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Low-Temperature Chlorination of GaAs(100)

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The chemisorption and the reaction of chlorine and hydrogen chloride on the GaAs(100)-4 × 6 surface at 110 K are investigated using soft X-ray photoelectron spectroscopy which employs synchrotron radiation. At low exposures, Cl_2 and HCl dissociate and preferentially adsorb on the As atom, which causes As−Ga bond breakage to initiate chlorination of the Ga atom. As_xCl is proposed to form at initial chlorination, in which the Cl atom is bonded to a high coordination site. Subsequently, various $AsCl_x$ and $GaCl_x$ ($x = 1$, 2, and 3) species are formed on the GaAs surface, and their corresponding chemical shifts are assigned. At high exposures, chlorination of the GaAs surface is saturated, and the surface is mainly covered with physisorbed Cl_2 and HCl molecules. Synchrotron radiation on the chlorinated GaAs surface stimulates both the photodesorption of Ga and As chlorides and the photodissociation of physisorbed Cl_2 molecules. A potential route for anisotropic cryogenic etching of the GaAs surface by the chlorine-containing compound under photon irradiation is discussed.

1. Introduction

Chemically assisted dry etching of semiconductor materials is an important technology for future integrated optical and microelectronic devices. Chlorine-based etchants are often used in the fabrication of GaAs surfaces because of the high reactivity of chlorine with GaAs and the high volatility of the generated products. It is becoming important to understand the reaction mechanisms involved in the chemical etching of the processing technology applied to III−V semiconductor substrates. There have been many attempts to utilize various approaches and analytical techniques to develop a complete picture of the overall etching process on the surface. The reactions of III−V semiconductor surfaces with halogen have been comprehensively reviewed.[1,2] The present work is focused on the surface reaction of GaAs(100) with chlorine. Although the GaAs(100) surface is known to present several reconstructions with different stoichiometries depending on the surface preparation process, it is the most commonly used surface in manufacturing opto-microelectronic devices.

The adsorption and the reaction of Cl_2 and HCl gases on GaAs have received great attention during the past decade. The previous studies were mostly focused on understanding the volatility of the reaction and the surface products formed by the adsorption and reaction of Cl_2 on GaAs at room or elevated temperatures. Because molecular Cl_2 is sufficiently reactive with GaAs, thermal reaction will result in an isotropic surface topography during the etching process.[3] It has been reported that cryogenic cooling of the substrate during the etching process can enhance etching anisotropy by suppressing thermally initiated reactions.[4,5] A detailed study of chlorine-based molecules on GaAs at low temperature is thus needed for better understanding the effect of the substrate temperature on the surface chlorination during the etching process.

It is known from the previous studies of the adsorption of Cl_2 on GaAs that Cl_2 dissociatively adsorbs on GaAs at room temperature. However, there is a controversy on the exact site where Cl adsorption takes place. It was concluded from different experimental results that chlorine may preferentially adsorb on either Ga or As or form nonselective bonding with both As and Ga.[6−12] A plausible explanation on the controversy is that the extent of Cl bonding to Ga or As is dependent on the starting property of the GaAs surface, such as the surface composition and imperfection.[13] Since Ga and As chlorides are volatile, they may desorb from the surface after being formed at dosing temperature during Cl_2 exposures. The surface composition, after GaAs is exposed to Cl_2, may thus vary accordingly at different substrate temperatures. In addition, the kinetics of the GaAs etching reaction is influenced to some extent by the temperature-dependent adsorption and desorption rate of the Cl_2 precursor.[14] Therefore, a critical factor in the determination of the preferential site of Cl adsorption on the GaAs surface is to keep the substrate below the desorption temperature of the reaction products.

In the study of the GaAs etching by Cl_2 and HCl, it was found that Cl_2 etches at temperatures as low as 50 °C, whereas HCl does not etch the surface up to 250 °C.[15] In a recent study using molecular beam scattering techniques, Su et al. found that HCl etches GaAs at a measurable rate only at temperatures above 670 K.[16] It was also concluded that GaAs etching by Cl_2 is controlled by the kinetics (formation/desorption) of the Ga removal from the surface as $GaCl_3$ while etching by HCl is limited by As evaporation as As_2. It is of interest to know the difference in the reactivity on GaAs between HCl and Cl_2, which may be derived from the analysis of the surface composition after the chlorination takes place.

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On the basis of the latent heat of vaporization, Furahata et al. suggested that the etching rate of GaAs by Cl_2 was limited by the desorption process of $GaCl_3$ at temperatures below ~423 K.[17] The etching rate, however, can be promoted by stimulating the surface via bombardment with high-energy ions, electrons, or photons.[18−25] In general, the device surface suffers from the damage induced by high-energy particle bombardment. On the other hand, the laser-driven chemical etching reaction of GaAs has been demonstrated as a damage-free method for low-temperature selective patterning of the III−V semiconductor.[4] However, etching with laser wavelengths longer than 193 nm (ArF) imposes restrictions with respect to the spatial resolution because of the diffraction effect. An extension of these studies to shorter wavelengths is thus desirable because the diffraction limitations on the spatial resolution are less stringent at short wavelengths.[26] Furthermore, many etching gases, adsorbates, and reaction intermediates and products have high adsorption cross sections in VUV and soft X-ray regions such that an increase in the excitation efficiency can be expected. Compared to conventional VUV light sources, synchrotron radiation (SR) offers the advantages of a continuum of wavelengths up to high energies, a small divergence, and a high intensity. Therefore, it is regarded as an ideal light source for the desired improvements on the structural resolution and efficiency.

