Passivation versus Etching: Adsorption of I_2 on InAs(001)

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Halogen adsorption on certain III-V semiconductor surfaces forms ordered overlayers, while other surfaces etch. The microscopic mechanism underlying this behavior is investigated by comparing the adsorption of I_2 on In- and As-terminated InAs(001) surfaces. On the In-terminated surface, a well-ordered (1×1) structure forms and all of the iodine attaches to In. The As-terminated surface becomes disordered, however, and iodine attaches to both In and As. These observations can be explained by assuming that iodine initially bonds to In atoms, whether they are in the first or the second layer. [S0031-9007(98)06834-3]

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One of the most remarkable aspects of modern surface science has been the ability to control the structures of solid surfaces with atomic precision. Such control will ultimately lead to major advances in both our understanding of solid-state physics and in the technology of small devices. Because III-V semiconductors have alternating layers of group III and group V atoms along the [001] direction, they are ideal candidates for making such atomically abrupt structures. Although much has been done in this regard with molecular beam epitaxy (MBE) [1,2], chemical processing offers a better method in terms of real applications. In order to use chemical methods with atomic precision, however, the details of the structure, and the chemical mechanisms of the reactions used to create that structure, must be understood.

Most dry etching processes used to fabricate devices employ halogens, since halogens readily form volatile compounds. It has been found that when molecular halogens react with certain III-V semiconductor surfaces, an ordered overlayer forms [3–9], while other surfaces become disordered [7,10–12]. When an ordered layer forms, the surface saturates with ~1 monolayer (ML) of adsorbed halogen atoms. Disordered surfaces, on the other hand, are formed as the material etches, or is at least in the preliminary stages of etching. Finding an explanation for this behavior has been difficult, however, due to the complexity of III-V surfaces. For even a single crystal face of a given III-V material, many different reconstructions are possible [13], each of which has a different stoichiometry in the outermost few atomic layers. It has been proposed that the surface stoichiometry is one of the crucial factors in determining whether a surface will passivate or etch [7]. Other work has indicated that the degree of surface order is also critical [14]. Despite this information, however, there has been no microscopic model that explains why certain surfaces passivate while others etch.

In this Letter, we compare the reaction of I_2 with In-terminated and As-terminated InAs(001). Iodine is less reactive than other halogens, such as chlorine [15] and is therefore a better probe of the surface reaction mechanism as each step in the process can be isolated. InAs(001) can be prepared to have a more well-ordered surface than other III-V's, such as GaAs, and is therefore better suited for a mechanistic study. Previous investigations of I_2 adsorption on InAs(001) involved only the In-terminated surface [16,17]. We find that the In-terminated surface passivates, in agreement with Refs. [16,17], but that the As-terminated surface instead becomes disordered. A direct comparison of soft x-ray photoelectron spectroscopy (SXPS) and low energy electron diffraction (LEED) data collected from these surfaces enables the formulation of a microscopic model. This is the first time that such a mechanism has been established, which has implications for any chemical process in which atomic precision is desired, such as atomic layer epitaxy or atomic layer etching.

SXPS and LEED measurements were made at beamline UV-8a of the National Synchrotron Light Source. Additional LEED measurements were made in our own laboratory. The SXPS spectra were collected using a 3 m toroidal grating monochromator and an angle-integrating ellipsoidal mirror analyzer, as in our earlier studies [11,12,14,18,19]. The total instrumental resolution was better than 0.15 eV. Photon energies of 79 and 102 eV were used to excite the In $4d$ and As $3d$ core levels, respectively, so that the photoelectrons all had similar kinetic energies (~50 eV) and thereby probed the same portion of the near-surface region.

Single crystal InAs(001) wafers (n-type, carrier concentration $= 3.0 \times 10^{16}\ \mathrm{cm}^{-3}$) were prepared by repeated cycles of Ar^+ sputtering at 500 eV and annealing to about 420 °C. All I_2 exposures and measurements were performed with the sample at room temperature.

Iodine was produced from a solid-state electrochemical cell, as described previously [16]. It is based on a AgI pellet, with Ag foil and Pt mesh as the electrodes. The cell was operated between 140 and 160 °C. Exposures are reported in μA min, i.e., the time-integrated operating

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current, which measures the number of I^- ions that diffuse through the pellet. On the surface of the pellet, the atoms combine to form I_2. Note that there may also be some atomic iodine emitted from the pellet, but this would not affect any of our analysis or conclusions. We estimate that a 10 μA min exposure corresponds approximately to one I_2 molecule impinging on each surface atom.

