting. The binding-energy shifts determined for the reacted components are given in Table II.

The chemically shifted components in the In 4d core-level spectra are identified as InCl, InCl_2 , and InCl_3 . To our knowledge there have been no previous reports of the In 4d binding-energy shifts for InAs reacted with Cl_2 , but the shifts are similar to those obtained from chlorine reaction with other III-V semiconductors.^{30,31} Note that these values are slightly larger than those reported in Ref. 32 for the reaction of chlorine with InP(100). The identification of InCl_3 as a surface reaction product is in contrast to chlorine reaction with GaAs(001), in which only GaCl and GaCl_2 are observed on the surface.³¹ This is because GaCl_3 is volatile, while InCl_3 is not.

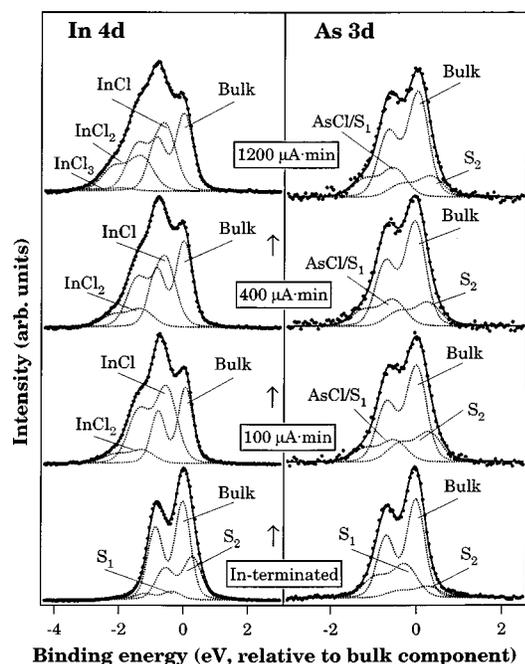


FIG. 6. High-resolution In 4*d* and As 3*d* SXPS spectra collected from the In-terminated surface following representative Cl₂ exposures. The raw data after background subtraction are shown as filled circles, the individual components of the numerical fits are shown as dashed lines, and the solid lines show the sum of the fit components.

The As 3*d* spectra for both terminations show some bonding to arsenic following Cl₂ reaction. The binding energy shifts found here for the arsenic chlorides are similar to those in the literature for chlorine adsorption on GaAs.^{9,30,31} For the In-terminated surface, the two surface components persist throughout the exposures, although they alter their relative intensities. Since the positions of the S₁ SSCL and AsCl components are quite close to each other, a single component on the high-binding-energy side of the bulk peak is used in the fitting. This same approach has also been used for Cl₂ reaction with GaAs.³¹ To obtain the best fit after chlorine adsorption, the binding energy of this feature increased to 0.51 eV from the SSCL value of 0.31 eV, and the Gaussian FWHM increased slightly. Note that for I₂ reaction with the In-terminated surface, the width of this component also increased following reaction, but the binding energy that produced the best fits was that of the SSCL. This suggests that for the Cl₂ reaction, most of the component intensity corresponds to AsCl, while for the I₂ reaction the component primarily arises from the SSCL. For the As-terminated surface, in addition to AsCl, a component identified as AsCl₂ appears in the As 3*d* core-level spectra. On both the In- and As-terminated surfaces, S₂ persists following Cl₂ reaction. As discussed above, S₂ not only arises from atoms on the clean surface, but also from tricoordinate atoms produced by the reaction. Similar to the I₂ reaction, tricoordinate As atoms are produced, but tricoordinate In is not observed.

The chloride coverages, calculated in the same manner as the iodide coverages in Fig. 4, are shown as a function of exposure in Fig. 8. On both the In- and As-terminated surfaces, InCl forms prior to the formation of higher chlorides. There is about 1 ML of InCl on both surfaces after a 100-

