

High-Resolution X-ray Photoelectron Spectroscopy of Chlorine-Terminated GaAs(111)A Surfaces

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Oxide-terminated and Cl-terminated GaAs(111)A surfaces have been characterized in the As and Ga 3d regions by high-resolution, soft X-ray photoelectron spectroscopy. The Cl-terminated surface, formed by treatment with 6 M HCl(aq), showed no detectable As oxides or As⁰ in the As 3d region. The Ga 3d spectrum of the Cl-terminated surface showed a broad, intense signal at 19.4 eV and a smaller signal at 21.7 eV. The Ga 3d peaks were fitted using three species, one representing bulk GaAs and the others representing two chemical species on the surface. The large peak was well-fitted by the bulk GaAs emission and by a second doublet, assigned to surface Ga atoms bonded to Cl, that was shifted by 0.34 eV from the bulk GaAs 3d emission. The smaller peak, shifted by 2.3 eV in binding energy relative to the bulk GaAs Ga 3d signal, is assigned to Ga(OH)₃. The data confirm that wet chemical etching allows for the formation of well-defined, Cl-terminated GaAs(111)A surfaces free of detectable elemental As, that can provide a starting point for further functionalization of GaAs.

I. Introduction

The surface chemistry of gallium arsenide is poorly understood relative to that of silicon. Consequently, few, if any, wet chemical methods have been developed that can chemically passivate GaAs surfaces. The chemistry of the GaAs(100) face has received the most scrutiny in recent years.^{1–7} However, the polar GaAs(111)A (Ga-rich) face provides several advantages in developing wet chemical methods for producing surfaces with a low density of electronic defects. For many chemical etches, particularly oxidizing ones, the GaAs(111)A face exhibits the slowest etching,⁸ suggesting that manipulations of this face might provide the best opportunity for effective chemical removal of surface oxides without the introduction of new defects. Furthermore, unlike the mixed GaAs(100) face, the dangling bonds on the GaAs(111)A face are only Ga-derived and are normal to the surface plane, minimizing possible steric interactions between groups bound to these surface atop sites.

Etching GaAs(111)A with a dilute solution of HCl(aq) has been shown to produce a well-ordered surface terminated with Ga–Cl σ bonds.^{9,10} This Cl-terminated surface should provide an excellent platform for further chemical functionalization reactions. A complete picture of this starting surface is required to understand fully the subsequent functionalization chemistry of such systems. We describe the characterization of Cl-terminated GaAs(111)A surfaces, as well as the native oxide initially present on GaAs(111)A surfaces, based on information obtained using X-ray photoelectron spectroscopy (XPS) from aluminum anode and synchrotron soft X-ray sources. XPS data obtained from a laboratory-based X-ray source provided information on all of the detectable atoms present on the functionalized surfaces, while the high-resolution synchrotron data

provided detailed information on the oxidation state of the surface Ga and As atoms.

II. Experimental Section

A. Materials and Methods. n⁺-GaAs(111) wafers (325- μ m-thick) that had been polished on the (111)A face were obtained from AXT, Inc. (Fremont, CA). The wafers were doped with Si to a carrier concentration of 1.7×10^{18} cm⁻³. All solvents and chemicals for the surface functionalization reactions were used as received from Aldrich Chemical Corp. H₂O with a resistivity of > 17.8 M Ω cm, obtained from a Barnsted Nanopure system, was used at all times.

Prior to performing any surface chemistry, all samples were cleaned and degreased by successive rinses in H₂O, CH₃OH, acetone, 1,1,1-trichloroethane (TCE), acetone, CH₃OH, and H₂O. To form the Cl-terminated GaAs(111)A surface, samples were etched at room temperature for 5–30 min in a 1:1 (by volume) (~6 M) mixture of concentrated HCl(aq)/H₂O, and then were dried, without rinsing, under a stream of N₂(g).

