

# Synchrotron Photoemission Analysis of Semiconductor/Electrolyte Interfaces by the Frozen-Electrolyte Approach: Interaction of HCl in 2-Propanol with GaAs(100)

Thomas Mayer,<sup>\*,†</sup> Mikhail V. Lebedev,<sup>‡</sup> Ralf Hunger,<sup>†</sup> and Wolfram Jaegermann<sup>†</sup>

TU-Darmstadt, FB Material- und Geowissenschaften, FG Oberflächenforschung, Petersenstrasse 23, 64287 Darmstadt, Germany, and A. F. Ioffe Physico-Technical Institute, Russian Academy of Sciences, Politekhnicheskaya 26, St. Petersburg, 194021, Russia

Received: November 4, 2005

Perspectives of a new approach for the synchrotron photoemission spectroscopic analysis of chemical processes at solid/liquid interfaces under UHV conditions have been explored. A thin layer of HCl–2-propanol solution was frozen-in on the semiconductor GaAs(100) wafer surface by cooling the substrate to liquid nitrogen temperature after etching off the native oxide layer under N<sub>2</sub> atmosphere. Chemical reactions induced in situ by exposure to synchrotron radiation (SR) and by stepwise heating have been monitored. Right after etching and freezing, the surface is covered by gallium chlorides with 1, 2, 3, and 4 Cl ions attached and lattice back-bonded to As atoms, as well as by elemental arsenic As<sup>0</sup> and 2-propanol. Exposure to SR at low temperature produces surface As chlorides at the expense of As<sup>0</sup>. The GaCl<sub>3</sub> and GaCl<sub>2</sub> emissions diminish while GaCl is enhanced. On the other hand, heating the sample to approximately 130 K just above H<sub>2</sub>O desorption causes the thermodynamically expected reaction of AsCl<sub>3</sub> with the substrate GaAs to form Ga chloride species and As<sup>0</sup>. Heating the sample to room temperature leaves only As<sup>0</sup> on the surface and for gallium the content of all surface chlorides is drastically reduced. By further heating to 400 K elemental arsenic starts to desorb and the Ga chloride surface content is reduced. Using different excitation energies the depth composition of the reaction products has been monitored indicating a tendency of decreasing chlorination numbers and increasing Ga vs As chloride content toward the pristine substrate at each stage of the reaction.

## I. Introduction

Wet chemical procedures are widely applied in device fabrication since such processes involving low-energy impacting species (as compared to dry vacuum etching and deposition processes) can minimize surface defect formation. Processes occurring at semiconductor/electrolyte interfaces are very complex and include the adsorption of ions, breaking of semiconductor surface bonds, as well as the formation of surface compounds, which may be soluble in the solution or passivate the surface.<sup>1</sup> A more detailed view of contact formation at semiconductor/electrolyte interfaces requires a precise knowledge of the microscopic structure of the phase boundary, e.g., the structure of the semiconductor surface and interfacial composition of the electrolyte.<sup>2</sup> Synchrotron photoemission spectroscopy (SXPS) can provide such information; however, ultrahigh vacuum (UHV) conditions are required prohibiting analysis of high vapor pressure liquids. Therefore SXPS was performed on room temperature (RT) emersed substrates giving access to the surface composition after electrochemical treatment and on coadsorbed electrolyte species as electrolyte model at liquid nitrogen (LN<sub>2</sub>) temperature enabling controlled concentration variations and giving access to intermediate reaction steps.<sup>3,4</sup> In this study we approach the SXPS analysis of semiconductor/electrolyte interface by freezing-in remnants of the electrolyte on the sample surface after emersion attempting to fix volatile reaction products for the analysis.

GaAs(100) is one of the most intensively studied semiconductor surfaces because of its significance in semiconductor device technology. Halogen-based etchants (dry and wet) are often used in the preparation and conditioning of GaAs surfaces because of the high halogen reactivity and the high volatility of the generated products. In previous SXPS studies on emersed nonpolar GaAs(110) surfaces, we reported on the final Ga rich composition of the surface after contact to Br<sub>2</sub>/Br<sup>−</sup> in H<sub>2</sub>O and compared the results to adsorption of Br<sub>2</sub> and coadsorption of H<sub>2</sub>O revealing intermediate reaction steps.<sup>3,4</sup> In the present study, we focus on the analysis of dynamic reaction processes induced by photo and thermal activation on the emersed and frozen GaAs (100) surface.

The reaction of HCl with GaAs has received great attention during the past decade. Previous studies were mostly focused on the study of the dry etching mechanism of the semiconductor.<sup>5–7</sup> To this end the adsorption of HCl and Cl<sub>2</sub> molecules from the gas phase at low temperatures was studied by photoemission spectroscopy.<sup>8,9</sup> In these investigations a number of volatile or back-bonded GaCl<sub>x</sub> and AsCl<sub>x</sub> species have been identified based on their chemical shift. Also it was found that at lower temperatures HCl is less reactive than Cl<sub>2</sub>. On the other hand, the chemical reaction mechanism and the reaction products should be considerably different in an electrolyte solution than in the gas phase, because, first, the HCl molecule is dissociated in the solution to an H<sup>+</sup> and Cl<sup>−</sup> ion pair and, second, the solvation shell can modify considerably the reactivity of the ions.<sup>10,11</sup> However, the interaction of HCl solutions with surfaces of III–V semiconductors is less studied. In particular, it was found that HCl in 2-propanol removes effectively the native oxide layer from GaAs<sup>12</sup> and InAs,<sup>13</sup> forming well-ordered

\* To whom correspondence should be addressed. E-mail: mayerth@surface.tu-darmstadt.de.

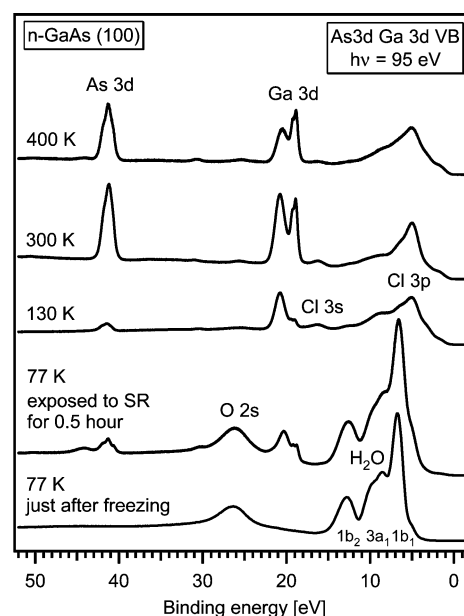
† Darmstadt University of Technology.

‡ A. F. Ioffe Physico-Technical Institute.