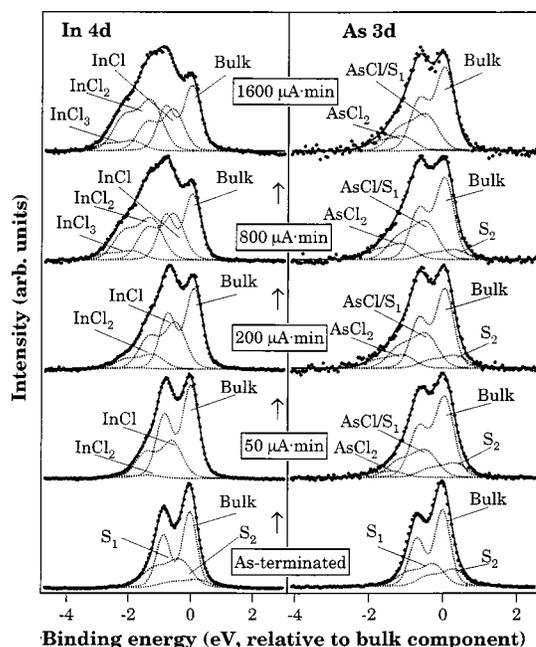


FIG. 7. High-resolution In 4*d* and As 3*d* SXPS spectra collected from the As-terminated surface following representative Cl₂ exposures. The raw data after background subtraction are shown as filled circles, the individual components of the numerical fits are shown as dashed lines, and the solid lines show the sum of the fit components.

μA min exposure. InCl₂ forms after ~100 μA min, and the amount of InCl decreases at the same point. This suggests that additional Cl bonds to In atoms that already have one Cl atom attached, converting them into InCl₂. InCl₂ is the major surface reaction product on the As-terminated surface after large Cl₂ exposures. On the In-terminated surface, the rela-

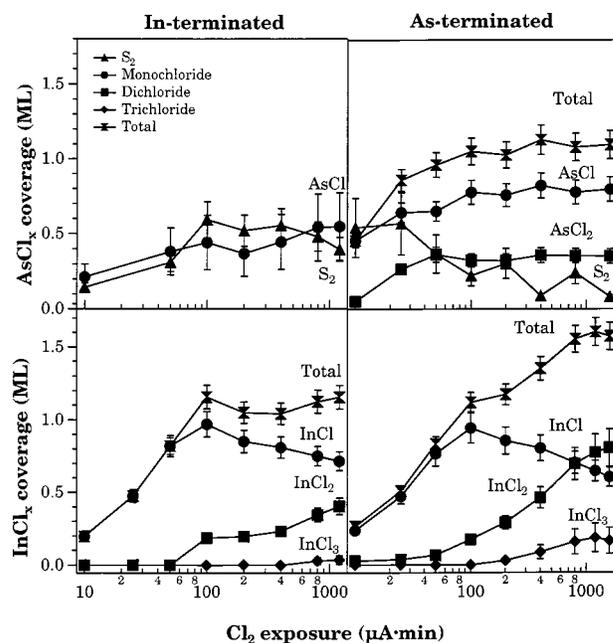


FIG. 8. Coverages of the various In and As iodides as a function of Cl₂ exposure. The panels on the left show the coverages on the initially In-terminated surface, while the panels on the right show the coverages on the initially As-terminated surface.

tive amount of dihalide is larger for chlorine than it was for iodine, and it is still increasing after the largest exposure employed here, which suggests that InCl_2 would also be the major reaction product on the In-terminated surface following larger exposures. The formation of an In dihalide species as a major surface reaction product is in sharp contrast to the reaction with iodine.

It is reasonable to assume that initially chlorine will also preferentially bond to the group-III surface atoms, as was suggested for I_2 adsorption, and there is additional experimental evidence that supports this supposition. A temperature-programmed desorption and Auger electron spectroscopy study of the reaction of Cl_2 with Ga- and As-terminated GaAs(100) suggested a preferential formation of Ga-Cl bonds on the surface.³³ The preferential bonding of chlorine to group-III atoms was also reported in Ref. 30, where it was observed that chlorine dissociates and bonds to both Ga and As atoms, with a preference for Ga bonding at low coverages.

With this in mind, it is likely that the reaction of Cl_2 with the In-terminated surface begins in a similar manner as for I_2 , but differs after larger exposures. Chlorine initially bonds to the outermost In atoms, with the extra electron needed to form InCl coming from the breaking of the dimer bond, as was the case for iodine. The difference between chlorine and iodine, however, is that dichlorides can readily form on the surface while di-iodides do not. If In dichlorides form, then the other electron needed to form the bond must come by breaking the bond to As. This begins the process of disordering the surface.