Soft X-ray photoelectron spectroscopy employing synchrotron radiation is well-suited for the identification of the surface products formed upon Cl_2 chemisorption, as the core-level binding energy shifts associated with halogen are large enough to be easily resolved.[27] In this study, XPS is used to study the surface reaction of GaAs with Cl_2 and HCl at a temperature as low as 110 K. At low coverage, chlorine first reacts with the more reactive As atoms on the GaAs surface to form As chlorides. It results in bond breaking of As−Ga, which subsequently allows Cl_2 molecules to react with Ga atoms and to form Ga chlorides at high exposures. In contrast to room-temperature chlorination, the GaAs surface is saturated at 110 K with the formation of $GaCl_x$ and $AsCl_x$ ($x = 1-3$) at high Cl_2 dosage, and physisorbed Cl_2 molecules accumulate on the surface. Under the irradiation of the unmonochromatized synchrotron radiation (i.e., zeroth-order or white light), the dissociation of physisorbed Cl_2 molecules can be initiated to further chlorinate GaAs. Because the thermally initiated reaction and desorption can be suppressed at low temperature, the SR irradiation stimulates the desorption of Ga and As chlorides and provides a potential route to achieve anisotropic etching with a high spatial resolution on the GaAs surface substrate.

2. Experimental Section

Experiments are performed in a UHV chamber equipped with a quadrupole mass spectrometer, LEED, and CLAM II electron energy analyzer. The XPS spectra are carried out at 6m LSGM and HSGM beamlines of SRRC (Synchrotron Radiation Research Center, Taiwan). The incident angle of photons to the surface normal was 55°, and photoelectrons were collected with the electron analyzer normal to the sample surface. The sample can be cooled to 110 K with liquid nitrogen and heated by resistive heating. The GaAs(100) sample (Si-doped n-type, $\sim 1.2 \times 10^{18}/cm^3$) is obtained from American Xtal Technology and is cleaned by Ar^+ bombardment (500 eV) with the ion beam at a 45° incident angle in UHV. Following the Ar^+ bombardment, the sample is annealed to ~850 K. A 4 × 6 LEED pattern is observed, which is characteristic of a Ga-rich GaAs(100) surface.[28] Cl_2 and HCl gases are introduced into the GaAs(100) surface by the background dosing through a leak valve.

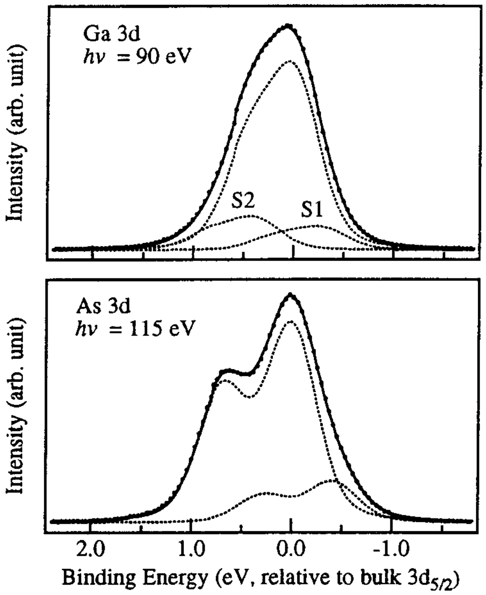


Figure 1. Soft X-ray photoelectron spectra of Ga and As 3d, collected from a clean GaAs(100)-4 × 6 surface at 110 K. The photon energy used to collect these spectra is 90 eV for the Ga level and 115 eV for the As level. The dots represent the collected data after background subtraction, the solid line is the curve fit to the data, and the various components are shown in dash lines. Two SSCLs (S1 and S2) are obtained for Ga 3d and one for As 3d.

All XPS spectra are taken at a sample temperature of 110 K. Due to the adsorption of Cl_2 on GaAs, the Fermi-level movement causes a change in the kinetic energy of photoelectrons. The binding energies in the collected spectra are referred to as the VBM (valence band maximum) levels, and then chlorine-induced chemical shifts in Ga and As 3d are presented with respect to the substrate peaks. The collected spectra are numerically fitted with Gaussian-broadened Lorentzian spin−orbit doublets, after Shirley background subtraction with a third-order polynomial to each side of the peak.[29] The spin−orbit splitting values of $3d_{3/2}$ and $3d_{5/2}$ are 0.45 eV for Ga and 0.69 eV for As.

The VUV and soft X-ray white beam used in this study is an unmonochromatized synchrotron radiation (zeroth-order light) via a reflection from a 900 lines/mm gold-coated grating with a grazing incident angle of 10°. The SR white beam has a photon energy distribution from ~20 to ~200 eV. The beamline is described in detail elsewhere.[30] The temperature increase, as monitored by a thermocouple, in the substrate during SR irradiation is negligible.

3. Results and Discussions

Figure 1 shows the XPS spectra of Ga and As 3d on a clean GaAs(100)-4 × 6 surface, measured with photon energies of 90 and 115 eV, respectively. The best fits were achieved with branching ratios of $3d_{3/2}$ to $3d_{5/2}$ components being 0.63 for Ga and 0.66 for As and a Lorentzian width of 0.16 ± 0.02 eV. The surface-shifted core levels (SSCL) obtained from our data fitting are −0.26 and +0.43 eV for Ga 3d and −0.44 eV for As 3d, compared to the substrate peaks. The intensity ratios of two Ga SSCLs to bulk are about 0.12 (S1) and 0.18 (S2). In the As 3d spectrum, the intensity of SSCL is about 0.20 of the bulk contribution. These values vary slightly for each cycle of surface cleaning by Ar^+ bombardment and annealing because of the sensitive temperature dependence of the GaAs(100) surface composition. There is a slight difference between previously reported values and our fitted results in the Ga and

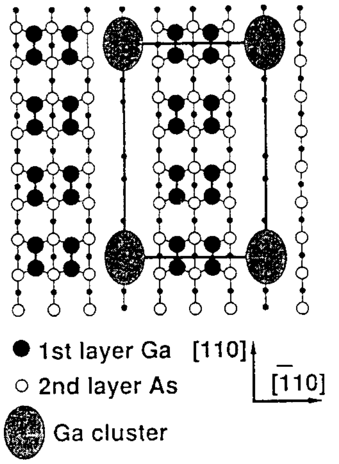


Figure 2. Proposed structure model for the GaAs(100)-4 × 6 surface (after ref 33). The 4 × 6 phase is the Ga-rich 4 × 2 phase with Ga cluster orderly distributed on the surface, which consists of two Ga dimers on the top layer.