In this study, we analyze in situ chemical reactions and formation of surface compounds that occur on the GaAs(100)/frozen-HCl-2-propanol interface after completely etching off the native oxide in HCl-2-propanol solution. The analysis is performed by means of high-resolution SXPS of the semiconductor surface with an ultrathin electrolyte layer emersed from the solution and stabilized on the surface by cooling the sample to low temperatures (“frozen electrolyte”). This type of experiment is considered as the missing link of previously performed studies to investigate the solid/electrolyte interface in ex situ UHV experiments, namely, emersion and transfer at RT with the expected loss of volatile species and coadsorption experiments with different concentrations and experimental parameters.<sup>2,18</sup>

The XPS experiments were performed at the undulator beam line U49/2 of the BESSY II storage ring, which provides photons in the energy range between  $h\nu = 90$  and 1400 eV. The spectra were obtained using a Phoibos 150 (SPECS) energy analyzer of the experimental system SoLiAS (Solid/Liquid Analysis System) permanently operated at BESSY. The emitted photoelectrons were detected in normal emission with an acceptance angle of  $\pm 9^\circ$ . A homemade electrochemistry chamber built from standard glass elements is integrated to the SoLiAS system, allowing for wet chemical processing under inert, dry, and carbon- and oxygen-free  $N_2$ -atmosphere and transfer to UHV without contact to ambient air. Details of the experimental setup and of the procedure of taking photoemission spectra can be found elsewhere.<sup>3,4,19,20</sup> In a special buffer chamber the wet processed sample can be cooled to LN<sub>2</sub> temperature while pumping to UHV. The sample may then be transferred actively cooled to the analysis chamber manipulator, which is cooled as well.

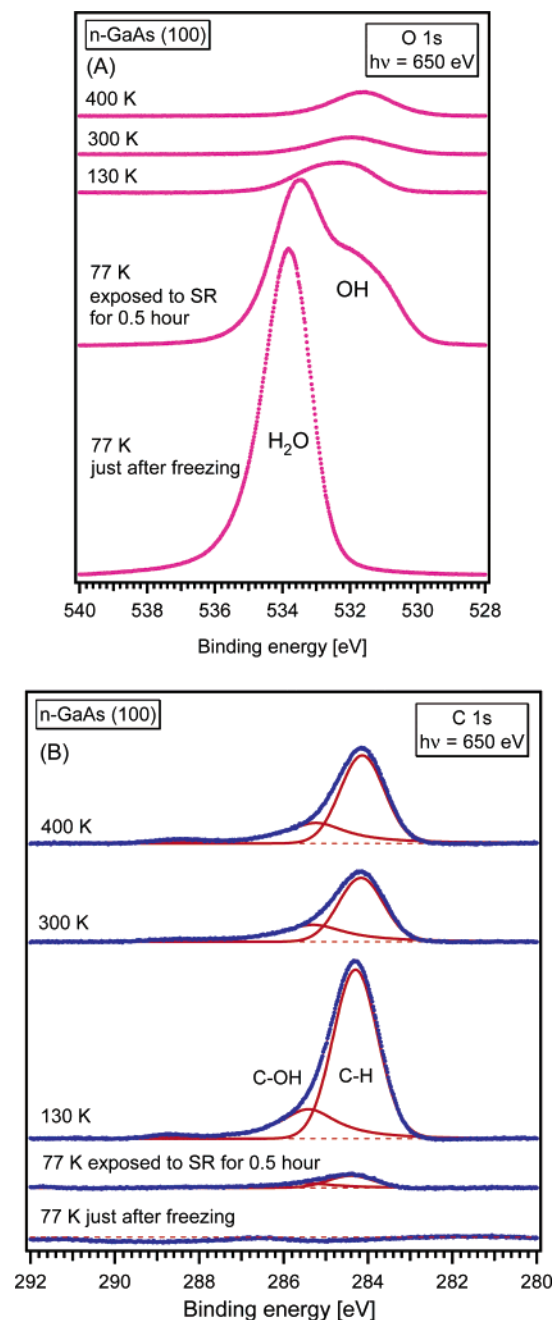
To induce chemical reactions and to achieve the successive desorption of volatile reaction products, a few distinct activation steps were performed. The first one was accomplished by exposure to SR radiation for 0.5 h. The second was performed by counterheating the sample through contact to a RT reservoir. As a result of sample heating, the base pressure in the analysis chamber started to raise showing desorption of volatile species. At the next stage the sample was heated to RT while stored in a separate vacuum chamber since the pressure rise was rather high in this case. After each of these heating steps, all sets of measurements were performed on the cooled manipulator. At



last, the sample was heated resistively to approximately 400 K in a separate vacuum chamber and measured at RT.

**A. Survey of the Analyzed Conditions of the GaAs/HCl-*i*-C<sub>3</sub>H<sub>7</sub>OH Interface.** Survey spectra of the GaAs/HCl-*i*-

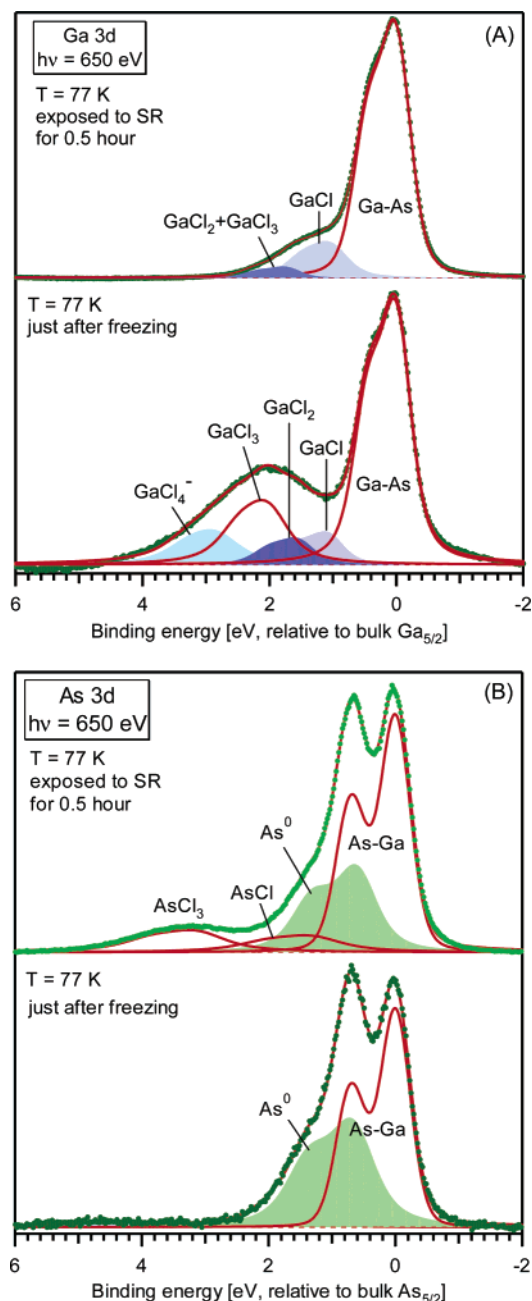
The ice layer was desorbed by exposing the sample to synchrotron radiation for extended times.<sup>25</sup> Because of partial desorption of H<sub>2</sub>O the substrate core levels appear in the 95 eV survey spectra after approximately half an hour of irradiation (Figure 1); prolonged irradiation did not result in further changes of the spectra. Besides ice desorption, also the splitting of water into OH and H is activated as indicated in the valence band by a low-energy shoulder of the 1b<sub>1</sub> emission assigned to the 1 $\pi$  orbital of OH<sup>22,23</sup> (see Figure 1) and in the O 1s core level by a new peak at lower binding energy, which has been assigned to OH groups<sup>4,22,23</sup> (see Figure 2a). But we cannot rule out that



