

Soft x-ray photoelectron spectroscopy study of the reaction of XeF₂ with GaAs

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The room temperature reaction of atomic F (via XeF₂ vapor) with GaAs(110) wafers is studied employing synchrotron-based soft x-ray photoelectron spectroscopy. Both film growth and etching occur simultaneously in this reaction, as the GaAs substrate is consumed in forming a GaF₃ film while the excess As is liberated. The intermediate reaction products GaF, AsF, and/or elemental As, as well as tricoordinate Ga and As atoms, are present at the GaF₃-GaAs interface throughout the various stages of film growth. © 1995 American Vacuum Society.

I. INTRODUCTION

The reaction of F with GaAs constitutes one of a rare class of surface reactions in which both film growth and etching occur simultaneously. This is similar to the reaction of WF₆ with Si, in which WF₆ decomposes on the Si surface, depositing a W film, while at the same time, the substrate is etched by the liberated F atoms.¹ However, instead of depositing metal, the reaction between F and GaAs forms a film of GaF₃, which is a 10 eV band-gap insulator, while As is etched from the surface.²⁻⁵ The fluorination of GaAs to form GaF₃ is a simple chemical process for growing an insulator on GaAs, similar in procedure to the oxidation of Si to form SiO₂, and therefore has potential technological importance.⁴ The ease with which GaF₃ films can be grown in this way has been shown using a variety of F compounds, including CF₄, CHF₃, and CCl₂F₂ plasmas,⁶⁻⁹ F₂ gas,⁵ atomic F,¹⁰ and F⁺ ions.⁸

Fundamental studies of the growth of GaF₃ on GaAs have been performed via fluorination with XeF₂ vapor.¹¹⁻¹³ XeF₂ is a convenient source of atomic F, as the relatively weak Xe-F bonds are broken in the vicinity of the surface, liberating atomic F and unreactive noble gas atoms.^{14,15} GaF₃ films grown via XeF₂ exposure have been shown to grow homogeneously and in a nearly identical fashion on GaAs(100) and (110) wafers and on GaAs(110) cleaves.^{11,13} In addition, the films take on the electronic structure of bulk GaF₃ once their thickness exceeds 10 Å.¹³ In the present work, soft x-ray photoelectron spectroscopy (SXPS) is used to monitor the evolution of GaAs surfaces as they are exposed to increasing amounts of XeF₂ in an attempt to better understand the chemistry of the reaction at room temperature.

II. EXPERIMENTAL PROCEDURE

GaAs(110) wafers were first etched in a 1:1:200 solution of HNO₃:H₂O₂:H₂O, then rinsed with deionized water and dried with isopropanol. After being placed in the ultrahigh vacuum (UHV) chamber, they were further cleaned by sputtering with 500 eV Ar⁺ ions followed by annealing to ~825

K. Samples were exposed to XeF₂ in a separate stainless steel UHV chamber that had a typical base pressure of ~5×10⁻¹⁰ Torr. Sample transfers between the dosing chamber and the analysis chamber were conducted entirely under UHV. In order to reduce vapor phase transport of metal fluorides to the sample surface, the dosing chamber was passivated with a large amount of XeF₂ prior to the introduction of any GaAs samples.¹⁶ As an extra precaution, the pressure in the dosing chamber was monitored with a cold cathode ion gauge to prevent possible contamination from metal fluorides or radical species created by the hot filament of a conventional ion gauge. As a result, no evidence of metal contamination was apparent in any of the SXPS spectra.

The measurements were performed at the National Synchrotron Light Source, Brookhaven National Laboratory, on beamline UV-8a, employing an angle-integrating ellipsoidal mirror spectrometer that accepts particles within an ~85° cone centered about the surface normal.¹⁷ Photon energies were selected with a 3 m focal length grazing incidence toroidal grating monochromator. The high-resolution SXPS spectra have a combined energy resolution of better than 0.2 eV. The measured photoelectron intensity was normalized by the incident photon flux measured via the total photocurrent at the final focusing mirror. After each exposure, care was taken to consistently reposition the sample in the analyzer so that spectra from different exposures could be compared directly.