As 3d surface-induced shifts and the surface composition ratio.[28,31,32] Given the complex nature of the GaAs(100) reconstruction surface, no attempt is made to interpret the origin of these differences. However, the surface-induced shifts determined in our data fitting are to ensure that the unreacted surface atoms are adequately presented in the fits to the spectra for the surfaces exposed to chlorine.

The lone peak from the surface As atom exhibits an electron-acceptor character with a −0.44 eV shift. Two surface contributions (S1 and S2) for the Ga 3d are attributed to the two kinds of surface Ga atoms present in two different surface reconstruction domains.[28] Based on a MBE-STM study, a 4 × 6 reconstruction on GaAs(100) was proposed as shown in Figure 2. The GaAs(100)-4 × 6 surface structure accommodates a periodic array of Ga clusters at the corner of 4 × 6 unit on the top of a 4 × 2 phase with Ga dimers.[33] The cluster size was estimated to be about 6 or 8 atoms on average. Each of the Ga atoms in the dimer bonds directly to the As atom (an electron acceptor). It is therefore proposed that the +0.43 eV shift (S2) peak is contributed from the dimeric Ga atom on the surface, which lies on its usual electron-donor position.[32] The binding energy of the −0.26 eV shift (S1) is thus attributed to the Ga atom in the cluster. The surface Ga atom (S1) is shifted toward a lower binding energy than the bulk atoms. It indicates that only a small amount of charge is transferred from the bulk and is in agreement with a cluster configuration proposed by the model. Assuming that the amount of surface Ga is proportional to its 3d photoelectron intensity, the intensity ratio of S1 to S2 is 0.67. This value is close to the ratio (0.5−0.67) of the number of Ga atoms in the clusters to that in dimers of the 4 × 2 phase, as proposed by the model shown in Figure 2.

The chlorine-induced Ga and As 3d chemical shifts on the GaAs surface that is exposed to 6.0 langmuirs of Cl_2 at 110 K are shown in Figure 3. For simplicity and clarity, only the spectra with the $3d_{5/2}$ components are presented here. They are obtained after $3d_{3/2}$ parts are numerically removed from the collected 3d spectra. In the spectrum of As 3d, there are three well-resolved features with chemical shifts peaked at 1.38, 2.34, and 3.43 eV higher in binding energy than the substrate peak. These peaks are assigned to AsCl, $AsCl_2$, and $AsCl_3$ surface species, respectively. The chlorine-induced chemical shifts of As 3d for AsCl and $AsCl_2$ species are much higher than the values reported previously (0.5−0.7 eV for AsCl and 1.3−1.7 eV for $AsCl_2$).[6,28,29,34,35] The chemical shift for $AsCl_3$ has never been assigned before. In this study, the GaAs sample is cooled to 110 K before being exposed to chlorine, while in the previous studies the GaAs sample was held at room temperature. The arsenic chlorides formed on the GaAs surface under chlorine exposure should remain on the surface when the sample is kept below their desorption temperatures. Three well-resolved As 3d peaks thus correspond to three different kinds of As chlorides formed at low temperature. On the other hand, when the surface is exposed to chlorine at room temperature, some of the reaction products may desorb from the surface because of their low desorption temperatures. The etching of the GaAs sample by Cl_2 may thus lead to the formation of a rough surface at room temperature and result in an As 3d spectrum which has a broad tail at the high binding energy side. The broad tail may cause difficulty and uncertainty in determining the exact chemical shift of As from an etched GaAs surface.

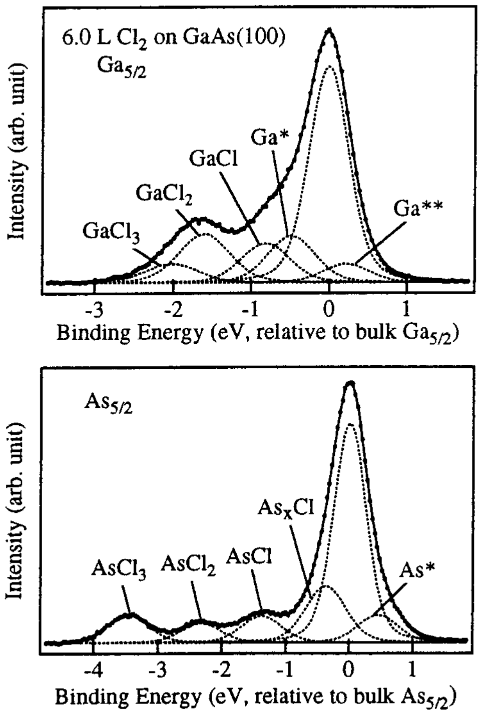
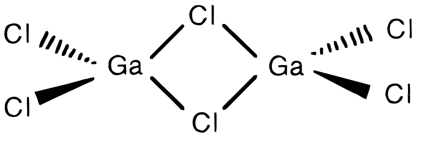


Figure 3. Soft X-ray photoelectron spectra of Ga and As $3d_{5/2}$ collected from the GaAs (100)-4 × 6 surface exposed to 6 langmuirs of Cl_2 at 110 K. The spectra are obtained by numerically removing the $3d_{3/2}$ component. Refer to the caption of Figure 1 for details.