**Figure 2.** Core level O 1s (a) and C 1s (b) spectra of the GaAs/HCl-*i*-C<sub>3</sub>H<sub>7</sub>OH interface at the examined conditions. The excitation energy was 650 eV. The spectra scale in intensity.

at this stage some of these OH groups belong to 2-propanol solvent molecules. Photolysis and photodesorption of H<sub>2</sub>O has been observed on several substrates before<sup>25</sup> and are not in the scope of this publication. The reaction of the GaAs substrate with the condensed H<sub>2</sub>O layer can be excluded as will be discussed in detail in section IIIB.

After exposing the sample for 0.5-hour to synchrotron radiation, also the C1s line addressed to 2-propanol (Figure 2b) and the Cl 2p line addressed to reaction products and to a minor extent to the solute become apparent. Obviously, the electrolyte has been frozen in. In the next paragraph we show that also the amount of As chlorides has been increased while the amount of Ga chlorides was decreased. As surface reactions and desorption may also be activated by increased temperature, we analyzed the surface composition after heating the sample to a temperature just above H<sub>2</sub>O desorption and below the desorption



**Figure 3.** Photoemission spectra (650 eV) of Ga 3d (a) and As 3d (b) core levels collected from GaAs(100)/(frozen) HCl-2-propanol interface just after freezing-in the electrolyte layer and after exposure for 0.5 h to SR. The dots represent the collected data after background subtraction. The spectra have been deconvoluted in the assigned components by a fitting routine.

temperature of AsCl<sub>3</sub> which is known to be 170 K.<sup>26</sup> All traces of water disappeared and Cl 3p and Cl 3s become apparent at 6 and 16 eV, respectively, in the 95-eV survey spectra (Figure 1). In the O 1s level (Figure 2a) only the OH emission remains, which we now address to 2-propanol. Because of H<sub>2</sub>O desorption, the C 1s peak rises in intensity (Figure 2b). Two main emissions can be discriminated, which we assign to C-H and C-OH bonds of the CH<sub>3</sub>-HCOH-CH<sub>3</sub> molecule. After extended exposure to synchrotron radiation a small C 1s emission shifted by 4.5 eV to higher binding energy becomes apparent, which coincides with carbonates. At 300 K, its intensity is decreased, but it grows back after annealing at 400 K. Therefore we tentatively address this small emission to a reaction product of 2-propanol. As the sample was emersed at



RT—the usual condition for conventional noncooled emersion experiments—next we also analyzed the surface composition at this temperature. An increase in intensity of the substrate emissions (Figure 1) and a reduction of the O 1s (Figure 2a) and C 1s (Figure 2b) intensities indicate partial desorption of physically adsorbed solvent molecules. Further desorption of still present electrolyte, as well as some remaining reaction products, was attempted by heating to 400 K. Modifications of the shapes of Ga 3d and As 3d core level emissions are observed while the C 1s emission is unchanged. Dipolar 2-propanol (1.85 D), stabilized probably by  $\text{Cl}^-$  ions bound to back-bonded surface Ga atoms, is still present on the surface after heating to 400 K.

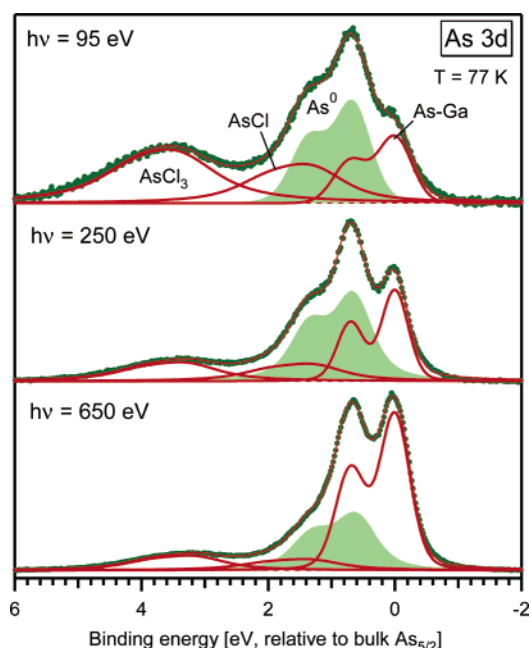
### B. High-Resolution Depth and Temperature-Dependent Analysis of GaAs (100) after Interaction with HCl Solution.

The analysis of the surface layer of GaAs was performed by Ga 3d and As 3d core level spectroscopy using three different excitation energies: 95, 250, and 650 eV. Spectra measured with different excitation energies provide information from the surface layers of different thickness due to the difference in the electron inelastic mean free paths  $\lambda$ , which for the As 3d level in GaAs for these energies are approximately 4.5, 7.3, and 15.1 Å, respectively.<sup>24</sup> After background subtraction, the fitting of the core-level spectra was carried out using Voigt functions with the parameters (Gaussian and Lorentzian width, spin–orbit splitting, branching ratio) similar to those used in ref 27.