III. RESULTS

SXPS survey spectra, which display the valence band as well as the F 2s, Ga 3d, and As 3d core levels, are shown in Fig. 1 in order of increasing exposure to XeF₂. The binding energy (BE) scale in Fig. 1 is given with respect to the GaAs valence band maximum (VBM) and was calibrated by assigning a value of 18.6 eV to the Ga 3d_{5/2} bulk component.¹⁸ The increasing intensity of the F 2p contribution to the valence band, as well as the appearance of a F 2s core level, indicates that F accumulates on the surface with increasing XeF₂ exposure. After a small exposure, the Ga 3d core level broadens towards higher BE. After larger exposures, a distinct second peak, attributed to GaF₃, appears and eventually

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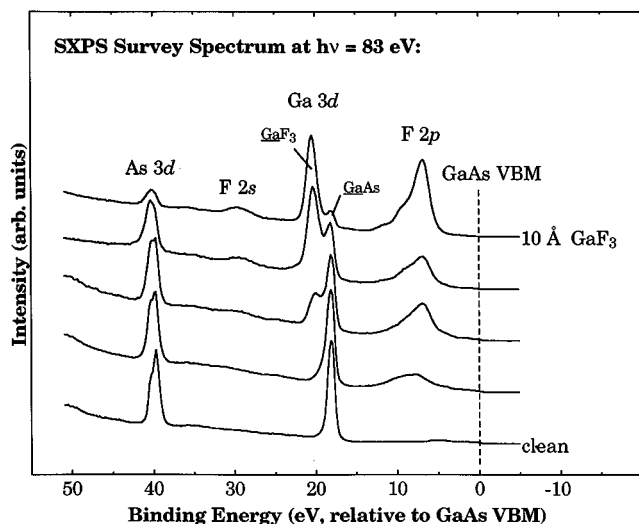


FIG. 1. SXPS survey spectra, displaying the valence band and low-lying core levels, of GaAs(110) wafers after various exposures to XeF_2 . The exposure increases from the bottom to the top of the figure.

dominates the Ga 3d core-level intensity. The As 3d core level also broadens after small XeF_2 exposures, but is attenuated following the largest exposures.

High-resolution Ga 3d and As 3d core-level spectra, given with respect to the substrate $3d_{5/2}$ component, are shown in Figs. 2 and 3, along with numerical fits to the data.

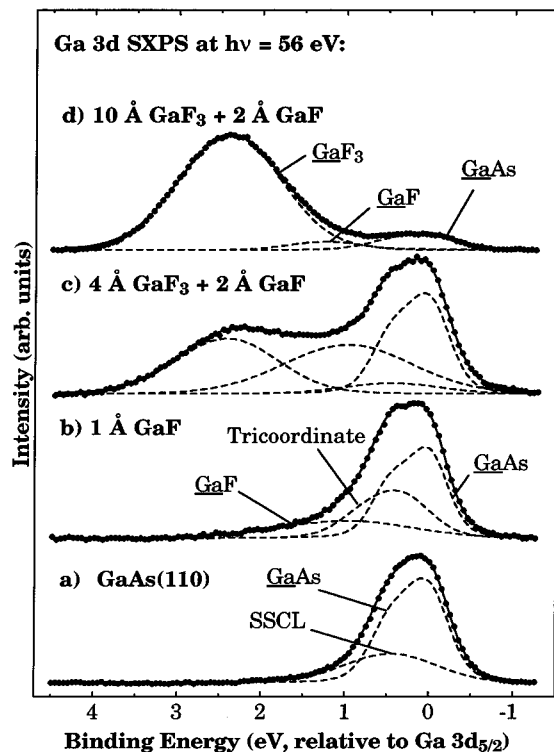


FIG. 2. High-resolution SXPS spectra of the Ga 3d core level, collected from GaAs(110) before and after exposure to XeF_2 , are shown along with the results of numerical fits to the data. The background-subtracted raw data are shown as filled circles. The dashed lines indicate the individual components of the fit and the solid line shows the sum of the components.

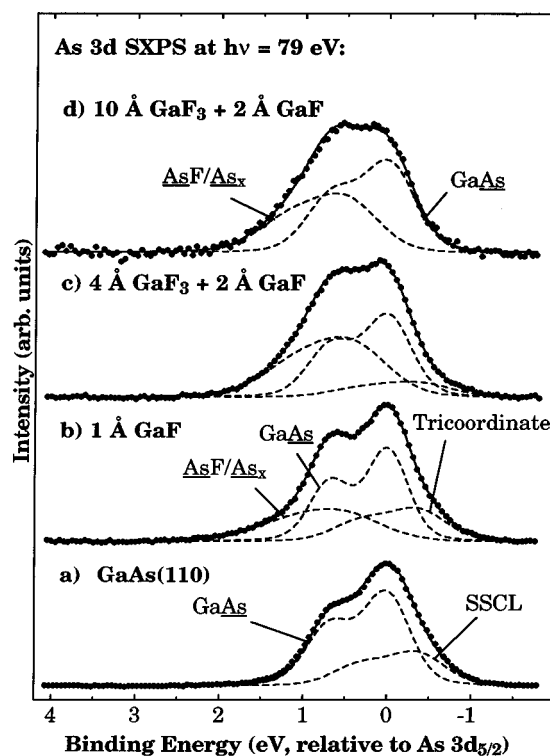


FIG. 3. High-resolution SXPS spectra of the As 3d core level, collected from GaAs(110) before and after exposure to XeF_2 , are shown along with the results of numerical fits to the data. The background-subtracted raw data are shown as filled circles. The dashed lines indicate the individual components of the fit and the solid line shows the sum of the components.