The withdrawal of the charge changes the potential felt by the core electrons and causes a shift in the binding energy. In agreement with the fact that oxygen and chlorine have similar electronegativities, the observed As chemical shift of 3.43 eV is close to the value (3.2 eV) obtained for the native As(+3) oxide (As_2O_3) on GaAs.[36] This shift is thus attributed to the contribution of $AsCl_3$. Further, the core-level chemical shift usually increases in a linear fashion with the number of the attached halogens.[1] This makes the identification of chemically shifted core-level components straightforward. The chemical shifts of As for AsCl and $AsCl_2$ are expected to be about one-third and two-thirds of that for $AsCl_3$, respectively. The obtained values of 1.38 and 2.34 eV are thus assigned to the contribution of AsCl and $AsCl_2$ species.

The difference in the As chemical shift between $AsCl_3$ and $AsCl_2$ (1.09 eV) is significantly greater than that between $AsCl_2$ and AsCl (0.96 eV). It is expected that the consecutive difference in chemical shifts between two As chlorides ($AsCl_x$, $x = 0-3$) is nearly constant or decreases slightly with the increase of the number of halogen atoms attached to the As atom. The observed larger difference in the As chemical shift between $AsCl_3$ and $AsCl_2$ implies that, when GaAs is exposed to Cl_2, "individual" $AsCl_3$ molecules are formed and weakly adsorb (physisorb) on the surface substrate at low temperatures. The As atom in the "individual" $AsCl_3$ molecule is positively charged because of the withdrawal of electrons by the three attached chlorine atoms without electronic (charge) buffering from the substrate. The weakly adsorbed $AsCl_3$ molecules desorb from the surface at temperatures as low as 170 K, consistent with the previous TPD results.[8] On the other hand, both AsCl and $AsCl_2$ are chemically bonded to the substrate. Electronic buffering from the substrate is expected to take place on these structures.

Regarding the chemical shifts of the chlorinated Ga atoms, a good fit can be obtained for the Ga 3d spectra by including three reaction components with chemical shifts of 0.80, 1.58, and 2.02 eV, as shown in Figure 3. These peaks are attributed to Ga chlorination products of GaCl, $GaCl_2$, and $GaCl_3$ on the surface. In a previous XPS study, a similar Ga 3d spectrum was obtained on the GaAs(110) surface that was exposed to Cl_2 at room temperature.[37] Their values of the Ga chemical shifts are significantly different from our reported ones. The main difference may originate from an assumption taken in the previous data fitting that the desorption of $GaCl_3$ occurred at room temperature, such that $GaCl_3$ did not accumulate on the surface. Other TPD results showed that $GaCl_3$ was formed on the GaAs surface after the adsorption of Cl_2, of which some can exist on the surface at room temperature.[8] Therefore, the $GaCl_3$ component needs to be included in the fitting of the collected spectra of the GaAs surface exposed to Cl_2 at 110 K, which is below the onset temperature, ~230 K, of $GaCl_3$ desorption. The 2.02 eV shifted feature for $GaCl_3$ persists on the surface when the surface is heated to the room temperature, consistent with TPD results. Compared to $AsCl_3$, the product $GaCl_3$ has higher desorption temperature on the GaAs surface. It may be due to the presence of an empty sp^3 orbital in the Ga atom of $GaCl_3$, which can form a dative bond with the substrate to release the positive charge generated by three attached Cl atoms of high electronegativity. There is another possible reason for the higher desorption temperature of $GaCl_3$. The molecule may be formed in a configuration as a discrete dinuclear species, as found in the crystal halides.[38,39] The configuration of dinuclear $GaCl_3$ with a coordination number of 4 is shown below.



To achieve good fits to the collected Ga and As 3d spectra of the chlorinated GaAs surface, it is necessary to include the components with shifts in binding energies from the substrate peak of −0.44 eV (As*) for the As atom and of −0.26 (Ga**) and 0.43 eV (Ga*) for the Ga atom. As shown in Figure 1, these shifts in binding energy are due to the presence of atoms on the surface and were labeled as the SSCL components. Similar persistence of SSCL was also seen for the GaAs surfaces exposed to XeF_2 and to Cl_2.[37,40] They were attributed to Ga and As atoms generated in the substrate with a tricoordinate configuration as a result of bond breaking during the halogenation, which have similar binding shifts as the surface-induced chemical shifts. Tricoordinated atoms are buried in the chloride layer and the substrate interface, where the chlorination reaction occurs, and they are continuously created and removed as the chloride layer grows. The intensity of the component (Ga**) at the chemical shift of −0.26 eV, assigned as due to the presence of the surface Ga cluster, decreases with increasing chlorine exposures, although a certain amount of Ga clusters persists at the saturation coverage. This indicates that the Ga atoms inside the cluster may be inert to further chlorination while those on the outside are subject to it.