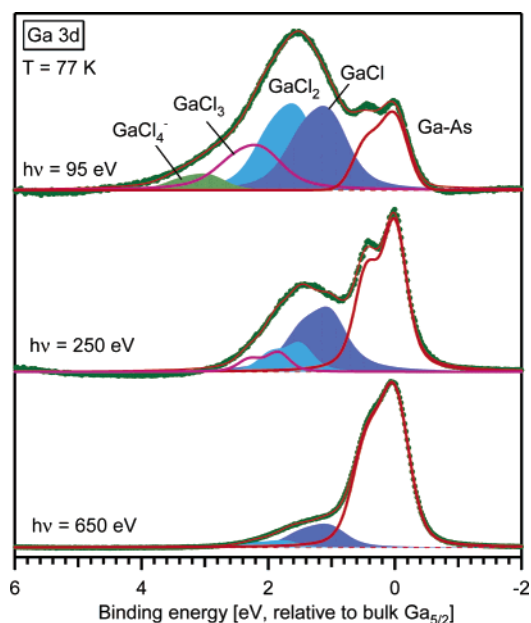
While shortly after freezing the Ga 3d and As 3d core levels cannot be observed with 95 eV photon energy, the condensed ice layer is transparent to these core electrons excited with 650 eV (Figure 3). The Ga-to-As ratio calculated taking into account the energy dependent photoemission cross-section correction<sup>28</sup> is equal to 2.75. The Ga 3d line can be reasonably fitted by 4 components shifted from the Ga–As bulk emission to higher energies by 1.1, 1.55, 2.0, and 2.9 eV, respectively. The following chemical shifts were found in the literature for surface components related to Ga–Cl bonds: 0.6–0.9 eV for  $\text{GaCl}$ ,<sup>9,29,30</sup> 1.6–1.7 eV for  $\text{GaCl}_2$ ,<sup>9,29</sup> and 2 eV for  $\text{GaCl}_3$ .<sup>9</sup> Accordingly, the first component can be assigned to  $\text{GaCl}$ , the second to  $\text{GaCl}_2$ , and the third component to  $\text{GaCl}_3$ . The fourth component with the highest chemical shift can be related to  $\text{GaCl}_4^-$ .<sup>31</sup> While  $\text{GaCl}_3$  may be formed as a discrete dinuclear species  $\text{Ga}_2\text{Cl}_6$ ,<sup>9</sup>  $\text{GaCl}_2$  and  $\text{GaCl}$  are surface species back-bonded to surface As atoms of the GaAs substrate.

Just after freezing the As 3d core level shows a strong component shifted from the As–Ga bulk emission to higher binding energies by 0.65 eV, which is often observed in spectra of GaAs especially when etched with different solutions as, e.g., ammonia,<sup>32</sup> and is usually assigned to excess elemental arsenic.<sup>27</sup> It is possible that some contribution of surface As with H attached is included into this component as well because such bonds can be formed on the GaAs surface in acidic solutions at certain conditions<sup>33</sup> and due to the similar electronegativity of As and H a similar binding energy is expected. Interestingly, no As chlorides are found on the surface right after freezing (Figure 3). We conclude that, due to its high solubility,  $\text{AsCl}_3$  has been dissolved into the bulk electrolyte, which was blown off. However,  $\text{AsCl}_3$  is formed during extended exposure to synchrotron light (Figures 3 and 4). As there are no indications of oxide species on the surface, it is clear that the condensed  $\text{H}_2\text{O}$  is situated on top of the substrate/electrolyte interface initially formed in solution and does not take part in the reaction.

High-resolution As 3d and Ga 3d core-level spectra of the sample measured with 3 different photon energies after freezing and partial synchrotron induced evaporation of the attenuating ice layer are shown in Figures 4 and 5. The spectra measured



**Figure 4.** Photoemission spectra of the As 3d core level collected using various excitation energies from the GaAs(100)/(frozen) HCl–2-propanol interface after freezing-in the electrolyte layer and exposure of the interface at low temperature to synchrotron radiation for 0.5 h to desorb the condensed ice layer (see text for details). The dots represent the collected data after background subtraction. The spectra have been deconvoluted in the assigned components by a fitting routine.



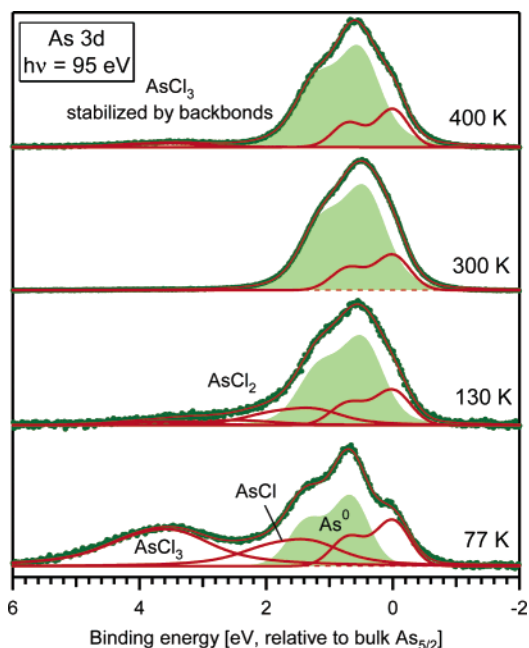
**Figure 5.** Photoemission spectra of the Ga 3d core level using various excitation energies from the GaAs(100)/(frozen) HCl–2-propanol interface after freezing-in the electrolyte layer and exposure of the interface at low temperature to synchrotron radiation for 0.5 h to desorb the top water ice layer (see text for details). The dots represent the collected data after background subtraction. The spectra have been deconvoluted in the assigned components by a fitting routine.

with 650 eV are also added to Figure 3 for the sake of comparison. Comparing the 650 eV spectra before and after 0.5 h SR exposure (Figures 3) shows clearly the formation of additional As–Cl reaction products. While the content of higher chlorinated surface Ga species was reduced,  $\text{GaCl}$  increased. The best fit to As 3d is obtained with three additional components shifted from the bulk GaAs line to higher binding

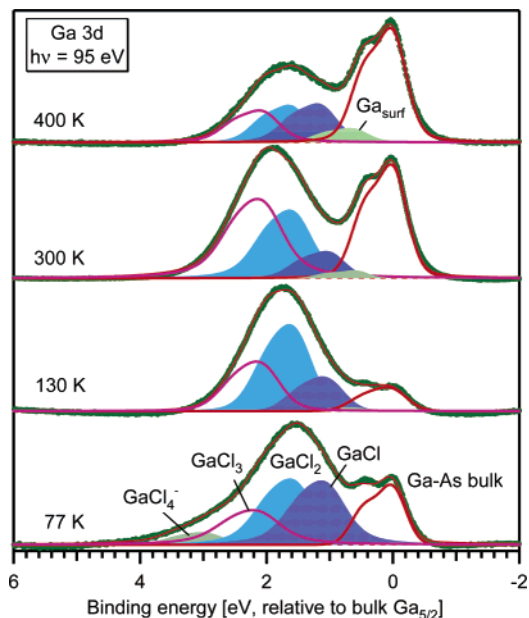
energies by 0.65, 1.3, and 3.1–3.4 eV. For the 3.1–3.4 eV species, the higher chemical shift is observed in the more surface-sensitive 95-eV spectrum. The first two components can be assigned to excess elemental arsenic<sup>27</sup> and surface-bound  $\text{AsCl}_3$ ,<sup>9</sup> respectively. The component with the chemical shift of about 3.4 eV, belonging to a volatile species, can be assigned to  $\text{AsCl}_3$ , in accordance with low-temperature HCl and  $\text{Cl}_2$  adsorption experiments in ref 9. While  $\text{AsCl}_3$  forms individual (volatile) molecules,  $\text{AsCl}$  (as well as  $\text{AsCl}_2$ ) is bound to the surface. Since the transition of Cl from surface Ga to As has not been observed before, we assume that the stabilization of the volatile reaction partners  $\text{GaCl}_3$  and  $\text{AsCl}_3$  by the frozen in solvent molecules is a necessary precondition. In the assignment of the As chlorides, we follow ref 9, which is in contradiction to the assignment given in RT adsorption experiment (ref 29) where the species with a shift of 0.65 eV was identified as an unresolved superposition of an As reconstructed surface core level and  $\text{AsCl}$  while the emission at 1.3 eV was addressed to  $\text{AsCl}_2$ . Assigning the 1.3-eV component to  $\text{AsCl}_2$  would result in too low binding energy for  $\text{AsCl}_3$ , which was clearly identified at 3.4 eV in ref 9.