B. Instrumentation. *1. XPS Measurements.* Preliminary spectroscopic data on functionalized GaAs(111)A surfaces were collected using an M-Probe XPS system that has been described previously.^{11,12} For these experiments, 1486.6 eV X-rays generated from an Al K α source illuminated the sample from an incident angle of 35° off of the surface. Photoelectrons emitted along a trajectory 35° off of the surface were collected by a hemispherical analyzer. After chemical functionalization, samples were inserted via a quick-entry load lock into the ultrahigh-vacuum (UHV) system and were kept at a base pressure of $\leq 1 \times 10^{-9}$ Torr. All samples were sufficiently electrically conductive at room temperature that no compensation for charging

effects was required. On each sample, a “survey” scan of core photoelectron binding energies from 1 to 1200 binding eV was collected to identify the chemical species present on the surface. Higher-resolution data were collected for atoms of interest, particularly those whose binding energy was too high to be examined with the synchrotron experiments, such as the Cl 2p and O 1s regions. Energies deduced from all of the XPS measurements are reported herein as binding energies.

2. SXPS Measurements. High-resolution soft X-ray photoelectron spectroscopy (SXPS) experiments were performed on beamline U4A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.¹³ The sample was introduced through a quick-entry load lock into a two-stage UHV system that was maintained at $\leq 1 \times 10^{-9}$ Torr. The beamline had a spherical grating monochromator that selected photon energies between 10 and 200 eV with a resolution of 0.3 eV. The selected excitation energy was not calibrated independently, because this study was principally concerned with shifts in core orbital binding energies relative to the bulk signals, as opposed to determination of absolute binding energies. Samples were illuminated at an incident energy of 90 eV, and the emitted photoelectrons were collected at normal to the sample surface by a VSW 100-mm hemispherical analyzer that was fixed at 45° off of the axis of the photon source. The energy resolution of the hemispherical analyzer was 0.1 eV. The beam intensity from the synchrotron ring was measured independently, and the data in each scan were normalized to account for changes in photon flux during the scan. No charging or beam-induced damage was observed on the samples during data collection. The limited range of excitation energies available at this beamline, although ideal for high-resolution core-level spectroscopy of surface species in both As 3d and Ga 3d regions, prevented the recording of survey scans of the surface that would have identified other atomic species present.

The escape depths of As and Ga photoelectrons were estimated using an empirical relationship described by Seah.¹⁴ For a photoelectron with kinetic energy E (in eV), with 0 eV the energy of an electron escaping from a pure element, the electron mean free path, λ_{el} , can be calculated from

$$\lambda_{el} = 0.41 a_{el}^{1.5} E^{0.5} \quad (1)$$

where λ_{el} and the atomic size of the element, a_{el} , are both in nanometers. For GaAs, a compound semiconductor made up of two atoms of similar size, an average size $a_{avg} = 0.283$ nm was calculated using

$$a_{avg} = \left(\frac{A_{avg}}{\rho_{GaAs} N_A} \right)^{1/3} \quad (2)$$

where A_{avg} is the average atomic weight of an atom in the GaAs lattice (72.322 g mol⁻¹), ρ_{GaAs} is the density of the crystal (5.319 g cm⁻³),¹⁵ and N_A is Avogadro's number. For a Ga 3d photoelectron with a kinetic energy of ~71 eV, eq 1 yields an electron mean free path of $\lambda_{Ga} = 0.52$ nm. For an As 3d photoelectron with a kinetic energy of ~49 eV, $\lambda_{As} = 0.43$ nm. Because the distance between two (111)A planes is 0.326 nm, the majority of the Ga and As 3d signals will therefore arise from the top two atomic layers of Ga and As, respectively.

Before fitting the data, a Shirley background was calculated and subtracted from the original spectra.^{16–18} A least-squares method was then used to fit the spectra to a series of Voigt functions. The Gaussian/Lorentzian ratio of the line shape was allowed to float but was constrained to be the same for all peaks in a given spectrum. The experimental line width was not