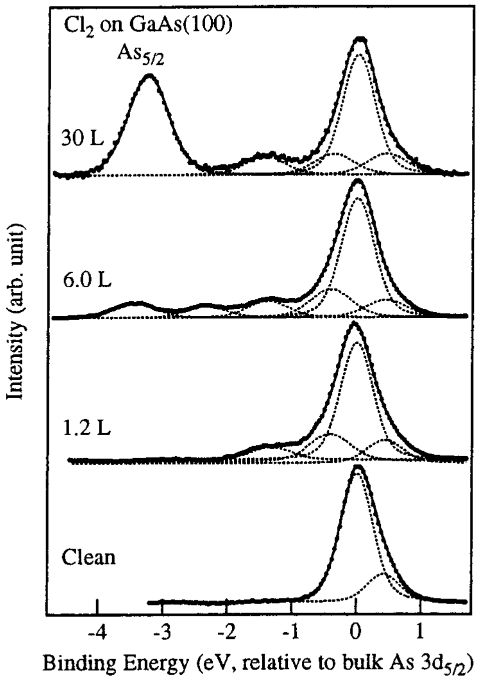


Figure 4. Soft X-ray photoelectron spectra of As $3d_{5/2}$ collected from the GaAs (100)-4 × 6 surface exposed to various amounts of Cl_2 at 110 K. The spectra are obtained by numerically removing the $3d_{3/2}$ component. Refer to the caption of Figure 1 for details.

Figure 4 and Figure 5 show the spectra of As and Ga $3d_{5/2}$ of the GaAs surface with various Cl_2 exposures at 110 K. At low Cl_2 exposures ($\leq$1.2 langmuirs), the development of new chlorine-induced chemical shifts is only observed in the As 3d spectrum, whereas the binding energy of the surface Ga 3d electron remains essentially unchanged. This indicates that during the initial chlorination the Cl_2 molecule reacts with the As atom on the surface to form As chlorides. The preference of Cl bonding to the As atom may be due to the reactive property of the filled dangling bond of the surface As atom with chlorine, as compared to that of the empty dangling bond of the surface dimer Ga atom. The preference of initial chlorination on the As adatom supports the notion that Cl_2 may be first dissociated at an electron-rich Lewis-base site.[41] On the basis of comparisons with results from the tight-binding calculation of the valence-band local density of states, it was concluded that after Cl_2 adsorption on GaAs(110) Cl atoms bond exclusively in the atop site to the As anions and not to the Ga cations.[10]

The As component with a ~0.4 eV chemical shift is the first feature to appear at initial chlorination with low Cl_2 exposures, prior to that peaked at 1.38 eV (AsCl). The 0.4 eV shifted feature is attributed to the formation of As_xCl in which the chlorine atom adsorbs at a high coordinate site on the As atom layer, instead of the on-top site to form AsCl species. The high coordinate site is favorable for the withdrawal of electrons from several As atoms to the Cl atom. Considering that the As 3d chemical shift of 0.4 eV is only about one-fourth of that of AsCl (1.37 eV), $AsCl_4$ is the most possible one of all the high coordinate configurations that may form on the surface. The

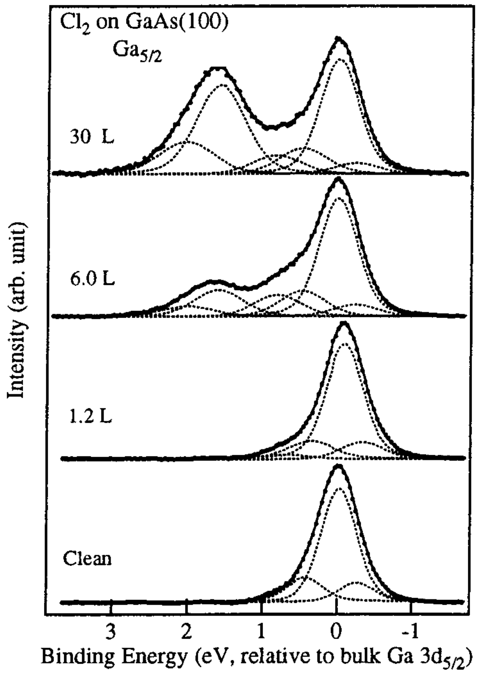


Figure 5. Soft X-ray photoelectron spectra of Ga $3d_{5/2}$ collected from the GaAs (100)-4 × 6 surface exposed to various amounts of Cl_2 at 110 K. The spectra are obtained by numerically removing the $3d_{3/2}$ component. Refer to the caption of Figure 1 for details.

chlorine-induced chemical shift of 0.4 eV with respect to the bulk As position was also obtained on GaAs(110) at room temperature.[6]

After the presence of As_xCl, AsCl(+1) species begins to form on the surface by further chlorinating As_xCl at increasing Cl_2 exposures. At this stage, the Cl atom is bonded on the top of one As atom (the on-top site). Chlorination of the more reactive As component on the GaAs surface to form AsCl results in breaking of the Ga−As bond and subsequently allows Cl_2 molecules to react with Ga atoms to form Ga chlorides at higher Cl_2 coverages. The Ga and As components on GaAs then proceed to form higher chlorides step by step, as shown in Figures 4 and 5.

The previous TPD results showed that the desorption of GaCl, As, and As_x clusters, but not of AsCl, was observed on the GaAs surface with low Cl_2 exposures.[7] The GaCl layer on the surface was proposed to be preferentially formed at early chlorination at 85 K. However, our XPS data show that, instead of Ga chlorides, As_xCl and AsCl are formed on the surface during the initial chlorination at 110 K. The desorption of GaCl rather than AsCl may be due to the slightly stronger Ga−Cl bond (4.99 eV), compared to the As−Cl bond (4.69 eV). This implies that, during thermal desorption, the Cl atom in the As_xCl or AsCl species is transferred to the Ga atom to form gaseous GaCl species, which desorbs along with As or As_x clusters.