The best fit of the Ga 3d spectrum measured using 95-eV excitation energy is obtained when five components are used. These are the Ga–As bulk emission and emissions chemically shifted by 1.0, 1.6, 2.0, and 3.0 eV (Figure 5). Three of these shifted emissions were observed previously in ref 9, where they were assigned to  $\text{GaCl}$ ,  $\text{GaCl}_2$ , and  $\text{GaCl}_3$  species, respectively, with  $\text{GaCl}$  and  $\text{GaCl}_2$  bound to the surface and  $\text{GaCl}_3$  forming discrete molecules in the form of  $\text{Ga}_2\text{Cl}_6$ . The component with the highest chemical shift (3.0 eV) was observed also in the 650-eV spectrum just after freezing displayed in Figure 3 and can be assigned to  $\text{GaCl}_4^-$ . In the spectrum measured with 250 eV, there is no  $\text{GaCl}_4^-$  component and the intensities of the other chemically shifted components are reduced with respect to the Ga–As bulk component. The spectrum measured with 650-eV excitation energy is characterized by the occurrence of two Ga–Cl-related emissions: one with a chemical shift of 1.0 eV due to surface bound  $\text{GaCl}$  and the other with a chemical shift of 1.8 eV, which we address to a mixture of  $\text{GaCl}_2$  and  $\text{GaCl}_3$  species that are not resolved due to low intensity. The spectra measured with different surface sensitivity clearly indicate decreasing Ga chlorination toward the bulk of the substrate. Less distinct, such a trend is also observed for the As chlorides (Figure 4).

Evolution of the high-resolution spectra of As 3d and Ga 3d core levels measured using 95 eV excitation energy as the sample is heated to different temperatures is shown in Figures 6 and 7, respectively. Clearly, the As chlorides formed by exposure to synchrotron radiation of the GaAs/frozen electrolyte interface are considerably removed with the first temperature step (130 K). In particular, only a small emission of the  $\text{AsCl}_3$  is left. On the other hand, a new small component with a chemical shift of 2.35 eV is formed, which is observed as well in the 250-eV spectrum (not shown). According to ref 9, this component can be assigned to  $\text{AsCl}_2$  bound to the surface. The area of the elemental As component as compared to the area of the As–Ga bulk component increases in the spectra measured with all excitation energies, whereas the area of the  $\text{AsCl}$  component decreases. For Ga we observe a strong increase of the chloride reaction products. The intensities of the  $\text{GaCl}_2$  and  $\text{GaCl}_3$  components increase considerably, whereas the  $\text{GaCl}$  component slightly decreases with respect to the Ga–As bulk emission. The  $\text{GaCl}_4^-$  component disappears completely, and a small component with a chemical shift of 0.6 eV appears in



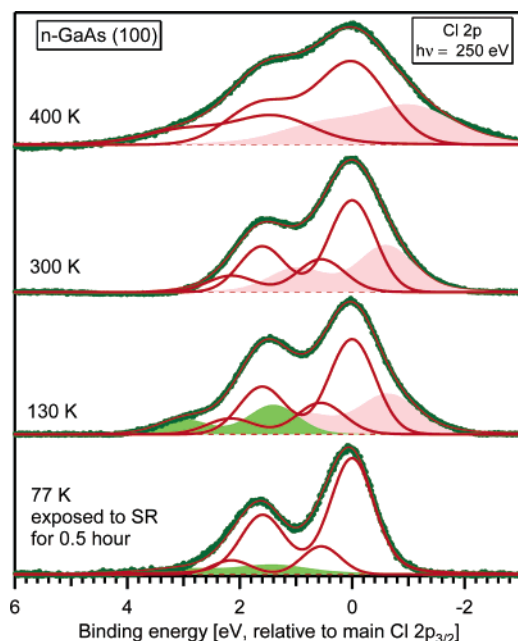
**Figure 6.** Photoemission spectra (95 eV) of the As 3d core level from the GaAs(100)/(frozen) HCl–2-propanol interface after heating to various temperatures. The spectrum corresponding to 77 K was taken after exposure of the interface to synchrotron radiation for 0.5 h to desorb the top water ice layer (see text for details). The dots represent the collected data after background subtraction. The spectra have been deconvoluted in the assigned components by a fitting routine.



**Figure 7.** Photoemission spectra (95 eV) of the Ga 3d core level from the GaAs(100)/(frozen) HCl–2-propanol interface after heating to various temperatures. The spectrum corresponding to 77 K was taken after exposure of the interface to synchrotron radiation for 0.5 h to desorb the top water ice layer (see text for details). The spectra have been deconvoluted in the assigned components by a fitting routine.

the spectrum (see Figure 7). The latter component was observed before in the spectrum of the clean GaAs(001)–(4 × 6) surface formed by sputtering and annealing<sup>27</sup> and was identified as the surface component probably due to Ga–Ga surface dimers.<sup>9,27,29</sup>

Heating the sample to RT causes complete removal of all As chlorides (Figure 6), while the intensity of elemental As further increases with respect to the As–Ga bulk emission. The



**Figure 8.** Photoemission spectra of the Cl 2p core level collected using 250-eV excitation energy from the GaAs(100)/(frozen) HCl–2-propanol interface after heating to various temperatures. The spectrum corresponding to 77 K was taken after exposure of the interface to synchrotron radiation for 0.5 h to desorb the top water ice layer (see text for details). The dots represent the collected data after background subtraction. An assignment of the deconvoluted components is given in the text.