LEED patterns were collected at each stage of the process. After sputtering and annealing, a pattern was obtained with fourfold symmetry in one direction and weak half-order streaky lines in the other, as shown in Fig. 1(a). This pattern is consistent with reports in the literature of a mixed $(4 \times 2)/c(8 \times 2)$ structure [20], and is indicative of an In-terminated reconstruction. As this surface was exposed to I_2, all of the LEED spots broadened. After an exposure of ~100 μA min, the higher-order spots faded away. At saturation (after ~600 μA min), a sharp 1×1 pattern was obtained, as shown in Fig. 1(b), whose spots were brighter than the first-order spots of the original clean surface, consistent with previous results [16]. After heating the sample to ~385 °C to remove all of the adsorbed iodine, the pattern shown in Fig. 1(c) was obtained, which is basically a 90° rotation of the original pattern. We interpret this to be a mixed $(2 \times 4)/c(2 \times 8)$ structure characteristic of a group V-terminated surface. The quality of this pattern was comparable to the original. When the $(2 \times 4)/c(2 \times 8)$ surface was exposed to I_2, the higher order spots quickly faded. After the largest exposures, the first-order spots also vanished, as shown in Fig. 1(d).

High-resolution In 4*d* and As 3*d* core-level spectra were collected after I_2 exposures ranging from 10 to 1000 μA min. Representative spectra, collected after 200 μA min exposures to both In- and As-terminated surfaces, are shown in Fig. 2. The spectra were numerically fit to a sum of Gaussian-broadened Lorentzian spin-orbit split doublets, as described in our previous work [11,12,14,16–19]. This procedure determines the binding energy shifts, areas, and Gaussian contributions to the full-widths at half maximum (FWHM) of each component. The Lorentzian FWHM's were fixed at 0.14 and 0.11 eV for In 4*d* and As 3*d*, respectively. The spin-orbit splitting and the branching ratio were fixed at 0.85 eV and 0.68, respectively, for In 4*d*, and 0.62 eV and 0.69, respectively, for As 3*d*.

The high-resolution SXPS spectra are used to identify the bonding configurations of the surface atoms. The chemically shifted components in the In 4*d* core-level spectra arise from InI and InI_2, i.e., In atoms with one or two iodine atoms attached. The binding energy shifts, relative to the bulk component, are 0.6 eV and 1.3 eV, respectively. Similarly, AsI and AsI_2 components with shifts of 0.7 eV and 1.6 eV, respectively, are identified from As 3*d* spectra collected from the I_2-reacted As-terminated surface.

On the In-terminated surface, InI forms when iodine bonds to a surface In atom. Since In is trivalent, surface InI is stable even if the surface dimer bond has broken. Furthermore, bonding of two I atoms to a single surface In is limited by repulsive interactions between neighboring

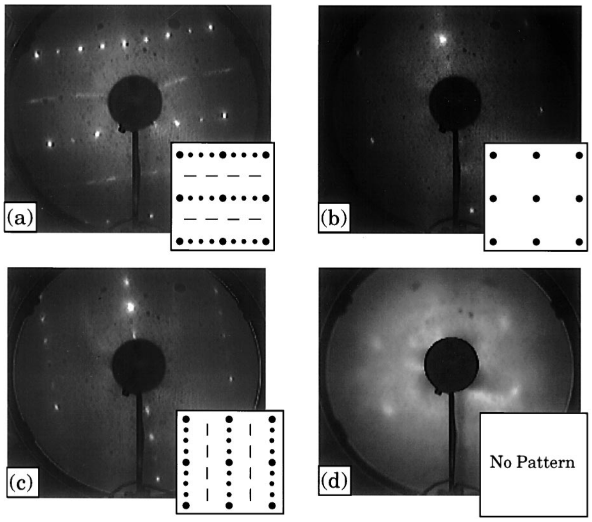

FIG. 1. LEED patterns collected from InAs(001) after (a) sputtering and annealing, which produces a mixed $(4 \times 2)/c(8 \times 2)$, (b) reaction with I_2, which forms a (1×1), (c) heating off the iodine, which produces a mixed $(2 \times 4)/c(2 \times 8)$, and (d) reacting with I_2, which removes the pattern. The electron beam energy was 30 eV in (a), (b), and (c), and 57 eV in (d). The insets show schematics of the observed patterns.