The As-terminated surface should initially react in a similar manner as with iodine. That is, the initial bonding should be with a second-layer In atom, which would act to remove charge from the filled orbitals of the surface As atom. The surface As atom then becomes reactive to additional chlorine. Eventually, this breaks In-As bonds as chlorine attaches to both In and As, and the surface becomes disordered. There is an additional pathway for producing reactive As atoms, however, since InCl_2 readily forms in the second layer. When InCl_2 is formed, another In-As bond breaks, and more reactive As sites are opened up. Thus, because there are essentially two operative mechanisms for producing reactive As sites, more surface products are produced on the As-terminated surface with chlorine than on In-terminated surface. This explains the larger uptake of Cl_2 on the As-terminated surface.

C. Comparison of iodine and chlorine reactions

The above results show that different pathways are followed for I_2 and Cl_2 reactions with InAs(001). The As-terminated surface behaves similarly for I_2 and Cl_2 in that it is disordered by both reactants, but there are still differences in terms of the distribution of reaction products. The In-terminated surface, however, shows a marked difference for I_2 and Cl_2 reactions. There are two main factors that could possibly contribute to these differences. The first is related to the charge transfer that occurs during bonding, and the second to the ability to form higher halides.

Surface disordering by chlorine may be partially due to the amount of charge that is transferred in forming a chemi-

cal bond. Chlorine has a higher electronegativity (3.0) than iodine (2.5).³⁴ Thus, in bonding to a first-layer In atom on the In-terminated surface, more charge will be transferred from the filled orbital of a second-layer As atom to Cl than to I. This suggests that chlorine could weaken the In-As bond more than iodine, thereby making the second-layer As atom reactive to additional chlorine. When chlorine has attached to both the first-layer In and second-layer As atoms, the In-As bond should break in order to provide the electrons needed in forming bonds to the halogens. This provides a path, in addition to the formation of In dichlorides, which could lead to surface disordering. This is not the dominant pathway, however, as the number of As chlorides on the In-terminated surface is not very large.

When any higher halide, such as InCl_2 or InI_2 , is formed on the surface, an In-As bond must also break to provide the electron needed. Thus the presence of higher halides is directly linked to the surface disorder. In the aggregate, the formation of higher halides is thermodynamically downhill. However, there are factors that act to limit the ability of higher halides to form on some surfaces.

On a well-ordered substrate, the formation of higher halides is limited by steric hindrance, i.e., the repulsion between neighboring halogen atoms. The effects of the repulsion would be greater for the larger iodine atoms than for chlorine, which is consistent with observations. The atomic spacing between two adjacent In atoms in the bulk crystal structure is 4.28 Å, while the atomic radii of I and Cl are 1.33 and 0.99 Å, respectively.³⁵ Figure 9 shows a schematic diagram of the InAs(001) surface onto which halogen atoms were placed at neighboring sites. The filled circles indicate the atomic radii of the halogens. Note that this diagram is not intended to accurately portray the adsorption sites, but only to show how the packing of halogens can be accommodated onto the surface. In Fig. 9(a), four iodine atoms are placed atop of In at neighboring sites. It can be seen that monoiodides easily fit into a single ordered atomic layer, but that the addition of more iodine, as would be needed to form diiodides, is restricted by I-I interactions. For the smaller chlorine atoms, however, at least some dichlorides can form in sites adjacent to monochlorides without restriction. This can be seen in Fig. 9(b), in which two Cl atoms were placed onto a single In site adjacent to a site containing a monochloride. This is, of course, not the actual adsorption geometry, as one of the underlying In-As bonds will break when the dichloride is formed. But this does show, however, that there is sufficient room to fit a significant number of chlorine atoms onto the surface as dichlorides. In fact, the distribution of surface species suggested by this simple packing argument would be 0.5 ML of monochlorides and 0.5 ML of dichlorides, which is close to the actual distributions reported in Fig. 8.