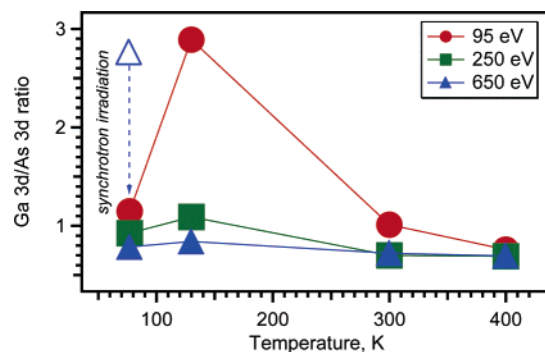
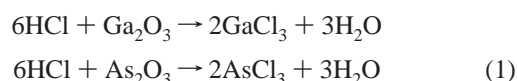
intensities of all chlorides decrease considerably in the Ga 3d emission (Figure 7).

After heating the sample to 400 K, the intensity of elemental arsenic decreases. Moreover, a small amount of a species with the same binding energy as AsCl<sub>3</sub> (about 4% of the total area) appears again on the surface as it is evidenced from the core-level spectrum. Since AsCl<sub>3</sub> molecules should already desorb at 170 K,<sup>26</sup> we assume that some new-formed AsCl<sub>3</sub> molecules are stabilized by back-bonds at the surface. In the Ga 3d spectrum, the intensities of GaCl, GaCl<sub>2</sub>, and GaCl<sub>3</sub> components continue to decrease, and the surface component shifted to higher binding energy from the Ga–As bulk emission by 0.6 eV becomes more pronounced (Figure 7).

We also measured the chlorine 2p emission at the different conditions of the GaAs/HCl–2-propanol interface (Figure 8). With increasing temperature, the Cl emission broadens but interestingly does not diminish. Clear decomposition and assignment to certain species was not possible in the complex surface composition of this study.

#### IV. Discussion

**A. Reactions Activated at the Semiconductor/Frozen Electrolyte Interface.** Right after etching and freezing we find a similar composition of the surface as observed with SXPS measurements on emersed GaAs (110) from HCl in H<sub>2</sub>O solution (not published) and from Br<sub>2</sub> in H<sub>2</sub>O solution at RT.<sup>3</sup> The surface is Ga enriched due to Ga halogenides, while arsenic is mostly found in its elemental form on the surface. We expect the formation of halogenides due to the interaction of the oxide layer on the GaAs surface with the HCl solution according to the following reactions



**Figure 9.** Ga 3d/As 3d intensity ratios for photoemission lines measured on the GaAs(100)/(frozen) HCl–2-propanol interface at different temperatures using various excitation energies. The open triangle corresponds to the spectra measured right after freezing the electrolyte layer using 650-eV excitation energy (shown in Figure 3).

The formation of other GaCl<sub>n</sub> (*n* = 1, 2) species proceeds in a similar way. Because of its high solubility in the liquid electrolyte, which is blown off, AsCl<sub>3</sub> is not found right after freezing. The elemental As we find at this stage has been formed already at the oxidized surface<sup>19</sup> and may be explained by the reaction of As<sub>2</sub>O<sub>3</sub> with bulk GaAs according to



as the heat of formation is higher (−283.6 kcal/mol) than the sum of the heats of formation of As<sub>2</sub>O<sub>3</sub> (−137.7 kcal/mol) and GaAs (−17 kcal/mol).<sup>34</sup>

Comparison of the 650 eV spectra in Figure 3b shows that AsCl and AsCl<sub>3</sub> have been formed under the influence of synchrotron radiation. Photoactivation of chemical reactions at low temperature is observed in many cases and was found, e.g., at the GaAs(110) surface covered with Cl<sub>2</sub> molecules and irradiated with ultraviolet laser light.<sup>35</sup> The reaction may be activated by secondary electrons of the photoemission process or by increasing the temperature due to SR exposure.

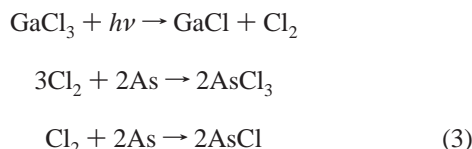
The temperature dependence of the ratios of integrated Ga 3d to As 3d emissions as measured with the different excitation energies and cross-section corrected<sup>28</sup> is illustrated in Figure 9. Right after freezing the surface is strongly Ga rich. After exposing the frozen sample to synchrotron radiation for 0.5 h at LN<sub>2</sub> temperature the near-surface atomic layer is slightly Ga rich (as evidenced from the ratio for spectra measured with 95 eV excitation energy), indicating desorption of Ga reaction products, whereas the layer below (about 25 Å thick) is As rich (as evidenced from the ratios for spectra measured with 250 and 650 eV excitation energies).

After the first heating step (at approximately 130 K) the Ga-to-As ratio in the near-surface layer (evidenced from the spectrum measured using 95-eV excitation energy) increases to a similar value as measured right after freezing with 650-eV excitation energy indicating desorption of volatile As-related surface species. On the other hand, the ratio in the deeper layers (evidenced from the spectra measured using 250-eV and especially 650-eV excitation energies) remains essentially the same as at 77 K. Further heating to RT causes desorption of Ga–Cl reaction products from the top surface layer, and at 400 K the Ga-to-As ratio is almost uniform over all surface information depths under study.

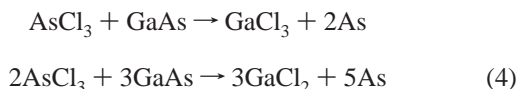
The development of the ratios of the various As and Ga reaction products to the corresponding bulk emission in the course of sample heating, as measured in the As 3d and Ga 3d spectra with different excitation energies, is illustrated in parts



a and b of Figure 10 beginning from the point where the sample was frozen to 77 K and exposed to synchrotron radiation for 0.5 h. At this point AsCl and AsCl<sub>3</sub> have been formed on the surface mainly at the expense of GaCl<sub>3</sub>. The reactions for these processes can be written as follows

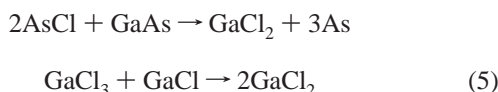


Heating the sample to 130 K causes decomposition of AsCl<sub>3</sub>. Only a small amount of AsCl<sub>3</sub> is still visible on the very top of the surface as evidenced from the corresponding As 3d spectrum (Figure 6). Along with AsCl<sub>3</sub> decomposition, the formation of AsCl<sub>2</sub> and some decrease in the AsCl content is found while As<sup>0</sup> increases. Simultaneously the GaCl<sub>2</sub> and GaCl<sub>3</sub> partial contents increase considerably while GaCl decreases slightly (especially in the deeper layer under study). This can be described by the following reactions