All the spectra shown were collected from the same GaAs(110) wafer. The photon energies were chosen so that the measured photoelectrons all have kinetic energies near 35 eV in order to maximize the surface sensitivity.¹⁹ In addition, using the same photoelectron kinetic energy for both core levels insures that the Ga and As 3d high-resolution spectra each indicate the composition of the same part of the near-surface region.

The Ga and As 3d core levels were numerically fit, following background subtraction, to a sum of Gaussian-broadened Lorentzian spin-orbit split doublets, using a least-squares optimization routine. The background was determined numerically by fitting a third-order polynomial to the data on each side of the photoemission peak. The fitting procedure was used to determine the BE, area, and Gaussian contribution to the width of each core-level component. In all of the fits, the Lorentzian full-width at half-maximum (FWHM) was fixed at 0.12 eV. For the Ga 3d core level, the spin-orbit splitting and branching ratio were fixed at 0.45 and 0.66 eV, respectively. For the As 3d core level, these parameters were fixed at 0.68 and 0.65 eV, respectively. These fitting parameters are consistent with previous treatments of GaAs surfaces.^{11,17,19,20}

The chemically shifted components in the Ga 3d core-level spectra have been identified previously as due to GaF and GaF_3 .^{2,8,11,21} Good fits were achieved for all of the Ga 3d core-level spectra by including only these two components. It was not necessary to include an additional compo-

nent to represent GaF_2 although, due to the large widths of the GaF and GaF_3 components, the presence of some GaF_2 on the surface cannot be ruled out. In the fits to core-level spectra collected after small XeF_2 exposures, the GaF BE was fixed at 0.8 eV relative to the substrate.¹¹ However, the BEs for both GaF and GaF_3 , relative to bulk Ga 3d, increase with exposure, presumably due to the decrease in screening by substrate electrons as the GaF_3 overlayer thickens.^{22,23}

For the As 3d core level, the formation of a shoulder on the high BE side with increasing fluorination indicates that there is at least one As reaction product present. The inclusion of only one reacted component with a higher BE than the bulk was sufficient to achieve good fits for all of the As 3d spectra. The position of this high BE component is consistent with either AsF (Ref. 11) or elemental As.^{19,24–26} Although it has been shown that this high BE component is due to elemental As for reactions at temperatures above 550 K,¹² it is not possible to determine from the present data whether this component is due to AsF, elemental As, or a combination of the two for reactions carried out at room temperature.

To achieve good fits to the GaAs(110) 3d spectra collected from samples having fluoride films as thick as 5 Å, it was also necessary to include components shifted in BE ~ 0.3 and ~ 0.4 eV from the substrate Ga and As components, respectively. For clean GaAs(110), components at these BEs arise from the outermost surface atoms being in a tricoordinate geometry and are thus labeled as surface-shifted core levels (SSCL's). However, the SSCL's in spectra collected from the fluorinated samples are thought to have an additional contribution from buried tricoordinate atoms, created in the substrate by the reaction, which exhibit BE shifts similar to those of the surface atoms.^{13,27} Since the two contributions cannot be resolved, they are treated collectively in this analysis. It is expected that the buried tricoordinate atoms are located at the GaF_3 –GaAs interface, where the reaction occurs, and that they are continually created and removed as the film grows.