The atomic radii, however, actually represent a lower limit to the sizes of the adsorbates. Since the halogen bonds are partially ionic, the ionic sizes can be considered at upper limits. For I and Cl, the ionic radii are 2.20 and 1.81 Å, respectively,³⁶ and are shown as dashed circles in Fig. 9. A consideration of the ionic sizes might lead to the conclusion that neither iodine nor chlorine would be able to form dihalides. Some of the steric hindrance introduced by the formation of dichlorides can, however, be accommodated via twisting of the substrate bonds, as was suggested for fluorine

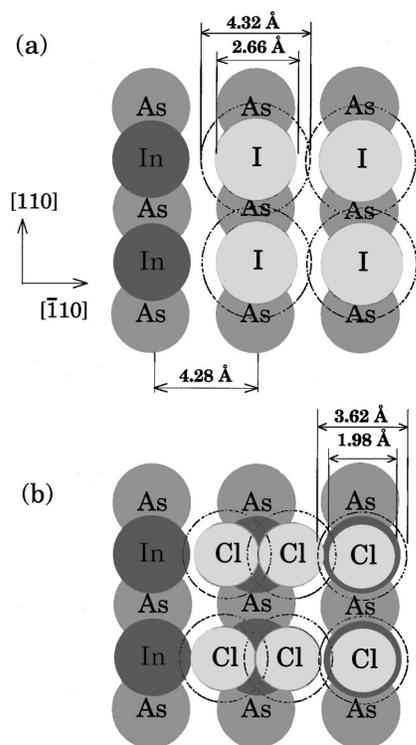
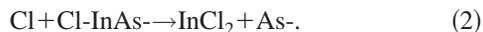
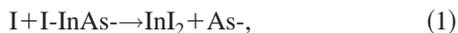


FIG. 9. Schematic top view of the In-terminated InAs(001) surface illustrating (a) I and (b) Cl adsorption. The monohalides are assumed to be located directly atop an In site. The sizes of the filled circles show the atomic radii, while the dashed circles denote the ionic radii. Monoiodides only are shown in (a). In (b), a dichloride is shown located next to a monochloride.

adsorbed on Si(001).³⁷ In addition, since underlying In-As bonds will break when dichlorides are formed, more degrees of freedom are available for the surface species to reorient themselves. Bond breaking and substrate disorder are thus necessary in order to accommodate the coverages of dichlorides reported in Fig. 8.

Formation of InCl₂ is also thermodynamically more favorable than InI₂, which further increases the likelihood that it forms. Consider the conversion of an In monohalide to the dihalide. For iodine and chlorine, this can be written as



These equations assume that an InAs bond is broken when the dihalide is formed. The In-As bond energy is 2.08 eV, while the bond energies of In-I and In-Cl are 3.43 and 4.55 eV, respectively.³⁶ Thus only 1.35 eV is gained in forming a

di-iodide as in Eq. (1), but 2.47 eV is gained when the dichloride is formed as in Eq. (2). Due to the steric limitations, however, there must also be some movement of the substrate atoms in order to accommodate two halogen atoms on the surface. This introduces strain into the system that will reduce the energy gained from the exothermicity of the reaction. Note that the amount of energy needed for twisting the lattice in order to fit two F atoms onto Si(100) was calculated to be on the order of 1.3 eV or more.³⁷ Thus, despite some rearrangement of the lattice, the total energy of the system is likely to be reduced in forming InCl₂, but lattice rearrangements may require too much energy to make the 1.35 eV gained in forming the second In-I bond thermodynamically favorable.

IV. CONCLUSIONS

The adsorption of I₂ and Cl₂ on In- and As-terminated InAs(001) was investigated with SXPS and LEED. It was shown that the competition between passivating and etching is controlled by the complex details of the charge distribution of the clean surface, the evolution of that distribution during the reaction, and the chemical pathways that are available to the reactants due to steric constraints.

Iodine passivates the In-terminated InAs(001) surface, forming a well-ordered overlayer. In this case, the reaction occurs with first-layer In atoms and does not perturb the charge distribution of the system sufficiently as to make any other sites reactive.

Disordering is seen for chlorine adsorption on both surfaces and for iodine adsorption on the As-terminated surface. The bond breaking and surface disordering indicate the onset of etching of the substrate; i.e., for continued exposure, or for reaction under high pressure, these surfaces will spontaneously etch. In the regime probed here, however, the etching has not yet begun. These results do, however, illustrate the initial reaction pathways that precede etching reactions.

ACKNOWLEDGMENTS

We are grateful to J. Kanski for providing the InAs(001) samples, and to A. C. Kummel for useful discussions. This work was supported by the U.S. Army Research Office under Grant No. DAAH04-94-G-0410. Partial support was given by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. SXPS spectra were collected at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the Department of Energy (Division of Materials Sciences and Division of Chemical Sciences, Basic Energy Sciences) under Contract No. DE-AC02-76CH00016.

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