The small amount of AsCl<sub>2</sub> found at this stage may be attributed to a partial reaction 4. AsCl<sub>3</sub> decomposition and enrichment of GaCl<sub>2</sub> and GaCl<sub>3</sub> at the surface are the cause for the increase in the Ga-to-As ratio at 95-eV excitation energy (Figure 9). So, we are following the etching reaction with chlorination of lower As and Ga chlorides to higher chlorides (AsCl<sub>3</sub> and GaCl<sub>2</sub> and GaCl<sub>3</sub>) and the preferential etching (desorption) of AsCl<sub>3</sub>. Enrichment of the Ga reaction products and of elementary As<sup>0</sup> indicates the ongoing etching attack on the substrate. The chlorination of GaCl to GaCl<sub>3</sub> at low temperatures was also observed previously in the case of Cl<sub>2</sub> interaction with the GaAs(100) surface.<sup>36</sup>

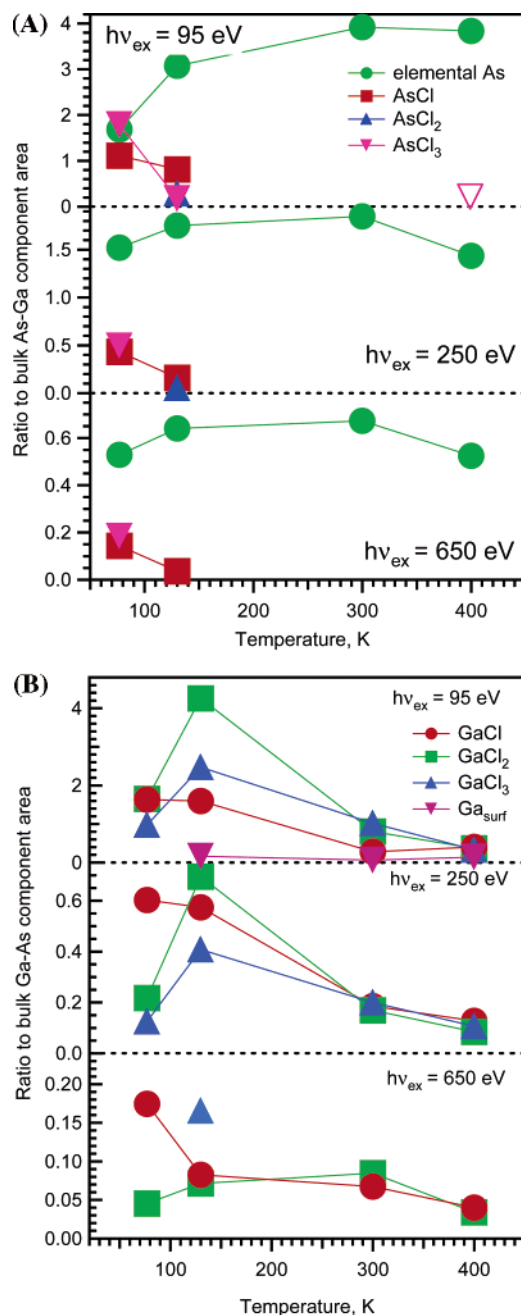
After heating the sample to RT the As chlorides completely disappeared and the content of all Ga chlorides decreases considerably (over all thickness under study of the sample (Figure 10b)). On the other hand, the intensity of As<sup>0</sup> increased, so there is no further chlorination of surface atoms at this stage and the Ga-to-As ratio decreases (Figure 9). Comparison to temperature-programmed desorption (TPD) results allows us to conclude that the partially chlorinated arsenic is converted to As<sup>0</sup> remaining on the surface and GaCl<sub>2</sub>, which is removed from the surface.<sup>26</sup> Thus, the following reactions can be written for this stage



Heating the sample to 400 K results in further reduction of all Ga chloride components and elemental arsenic starts to desorb (parts a and b of Figure 10) in the form of As<sub>2</sub> as found in TPD measurements.<sup>37</sup>

We found considerable removal of the GaCl<sub>2</sub> surface species as the temperature increases to 300 K. This contradicts the results of quantum chemical calculations<sup>38</sup> but confirms the GaCl<sub>2</sub> desorption found at 240 K in TPD.<sup>26</sup>

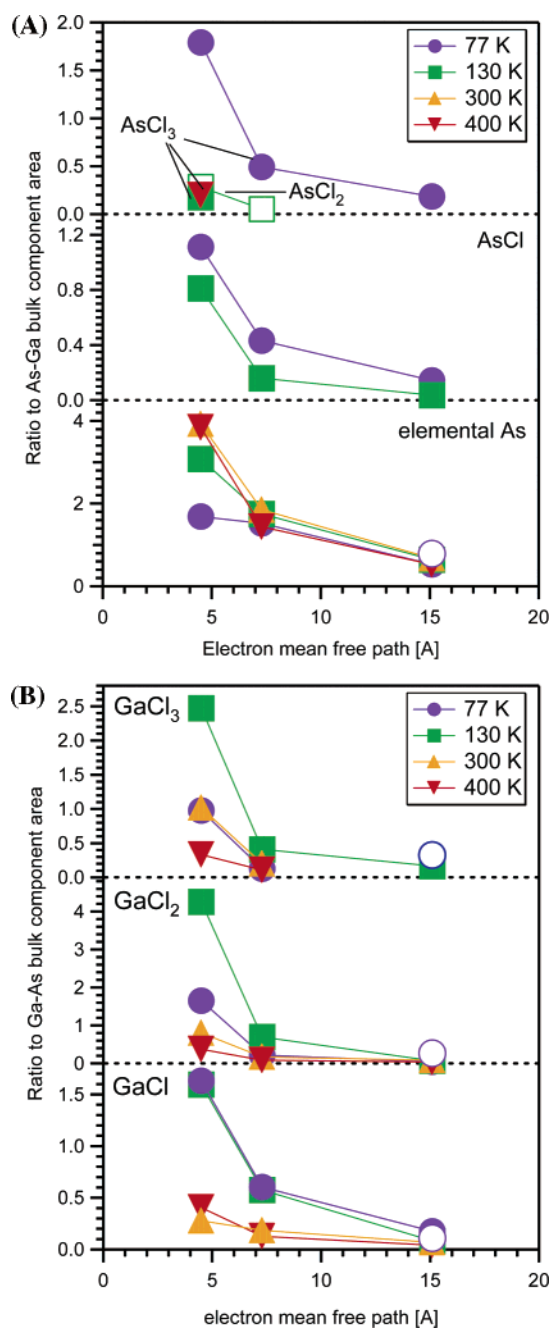
**B. Depth Structuring of Reaction Products.** We consider now the distribution of the reaction products over the near-surface layer of GaAs(100) at different temperatures (parts a and b of Figure 11). The electron inelastic mean free path, which



**Figure 10.** (a) Intensity ratios of elemental arsenic, AsCl, AsCl<sub>2</sub>, and AsCl<sub>3</sub> components to the As-Ga bulk intensity of the GaAs(100)/(frozen) HCl-2-propanol interface in dependence of the heating temperatures for different excitation energies. The open reverse triangle represents a species, which we assigned to AsCl<sub>3</sub> stabilized by back-bonds (see Figure 6). (b) Intensity ratios of GaCl, GaCl<sub>2</sub>, GaCl<sub>3</sub>, and surface gallium components to the intensity of the Ga-As bulk component of the GaAs(100)/(frozen) HCl-2-propanol interface in dependence of heating temperatures for different excitation energies.

is the depth where the intensity of photoemission is attenuated by a factor of  $e$ , characterizes the information depths. By use of a simple layer model for the interfaces, we now discuss the arrangement of the reaction products for the different analyzed conditions of the GaAs/HCl-2-propanol interface.