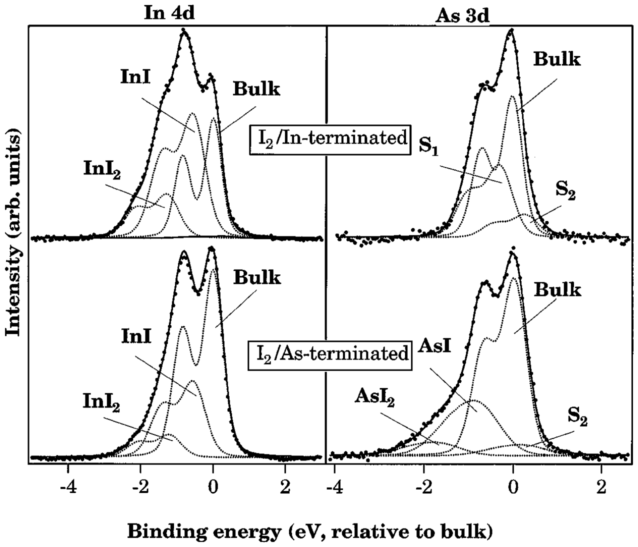

FIG. 2. Representative high-resolution SXPS spectra of In 4*d* and As 3*d* collected from In- and As-terminated InAs(001) after 200 μA min I_2 exposures. The raw data after background subtraction are shown as dots. The individual components of the numerical fits are shown as dashed lines. The solid lines are the sum of the fit components.

I atoms. Hence, the small amount of InI_2 detected is likely to have formed at defect sites.

The As 3*d* spectra collected from the reacted In-terminated surface contain components labeled S_1 and S_2. These components have binding energy shifts similar to the surface core level shifts (SCLS) of the clean surface [16], but have slightly larger Gaussian widths. The persistence of these SCLS components suggests that, on the In-terminated surface, the As atoms are not strongly affected by iodine adsorption.

The As 3*d* spectrum collected from the I_2-reacted As-terminated surface, however, contains only the S_2 SCLS component (in addition to the As iodide components). If iodine were to break an In-As bond in attaching to In, the As atom would then be bonded in a tricoordinate configuration. Group V elements are stable in such a configuration, as the two nonbonded electrons pair up. Such tricoordinate As defects, which have been reported following reaction of Cl_2 [11,12] and XeF_2 [18,19] with GaAs, have a similar binding energy shift to S_2. Although S_2 collected from the reacted As-terminated surface could also have a contribution from As in unreacted portions of the surface, it was not possible to obtain a good fit by including a component at the position of S_1. Thus, S_2 most likely corresponds solely to tricoordinate As defects produced by the reaction.

The results of the core-level fitting and LEED measurements can be summarized as follows. For the In-terminated surface, InI is the primary reaction product and no As iodides are formed. Thus, I_2 dissociates and bonds only to the outermost In atoms, forming an ordered overlayer. On the I_2-reacted As-terminated surface, both In and As iodides form, which indicates that In-As bonds are broken by the reaction. Such bond-breaking, which is a prelude to etching, causes the surface to become disordered. Thus, both LEED and SXPS show a clear difference in the behavior of the two surfaces when reacted with I_2. Because the difference is clear, and because we have microscopic chemical information about how the reaction proceeds, we can reach certain conclusions about the reaction mechanism.

In general, on reconstructed clean surfaces of III-V semiconductors, the group III element dangling bond orbitals are empty and the group V element dangling bond orbitals are full [21,22]. When a III-V surface is exposed to I_2, the interactions of the closed-shell I_2 molecular orbitals with the empty dangling bond orbitals are attractive, while the interactions with the filled dangling bond orbitals are repulsive. Hence, the surface group III atoms should be more reactive to I_2 than group V atoms.

The idea that group III elements are more reactive than group V elements is supported by previous work. A theoretical investigation determined that Cl_2 adsorption above the Ga dimers on Ga-terminated GaAs(001)-(4 × 2) occurs with no potential barrier, while the adsorption of Cl_2 on an As-dimer on As-terminated GaAs(001)-(2 × 4) is an activated process with an energy barrier of 0.9 eV [23]. The adsorption of Cl_2 to a second layer Ga atom, i.e., in a missing row, is exothermic with no potential barrier. These results thus suggest that molecular halogens would preferentially bond to the group III element on either group III-terminated or group V-terminated surfaces. This assertion is further supported by experimental investigations. Mokler *et al.* found that the sticking probability of Cl_2 on GaAs(001) was much higher for a Ga-terminated than for an As-terminated surface [24]. Liu *et al.* recently reported scanning tunneling microscopy (STM) studies of monoenergetic Br_2 adsorption on As-terminated GaAs(001)-(2 × 4) [25]. They collected images at a 0.039 ML coverage and concluded that Br atoms initially adsorb at second layer Ga sites.