As is seen in Figs. 2 and 3, the components sharpen noticeably following small exposures to XeF_2 . This is most likely due to the removal of surface defects by the highly reactive F atoms. It should be noted that the starting surfaces were not of the highest quality since they were generated by multiple cycles of sputtering and annealing, which tends to induce many defects. The poor quality of the starting surfaces is reflected in the large widths of the Ga and As 3d components in the spectra collected from the clean surfaces. However, the initial crystallinity of the surface is of little importance in this reaction since (1) the etching and film growth alter the surface morphology rather quickly, and (2) it has been shown that the reaction product distribution is independent of both the initial crystal face and initial surface order.¹³

The F uptake varied greatly over the exposure range studied, as well as from sample to sample. Thus, the XeF_2 exposure is not the best measure of the amount of F that has reacted with the surface. Instead, the GaF_3 film thickness, calculated using relative core-level component intensities determined from the fits to the high-resolution Ga and As 3d spectra, is used to label the spectra. The film thickness cal-

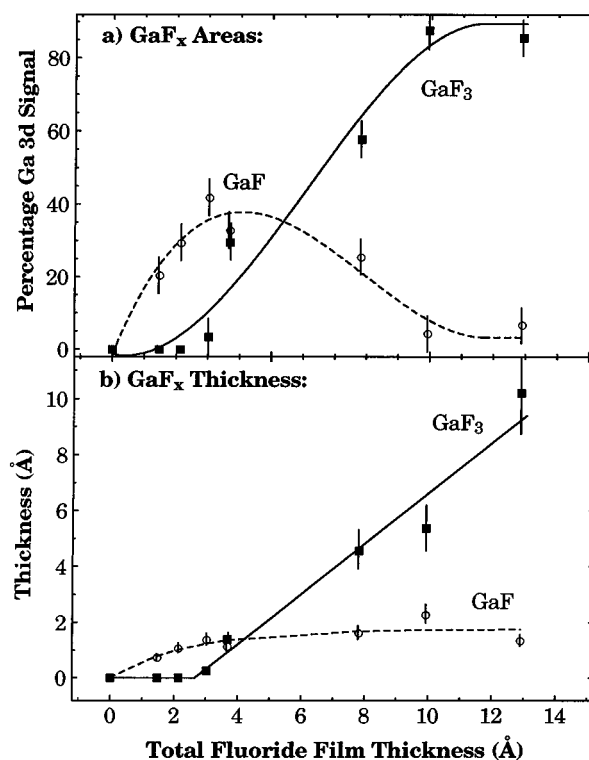


FIG. 4. (a) The relative contributions of the GaF component (open circles) and the GaF_3 component (filled squares) to the total Ga 3d intensity are shown vs total fluoride film thickness, for all of the surfaces studied. (b) The amount of GaF and GaF_3 on the surface that corresponds to the relative intensities shown in (a).

culution used here is explained in detail in Ref. 12.

A summary of the GaF and GaF_3 areas, determined from fits to the Ga 3d spectra, is given in Fig. 4(a). The areas are reported as a percentage of the total Ga 3d intensity and are given as a function of the total fluoride film thickness, which includes the thickness of the GaF_3 film and the interface region between the film and the substrate. Figure 4(b) shows the amount of GaF and GaF_3 on the surface, given in Å of GaF_x , that corresponds to the areas of the Ga 3d core-level components given in Fig. 4(a). As before, the film thicknesses reported are calculated using the model presented in Ref. 12.

IV. DISCUSSION

Based on the results presented in Figs. 1–4, the following reaction mechanism is proposed. The reaction begins with the dissociation of XeF_2 molecules on the surface, liberating F atoms which react rapidly with the GaAs substrate. In reactions with Si surfaces, XeF_2 has been shown to have a higher etch rate than atomic F.^{28,29} This is presumably because the polar XeF_2 molecule has an image attraction to the surface, and hence a longer residence time before dissociation occurs—an effect that may carry over to reactions with GaAs as well. However, since many different F-containing precursor molecules, including some that are polar, have been shown to grow GaF_3 films, it can be assumed that the reaction mechanism proposed here adequately describes the fundamental aspects of the interaction of atomic F with

GaAs, and that the only differences between the reactions of various F-containing precursors are quantitative.

Throughout the reaction, Ga–As bonds are broken, generating tricoordinate Ga and As atoms at the interface between the fluoride layer and the substrate. Also, it is apparent from Fig. 4 that, once formed, ~ 2 Å of GaF remains at the interface throughout the process whereas the amount of GaF₃ steadily increases with additional fluorination. Although the reaction initially takes place at the surface, once the surface Ga atoms are fully fluorinated, the reaction must occur beneath the surface at the GaF₃–GaAs interface. Thus, F atoms must diffuse from the surface to the interface, where they react with substrate Ga atoms to form GaF, as well as convert GaF to GaF₃. At the same time, As products are removed from the interface, diffusing to the surface where they desorb. In this way, the GaF₃ film grows down into the substrate, consuming GaAs as the film grows.