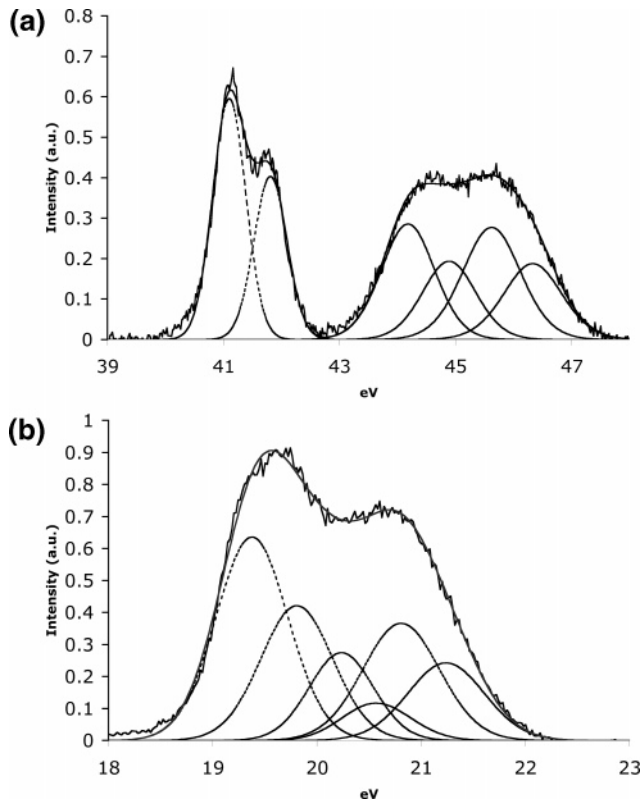


Figure 1. SXPS spectra (solid line) and Voigt function fits (dashed lines) of the native oxide for (a) the As 3d region and (b) the Ga 3d region. Each Voigt function fit includes both the $d_{5/2}$ and $d_{3/2}$ components of each signal. The binding energy values are reported for the $d_{5/2}$ components of the fit.

measured independently, but was estimated as ~0.32 eV on the basis of the photon resolution and detector resolution. States with short core-hole lifetimes will yield significantly broader, predominantly Lorentzian, line widths, whereas those with significantly narrower inherent line widths will appear predominantly with a Gaussian line shape. The line shapes of the As native-oxide peaks were ~90% Gaussian, while As line shapes for the Cl-terminated (111)A surface were >99% Gaussian. These results are consistent with significant broadening of the inherent Lorentzian line shape of the As oxide peaks.¹⁹

In accord with reported procedures, the As 3d spectra were fitted to a series of doublets to account for the $3d_{5/2}$ and $3d_{3/2}$ components of each peak. The peaks that composed each doublet were mutually constrained to have the same peak width, to be separated by 0.70 ± 0.01 eV, and to have an area ratio of $(1:0.667) \pm 0.01$.²⁰ A similar procedure was used for the Ga peaks, except that the energy separation between the $3d_{5/2}$ and $3d_{3/2}$ peaks was set to (0.44 ± 0.01) eV.²⁰ Binding energies for all spectra were referenced to the As $3d_{5/2}$ peak of GaAs, whose binding energy was taken to be 41.1 eV.

III. Results and Discussion

Figure 1a shows the SXPS data for the As 3d region prior to etching and Cl-termination of the GaAs surface. In addition to the energy-resolved spin-orbit doublet arising at 41.1 eV from the lattice As atoms of the bulk GaAs crystal, broader emissions were observed at 44.2 and 45.6 eV. These latter two peaks are assigned to As_2O_3 and As_2O_5 , respectively.²² The SXPS spectrum of the Ga 3d region (Figure 1b) showed a broad oxide peak at 20.81 eV that can be assigned to Ga_2O_3 .²² The broader feature at lower binding energy was fitted by peaks at 19.38