Figure 3 shows an atomic-scale schematic of the In- and As-terminated surfaces. The structures on these surfaces are composed of arrangements of 4 × 2 (or 2 × 4) units, such as those shown. On the In-terminated surface, the outermost layer consists of In-In dimers and missing rows. In the missing rows, there are exposed second layer As atoms. On the As-terminated surface, the outermost layer consists of As-As dimers, and in the missing rows are exposed second layer In atoms. Based on the above considerations, the reaction of I_2 with InAs(001) would proceed as follows.

On the In-terminated surface, iodine simply attaches to the outermost In atoms. Since this process does not involve any disruption of the underlying lattice, a stable, ordered overlayer is formed which saturates at ~1 ML

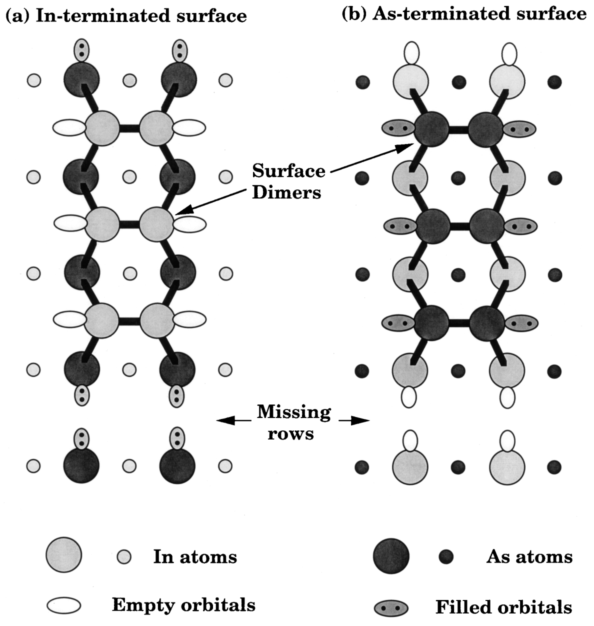

FIG. 3. Top view schematic of 4 × 2 and 2 × 4 units of the (a) In-terminated and (b) As-terminated (001) surfaces, respectively, showing the dimers and missing rows.

coverage. Thus, we observe primarily an InI component in the SXPS spectra and a sharp 1 × 1 LEED pattern. Note that the removal of the higher order spots does indicate that there was some lateral diffusion of surface atoms, as discussed in Ref. [16].

On the As-terminated surface, it is apparently more favorable for iodine to initially react with the second layer In atoms. Charge is transferred to iodine in forming a bond to In, some of which may come from the filled dangling bond orbital of the first layer As. This, in turn, makes the surface As atoms more reactive towards additional incoming I_2. When iodine attaches to both the surface As and second layer In, the In-As bond will break. This bond breaking begins the process of disordering the surface, which eventually will result in the removal of material in the form of volatile iodides. Note that, in contrast to the STM studies mentioned above [25], we cannot measure surfaces until they have adsorbed an appreciable amount of iodine since the core-level shifts are not detectable at a very low coverage. Thus, even at our lowest exposures, both In and As iodides are observed in the SXPS spectra. At the highest exposures employed here, the extent of the disorder is sufficient that the LEED pattern disappears. Note that this mechanism may not apply to all III-V materials, as a well-ordered overlayer was obtained from I_2-reacted GaAs(001)-$c(2 \times 8)$ [16], which should have a local structure similar to that of As-terminated InAs(001).

In summary, the adsorption of I_2 on In- and As-terminated InAs(001) was investigated with SXPS and LEED. The In-terminated surface passivates with ~1 ML of adsorbed iodine, forming a well-ordered structure. The As-terminated surface becomes disordered, in a manner suggestive of etching. A microscopic mechanism is proposed to explain this behavior, in which iodine initially attaches only to exposed In atoms. These results are consistent with theoretical and experimental investigations of halogen reactions with other III-V semiconductors. These considerations could be used to explain a large class of chemical reactions with binary compound surfaces, and could also form the basis for processing materials with atomic precision.

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