If stepwise fluorination of Ga is assumed to occur, which is suggested by the data, then the relative rates of GaF_x formation can be inferred from the lack of appreciable GaF₂ photoemission intensity in the SXPS spectra. XeF₂ initially reacts with GaAs to form Ga monofluorides. The next step in the process would then be the formation of Ga difluoride. Since the data suggest that little or no GaF₂ is present on the surface during the reaction, it can be concluded that the difluorides quickly react to form the more stable trifluorides. Thus, it appears that the formation of GaF₂ from GaF is the rate-limiting step in the reaction of F with GaAs to produce GaF₃.

If the formation of GaF₂ is the rate limiting step in this reaction, a possible explanation is as follows. It is likely that GaF is produced at the interface when a F atom reacts at a tricoordinate Ga site. To accommodate this F atom, only a slight rearrangement of the lattice is necessary. To form GaF₂ from GaF, however, a much larger rearrangement would be necessary since a Ga–As bond must be severed and a F atom must be inserted into this space. Thus, from a steric perspective, it is expected that GaF₂ formation would be much slower than GaF formation. Once the steric barrier to form GaF₂ has been overcome, the final rearrangement needed for accommodation of GaF₃ is presumably less severe and can therefore occur more readily.

As GaF₃ is grown, arsenic is removed from the surface either as elemental As or as an As fluoride species. Although the identity of the gaseous As reaction product evolved at room temperature cannot be conclusively determined from the present data, the existing evidence suggests that it is unfluorinated As. It might be argued that elemental As is stable on GaAs at room temperature, since it is commonly used to cap GaAs surfaces, and thus would not be evolved as a gaseous reaction product. However, there is no evidence at present showing that adsorbed As is stable at room temperature on the surface of GaF₃, which is the outermost surface in this reaction. From studies of the reaction of Cl₂ with GaAs, it is known that the low-temperature As-containing reaction product is AsCl₃.^{30–32} At higher temperatures, the Cl₂ etching As-containing product distribution switches to a combination of As dimers and tetramers. Although this would suggest that AsF₃ should be the gaseous As-containing

product evolved after F reaction at room temperature, no evidence is seen for the AsF₂ intermediate species on the surface, while AsCl₂ has been observed on surfaces following room temperature reaction with Cl₂.²⁷ Furthermore, the need for the As reaction product to diffuse through the GaF₃ film suggests that the product should be a smaller molecule than AsF₃. Finally, a recent study of the effects of elevated temperature in the reaction of XeF₂ with GaAs found that above 550 K, the only As reaction product remaining on the surface is elemental As, and this result possibly extends to lower temperatures.¹² Although these considerations favor unfluorinated As as the major gaseous product evolved by the reaction, molecular beam scattering experiments are needed to conclusively identify the products.

As the GaF₃ film thickens, the rate of film growth drops off rapidly. In fact, once the film is 10–15 Å thick, an order of magnitude increase in XeF₂ exposure is needed to obtain a measurable increase in film thickness and an increase of several orders of magnitude is required to grow a thick film.¹² It is clear that the adlayer acts to block the access of F atoms to the underlying GaAs substrate. It is not clear, however, why the formation of a GaF₃ film slows the reaction. Diffusion of F to the interface and As from the interface is necessary for the reaction to proceed, but a diffusion-limited reaction has been ruled out by studying the temperature dependence of the process.¹² The reduction of the reaction rate could be simply due to the passivation of reactive surface sites. The fact that the reaction does not slow considerably until well over a monolayer of GaF₃ is formed then indicates that new reaction sites are generated during the initial stages of the film growth process, with the obvious candidates being tricoordinate Ga and As defects. It is also conceivable that XeF₂ molecules do not dissociate as well on a GaF₃ surface as they do on GaAs. If this were so, then the GaF₃ film would act to reduce the amount of atomic F generated at the surface, thus slowing the reaction. In actuality, it is likely that the reaction is slowed by a combination of such effects.

V. SUMMARY

The room temperature reaction of XeF₂ with GaAs is relatively unique in that both film growth and etching occur simultaneously, that is, the GaAs substrate is consumed by forming GaF₃ while liberating excess As. The reaction initially forms GaF, AsF, and/or elemental As at the surface. Further fluorination transforms GaF into GaF₃ and leads to the removal of As. Substrate Ga–As bonds are broken during the reaction, producing buried tricoordinate Ga and As atoms at the GaF₃–GaAs interface. Once the surface is covered with a complete layer of GaF₃, the reaction slows but does not stop. Instead, it continues below the surface at the GaF₃–GaAs interface, generating GaF and GaF₃ while removing As. Once formed, about 2 Å of GaF (~ 1 monolayer) is present at the interface throughout the GaF₃ film growth process, independent of the film thickness.

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