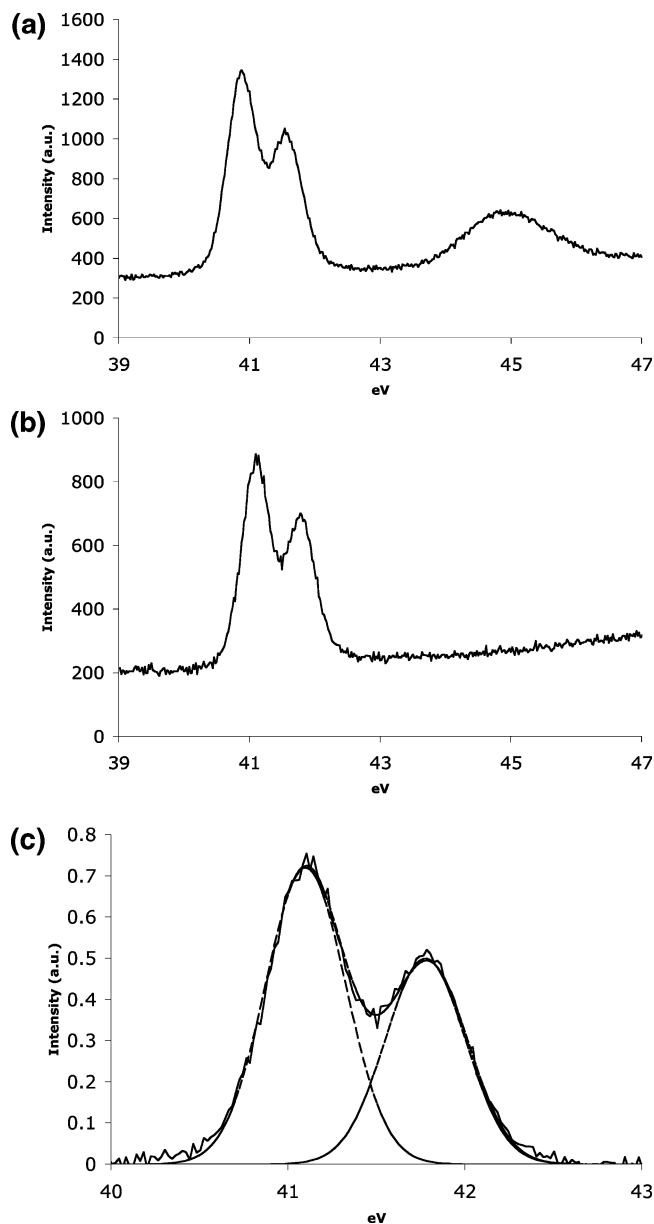


Figure 2. SXPS data for the HCl(aq) treated surfaces. (a) The As 3d region after 5 min in 6 M HCl(aq). (b) The As 3d region after 30 min in 6 M HCl(aq). (c) SXPS data (solid line) and calculated fits (dashed lines) for the As 3d spectrum of the Cl-terminated surface. No components other than the bulk As signal were evident.

and 20.24 eV, representing the bulk GaAs and Ga₂O signals, respectively. The coverage of the mixed oxide overlayer corresponded to 1.63 ± 0.25 equivalent monolayers.

Treating such oxidized GaAs(111)A surfaces in 6 M HCl(aq) for times as short as 5 min has been reported to form Cl-terminated GaAs(111)A surfaces.^{9,10} While etching for 5 min did remove all of the As₂O₅ from the surface, a significant amount of As₂O₃ oxide was still detectable using the very surface-sensitive SXPS method (Figure 2a). An observable amount of As₂O₃ was still present after etching the sample for 15 min. In contrast, Figure 2b depicts the As 3d SXPS data for the GaAs(111)A surface after a 30 min exposure to the HCl(aq) solution, in which no detectable oxide signals were observed to within the sensitivity of the SXPS instrumentation. Because a better Shirley background was obtained by omitting large regions that did not have any peaks, for this surface only the region known to contain the bulk GaAs and As⁰ (41.8 eV) peaks was fitted. After subtraction of the Shirley background from