Only a trace amount of $AsCl_2$ was found on the surface at high Cl_2 coverages (30 langmuirs) as shown in Figure 4. This means that $AsCl_2$ is a very reactive intermediate species, which can be easily further chlorinated to form $AsCl_3$. Among the Ga chlorides, $GaCl_2$ is the major reaction product at high Cl_2 exposures at 110 K and is chemically more stable than $AsCl_2$. It was proposed that $GaCl_2$ exists in a form of $-AsCl-GaCl_2$ on GaAs(110) at room temperature, based on the observation of equal amounts of $GaCl_2$ and AsCl on the surface.[37] It is obvious in our study that the amount of $GaCl_2$ is much greater than that of AsCl at high exposures, and $GaCl_2$ may exist in the manner of $Cl_2Ga-GaCl_2$ with a Ga−Ga bond.[38,39] The Ga dimer structure on the GaAs(100) surface facilitates the formation of Ga_2Cl_4 during the chlorination without breaking the Ga−Ga bond.

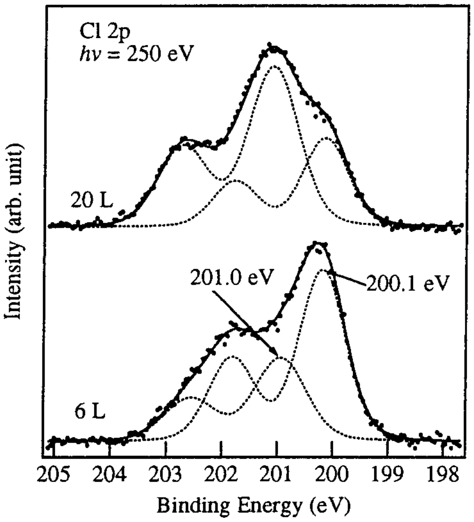


Figure 6. Soft X-ray photoelectron spectra of Cl 2p collected from the GaAs (100)-4 × 6 surface exposed to 6 and 20 langmuirs of Cl_2. The photon energy used to collect these spectra is 250 eV. Refer to the caption of Figure 1 for details

Figure 6 shows the spectra of Cl 2p taken from the chlorinated GaAs surface after Cl_2 exposures at 110 K of 6 and 20 langmuirs. A photon energy of 250 eV was used in the XPS measurement of Cl 2p, and a splitting of 1.6 eV and a branching ratio of 0.5 were used in the data fitting. There are two Cl $2p_{3/2}$ features with the binding energies of 200.1 and 201.0 eV, which are attributed to the Cl atom in the Ga and As chlorides and in the molecularly physisorbed Cl_2, respectively. Because of the accumulation of physisorbed Cl_2, the intensity of the component at the binding energy of 201.0 eV increases with the increase of Cl_2 exposures without reaching a saturation. It is difficult to estimate the exact thickness of the saturated chlorinated GaAs layer by calculating the attenuation of the photoemission intensity of the bulk Ga and As 3d, due to the presence of the physisorbed Cl_2 overlayer. With the exposure of GaAs to Cl_2 of more than ~30 langmuirs, Cl_2 molecules physisorb on the chlorinated GaAs surface without further chlorination. When the sample surface is heated to 140 K, the physisorbed Cl_2 molecules may either desorb from the surface or dissociate to grow more chloride layers.[42]

Figure 7 shows the Ga and As 3d photoemission spectra after GaAs is exposed to various amounts of HCl at 110 K. At a low HCl exposure of 0.8 langmuir, new chemical shift features appear clearly in As 3d spectrum, whereas the Ga 3d spectrum is almost unchanged, as compared to the spectra obtained from the clean surface. This indicates that HCl preferentially adsorbs on the As atom of the GaAs(100)-4 × 6 surface at low coverages, as is the case with Cl_2. A reaction model has been proposed, in which HCl was assumed to dissociatively add across Ga−As back-bonds at dimer vacancies on the GaAs surface at 85 K, with As bonding to H and Ga bonding to Cl. The model is based on an EELS study in which the As−H stretching mode was observed.[43] However, our XPS data show that both H and Cl atoms selectively bond to As atoms at the low exposure as shown in Figure 7, presuming that HCl dissociatively adsorbs on the GaAs surface. At high HCl exposures, chemical shifts due to the formation of the reaction products appear at the high binding energy side of the bulk peak for both Ga and As components. The collected Ga and As 3d

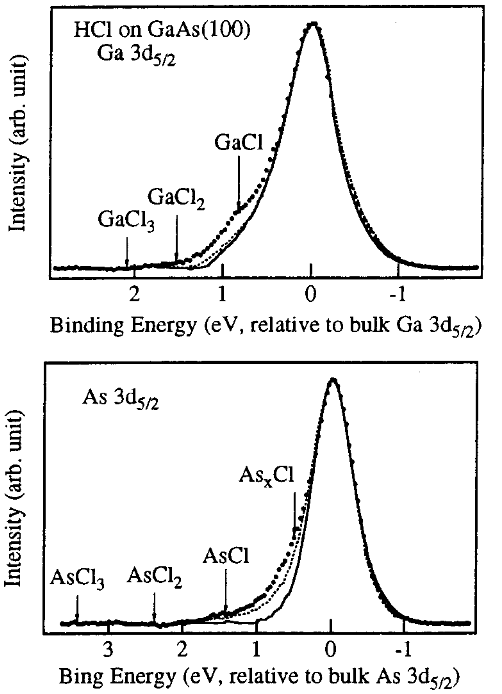


Figure 7. Comparison of soft X-ray photoelectron spectra of Ga and As $3d_{5/2}$ collected from a clean GaAs (100)-4 × 6 surface (solid line) with that of the GaAs surface exposed to 0.8 langmuir (dash line) and 4.0 langmuirs (dotted line) of HCl at 110 K. The spectra are obtained by numerically removing the $3d_{3/2}$ component.