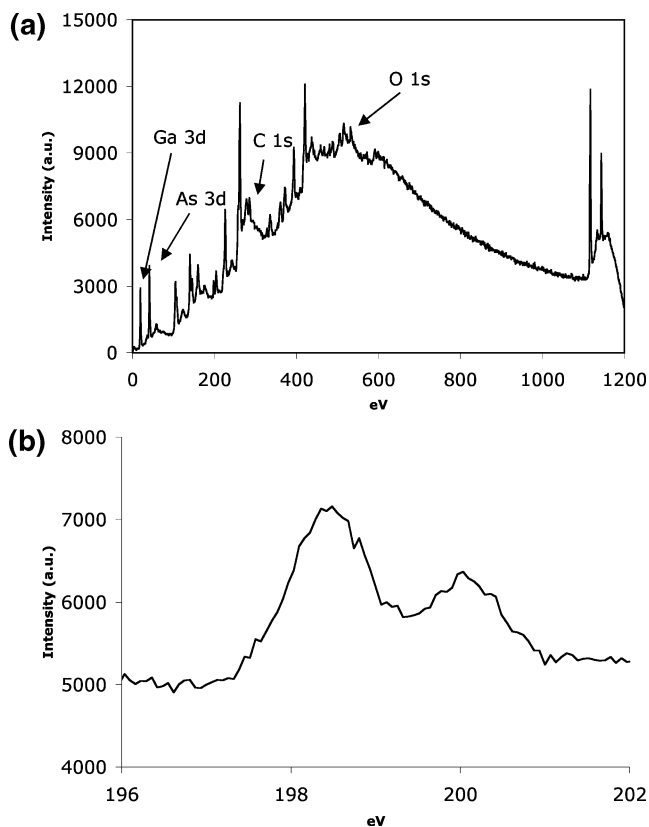


Figure 3. Al K α X-ray photoelectron spectra of the Cl-terminated GaAs(111)A surface prepared by a 30 min treatment in HCl (aq). (a) Survey scan from 1 to 1200 eV. The Ga 3d, As 3d, C 1s, and O 1s peaks are labeled. The Cl 2p peak is difficult to discern in the survey scan because of its close proximity to the As 3s peak at 204.7 eV. All other peaks are due to Ga and As photoelectron and Auger peaks. (b) Detailed scan of the Cl 2p region, showing the Cl 2p_{3/2} and 2p_{1/2} peaks.

this spectrum, the doublet peaks were each well-fitted by a single Voigt function (Figure 2c). Within the detection limits of the experiment, no elemental As was observed. As As⁰ is a potentially important trap state for carrier recombination, its absence is an important characteristic for the chemical preparation of surfaces having desirable electronic properties.

XPS survey scans of Cl-terminated GaAs(111)A surfaces showed the expected series of photoemission and Auger peaks arising from Ga and As (Figure 3a). Small O 1s (531.2 eV) and C 1s (284.6 eV) peaks were also observed. The Cl 2p (199.5 eV) peak was difficult to observe in the survey scan, due to its proximity to the As 3s (204.7 eV) signal,²¹ but the Cl 2p peak could be readily seen in a higher-resolution scan of the immediate area around 200 eV (Figure 3b). The Cl 2p_{3/2} and Cl 2p_{1/2} signals were also resolved from each other in this higher-resolution scan. Correcting for the relative sensitivity factors of Cl ($\sigma_{\text{Cl}} = 2.285$) and Ga ($\sigma_{\text{Ga}} = 1.085$), application of a simple substrate/overlayer model¹⁴ yielded a Cl coverage of 0.91 ± 0.12 equivalent monolayers. No Ga or As oxides were present in detailed scans of their respective 3d regions, indicating that the O 1s signal (0.56 ML) is primarily due to the observed Ga(OH)₃ as well as likely having a contribution from water and adventitious hydrocarbons that also contribute to the observed C 1s signal.

Etching with 6 M HCl(aq) for 30 min also led to the complete disappearance of the Ga 3d oxide signal and the appearance of a small, broad signal at 21.68 eV, i.e., 2.3 eV higher in binding energy than the Ga 3d signal in bulk GaAs (Figure 4a). The peak is not due to GaAsO₄, given the lack of a corresponding