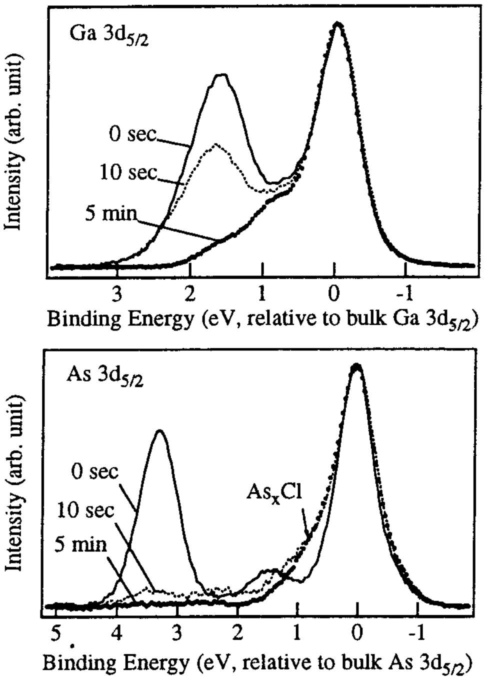


Figure 8. Soft X-ray photoelectron spectra of Ga and As $3d_{5/2}$ collected from a GaAs (100)-4 × 6 surface that is exposed to 6 langmuirs of Cl_2 and then irradiated by a SR white beam with the flux of ~1.1×10^{15} photons/s for various amounts of time. The sample current due to the emission of photoelectrons induced by SR irradiation is ~1.1 μA. The spectra are obtained by numerically removing the $3d_{3/2}$ component.

spectra are not deconvoluted into the individual reaction products, due to the complication of the possible contributions from both the Ga−H and the As−H bonds produced from the dissociation of HCl. The chemisorption of HCl on GaAs(100) is saturated up to the exposure of 4 langmuirs. Heating the sample to 450 K to desorb hydrogen leaves chlorides on the surface.[44] The Ga and As 3d spectra obtained after the sample being heated to 450 K are similar to the ones observed from Cl_2 adsorption, with chemical shifts corresponding to GaCl and As_xCl, respectively.

Contrary to that observed for the adsorption and reaction of Cl_2 on GaAs, no highly chlorinated Ga or As species ($AsCl_x$ and $GaCl_x$, $x = 2$ and 3) was found during the adsorption of HCl on GaAs. The GaAs surface is thus passivated against further reaction with HCl. The passivation is presumed as via the dissociative adsorption of HCl with the formation of AsCl, GaCl, and As and Ga hydrides. Since the etching involves the dissociative adsorption of the etchant molecules, the difference in the reactivity between Cl_2 and HCl on the GaAs surface may be due to the difference in their bond dissociation energies (E_{dis} = 4.48 eV (H−Cl) and 2.56 eV (Cl−Cl)). This explains why HCl does not etch GaAs up to 250 °C at which the surface GaCl species starts to desorb from the surface, whereas Cl_2 etches at a temperature as low as 50 °C.[16]

Figure 8 shows the Ga and As 3d photoemission spectra of GaAs after the sample is exposed to 6.0 langmuirs of Cl_2 at 110 K, followed by the irradiation of SR white light. The photon flux of the white beam is estimated to be about 1.1×10^{15} photons/s at a slit width of 80 μm when the electron current of the ring is at ~100 mA. The irradiated area on the surface is about 30−40 mm^2, and the sample current due to the emission of photoelectrons induced by SR irradiation is ~1.1 μA. As shown in Figure 8, most of the $AsCl_3$ species desorbs from the surface after a 10 s SR irradiation, whereas only less than half the amount of $GaCl_2$ and $GaCl_3$ desorbs. As the SR irradiation period is increased, all of the $AsCl_x$ ($x = 1-3$) species desorb from the surface, and As_xCl is the only As compound left on the surface. The amount of As_xCl increases when the sample is irradiated because of the formation of an etched and rough surface due to the desorption of Ga and As chlorides. SR irradiation also initiates the photodissociation of a fraction of Ga and As chlorides to form Cl particles (atoms or ions). Consequently, Cl particles may react with the As atoms on the kink or step sites of the etched surface. As stated above, these sites are the favorite ones for Cl to form a high coordinate configuration on the surface, i.e., As_xCl. After a 5 min SR irradiation, most of the $GaCl_3$ and $GaCl_2$ desorbs from the surface, and only GaCl is left on the surface. The persistence of GaCl during SR irradiation may be due to its insensitivity to SR irradiation or the high binding energy of GaCl to the substrate. The rise of the surface temperature due to the SR irradiation can be estimated to be less than a few degrees.[45] This suggests that Ga and As chlorides are not removed from the sample through a thermal reaction, but through an excitation via photoabsorption of chloride species or through a substrate-mediated desorption.[46]

To study the reaction induced by SR irradiation and occurring on the sample surface prior to chloride desorption, the SR photon flux and dose are reduced by decreasing the width of the beamline slit to less than 10 μm. Under such a condition, a sample current of 8−10 nA is obtained under SR irradiation. Figure 9 shows the spectra of Ga and As 3d from the GaAs surface after it is exposed to 6 langmuirs of Cl_2 and then irradiated by SR white light of low doses. As the irradiation time is increased, more $GaCl_2$ and $GaCl_3$ species are formed on the surface. As shown in Figure 6, Cl_2 physisorption already takes place on the GaAs surface at 110 K at an exposure of 6 langmuirs. The observed increase of $GaCl_2$ and $GaCl_3$ intensi-