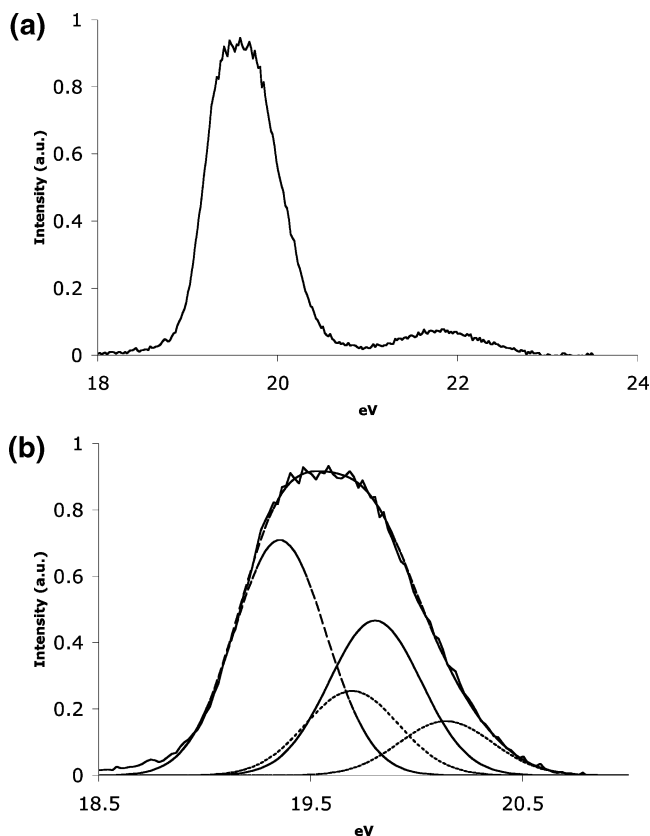


Figure 4. SXPS spectra of the Ga 3d region of the (111)A surface after 30 min in the HCl solution. (a) Raw data after Shirley background subtraction. The aqueous treatment has introduced a new peak at higher binding energy than the native oxides. (b) SXPS data (solid line) and Voigt function fits (dashed lines) of the bulk and Cl-bonded surface Ga species.

As signal 4.1 eV higher in binding energy than the bulk (Ga)-As peak (Figure 2b). The formation of Ga hydroxides has been observed during etching of GaAs in aqueous solutions.²² Thus, we assign this peak to Ga(OH)₃.

The remainder of the Ga 3d region was well-fitted using two peaks, one arising from the bulk signal at 19.36 eV and the second emission at 19.70 eV (Figure 4b). No Ga₂O or Ga₂O₃ signals were evident in the spectrum. The feature at 19.70 eV is assigned to Cl-bonded Ga on the GaAs(111)A surface. The lower binding energy of this peak relative to the binding energy of the Ga 3d emission from Ga₂O is consistent with expectations based on the smaller electronegativity of Cl relative to O. For comparison, the energy difference between the 2p photoelectron peaks of a Si⁺ bonded to O vs a Si⁺ bonded to Cl is 0.2 eV.²³ Assuming that the cross sections for photoemission from surface and bulk Ga atoms are the same, the ratios of the Ga peaks relative to the bulk Ga signal, in conjunction with the 0.52 nm escape depth of the Ga 3d photoelectrons at ~71 eV kinetic energy, yields a coverage of approximately 0.67 monolayers of Ga-Cl and 0.21 monolayers for the Ga(OH)₃ signal.²³ We suspect that the Ga(OH)₃ peak is possibly a contaminant on top of the Ga-Cl surface species, but cannot definitively evaluate the spatial distribution of these species from the available SXPS data. Regardless, we conclude that etching of GaAs(111)A for 30 min in 6 M HCl(aq) produces a well-defined Cl-terminated GaAs surface free of detectable elemental As and free of essentially all As and Ga oxides. Assignment of the peaks in this spectrum will aid in the characterization of surfaces formed by subsequent functionalization reactions, which will be discussed in forthcoming work.²⁴

IV. Conclusions

The photoelectron spectra of Cl-terminated GaAs(111)A have been measured using conventional and soft X-ray photoelectron spectroscopy. After treatment with 6 M HCl(aq), the presence of Cl atoms has been confirmed on the GaAs(111)A surface, and a binding energy of 19.70 eV, i.e., a shift of 0.34 eV from the bulk value, has been assigned to surface Ga atoms bonded to Cl. A 30 min treatment of the GaAs(111)A surface in 6 M HCl(aq) has been shown to yield a surface with a monolayer of Cl, while surfaces treated for only 5 min showed a significant amount of As₂O₃. The spectra also indicated that the surfaces were free of As⁰, to within the resolution of the SXPS experiment, suggesting that surfaces prepared by this method could provide an excellent platform for subsequent, well-defined, wet chemical functionalization reactions.

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