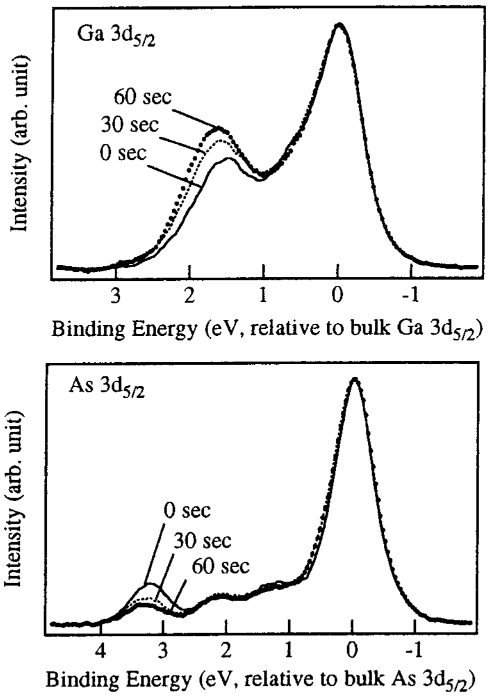


Figure 9. Soft X-ray photoelectron spectra of Ga and As $3d_{5/2}$ collected from the same GaAs surface as in Figure 8 except that the width of the beamline slit is reduced such that the sample current is 8−10 nA. The spectra are obtained by numerically removing the $3d_{3/2}$ component.

ties is thus caused by photodissociation of the physisorbed Cl_2, due to SR irradiation to further chlorinate Ga as described in reaction a.

photon-induced Cl_2 dissociation/chlorination

$$GaCl_{x(ad)} + Cl_{2(ad)} \xrightarrow{h\nu} GaCl_{2(ad)} \text{ or } GaCl_{3(ad)} \quad (x = 0-2) \quad \text{(a)}$$

The Cl_2 dissociation can be induced by SR via a direct absorption or a charge-transfer absorption that causes dissociative electron attachment, leading to the appearance of negatively charged ions.[47] Simultaneously, the photodesorption of Ga chlorides (reaction b) also occurs, as described above in the case of the high SR flux.

photon-induced desorption

$$GaCl_{2(ad)} \text{ or } GaCl_{3(ad)} \xrightarrow{h\nu} GaCl_{2(g)} \text{ or } GaCl_{3(g)} \quad \text{(b)}$$

The increase in the intensity of GaCl and $GaCl_2$ at low SR doses, as shown in Figure 9, indicates that the cross section of photodissociation of the physisorbed Cl_2 is greater than that for the photon-stimulated desorption of Ga chlorides. As observed in a previous kinetic measurement, the $GaCl_3$ has a low thermal desorption rate constant and tends to accumulate on the surface.[17,48] Its desorption barrier can be overcome by promoting the adsorbed $GaCl_3$ molecule to its electronically excited state, where the desorption rate of $GaCl_3$ is higher, via SR (VUV and soft X-ray) irradiation.

Figure 9 also shows that the amount of $AsCl_3$ gradually decreases with an increase of the SR irradiation time whereas the intensities of AsCl and $AsCl_2$ are nearly unchanged. This suggests that $AsCl_3$ is very sensitive to the photon-induced desorption, as compared to the photon-stimulated dissociation of Cl_2, leading to further chlorination of $AsCl_2$ and AsCl species. Therefore, the photon-driven etching process at the cryogenic condition involves different reaction kinetic mechanisms of the photoinduced dissociation/chlorination and desorption for the Ga and As components. The rate of removing Ga atoms from GaAs is limited by the photon-induced desorption of Ga chlorides, while the rate of etching As atoms is determined by the extent of chlorination of the As components due to the photodissociation of Cl_2.

The desorption of the generated chlorides on the GaAs surface is initiated at low temperature within the area irradiated by SR white light. We found that the sticking coefficient of Cl_2 on GaAs at 110 K is at least 1 order of magnitude more than that at room temperature. The increase of the sticking coefficient of Cl_2 on GaAs at low temperatures can increase the efficiency of the etching process. This may also explain Osgood's observation that the etching rate of GaAs assisted by an excimer laser was dramatically increased when the substrate was cooled below the Cl_2 desorption temperature.[4]

4. Conclusions

Soft X-ray photoelectron spectroscopy studies reveal that, during chlorination at 110 K, Cl_2 and HCl initially bond preferentially on the As atom of the GaAs(100)-4 × 6 surface to generate As_xCl and AsCl. The bonding induces the breakage of the surface As−Ga bond and initiates chlorination of the surface Ga atom to form GaCl. Cl_2 has higher reactivity with GaAs than HCl, due to its lower bond dissociation energy. Further exposure to Cl_2 causes the GaAs surface to be further chlorinated such that $AsCl_x$ and $GaCl_x$ ($x = 2$ and 3) are obtained. The population of these chlorides on the surface varies with the Cl_2 exposure and with the irradiation time and flux of the SR white light. After sufficient Cl_2 exposures, chlorination of the GaAs surface is saturated, and the surface is dominated by $GaCl_2$, $GaCl_3$, and $AsCl_3$ with the accumulation of physisorbed Cl_2 molecules.

Results of the present study provide insights into the reaction mechanism of the SR-induced etching of the GaAs surface by Cl_2 at low temperatures. The Ga and As chlorides that are formed after the GaAs surface is exposed to Cl_2 may be stimulated to desorb from the surface by SR irradiation. The SR irradiation also induces photodissociation of the physisorbed Cl_2 to further chlorinate the GaAs surface. The rate that Ga atoms are removed from GaAs is limited by the photon-induced desorption of Ga chlorides, while the rate at which As atoms are etched away is determined by the extent of chlorination occurring on the GaAs surface. By cryogenic cooling of the sample during photon-assisted etching, thermal reaction and desorption are suppressed. It provides a route for an anisotropic etching process with high resolution.

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