By increasing the information depths going from 95 to 250 eV photon energy at 77 K (circles in Figure 11a), the AsCl<sub>3</sub>/As<sub>bulk</sub> ratio falls considerably steeper (by a factor of 3.6) than AsCl/As<sub>bulk</sub> (factor 2.5) while As<sup>0</sup>/As<sub>bulk</sub> is almost constant (factor 1.1). This result clearly indicates layered formation of the chlorides on top of elemental As<sup>0</sup>. For the Ga chlorides



**Figure 11.** (a) Intensity ratios of elemental arsenic, AsCl, AsCl<sub>2</sub>, and AsCl<sub>3</sub> components to the intensity of the As-Ga bulk component of the GaAs(100)/(frozen) HCl-2-propanol interface in dependence of the electron mean free path after heating to various temperatures. The open circle corresponds to the elemental arsenic composition measured right after freezing the electrolyte layer (taken from Figure 3b). (b) Intensity ratios of GaCl, GaCl<sub>2</sub>, and GaCl<sub>3</sub> components to the intensity of the Ga-As bulk component of the GaAs(100)/(frozen) HCl-2-propanol interface in dependence of the electron mean free path after heating to various temperatures. The open circles correspond to the content of the corresponding components measured right after freezing the electrolyte layer (taken from Figure 3a).

(circles in Figure 11b), the GaCl<sub>2</sub>/Ga<sub>bulk</sub> and GaCl<sub>3</sub>/Ga<sub>bulk</sub> ratios change stronger (by factors of 7.6 and 7.8, respectively) than GaCl/Ga<sub>bulk</sub> (by a factor of 2.7), which also indicates that the chlorination number increases toward the top. The higher factors for the Ga chlorides compared to the As chlorides indicates the strong enrichment of the Ga chlorides at the surface due to preferential etching of As in the liquid etchant as discussed already for the measurements in just after freezing condition.

At 130 K, where AsCl<sub>3</sub> has been decomposed according to eq 4, the relative intensities vs the As bulk emission of AsCl<sub>2</sub> and AsCl decrease by almost similar values (factors of 5.5 and 5.1, respectively) when the information depths is increased by increasing the excitation energy from 95 to 250 eV while the relative intensity of elemental As decreases by a factor of 1.75 only (squares in Figure 11a). The relative intensities of GaCl<sub>3</sub> and GaCl<sub>2</sub> now change with similar values of 6.0 and 6.1, while GaCl changes by 2.8 (squares in Figure 11b). So a relatively homogeneous distribution of the Ga chlorides and the As chlorides on top of elemental As with intermixed GaCl is indicated. At RT the only strongly detectable As-related reaction product with 250 eV photon energy is elementary As while for Ga all the reaction products (Ga-Cl<sub>1,2,3</sub>) are detectable and the surface enrichment of Ga chlorides is still evident as the bulk related intensity ratios of 95–250 eV spectra decrease by factors of 1.5, 4.75, and 5 for GaCl/Ga<sub>bulk</sub>, GaCl<sub>2</sub>/Ga<sub>bulk</sub>, and GaCl<sub>3</sub>/Ga<sub>bulk</sub>, respectively (triangles in parts a and b of Figure 11).

After annealing at 400 K, the distribution of elemental arsenic, which is the only As-related surface species here, is similar to that obtained at the surface maintained at RT. The only distinction is that the decrease in elemental As bulk related intensity on increasing the information depth by changing the excitation energy from 95 to 250 eV becomes slightly higher (reverse triangles in Figure 11a) compared to the RT condition indicating that desorption proceeds from an interior (Ga chloride covered) As<sup>0</sup> layer. The depth distribution of Ga chlorides at 400 K (reverse triangles in Figure 11b) shows some increase in the surface GaCl content.

## V. Conclusion

The frozen electrolyte approach was introduced as a new method for the analysis of solid/liquid interfaces. The interaction of HCl (in 2-propanol) with the GaAs(100) wafer surface was analyzed with synchrotron radiation by freezing in a thin layer of the etchant after etching off the natural oxide layer. It was found that an ice layer that unavoidably condensed from background gas during cooling to LN<sub>2</sub> temperature could be desorbed by irradiation with synchrotron light without reacting with the substrate. The interaction of HCl in 2-propanol on GaAs(100) has been investigated starting from an oxidized wafer surface. The etching reaction has been performed and frozen-in under inert N<sub>2</sub> gas, and a Ga-rich composition similar to emersion experiments at RT was found initially. The etching reaction was then activated in situ by extended exposure to synchrotron radiation at LN<sub>2</sub> temperature at which volatile (soluble) reaction products cannot leave the interface. Formation of the highly chlorinated species AsCl<sub>3</sub> and GaCl<sub>3</sub> has been observed. By flashing to higher temperatures further etching reactions have been activated and the desorption of certain reaction products has been followed: Heating the sample to approximately 130 K causes the reaction of AsCl<sub>3</sub> with the pristine substrate to form Ga chlorides and elemental As. Heating the sample to RT results in desorption of GaCl-related species and reaction of AsCl with the substrate whereby the elemental arsenic content is increased further. By heating to 400 K elemental arsenic begins to desorb. By use of different excitation energies, i.e., information depths, decreasing chlorination numbers toward the pristine substrate have been evidenced for all stages of the reaction. Clearly in dependence on specific stages of the experiment very many different reaction species are formed leading to a complex distribution within the reaction layer.

The results demonstrate that a wealth of information on solid/electrolyte interfaces may be gained with synchrotron photo-



electron spectroscopy using the frozen electrolyte approach which complements adsorption and emersion experiments. Surprisingly soluble (volatile) species ( $\text{AsCl}_3$ ) have not been found right after blowing off the etchant and freezing but have been formed in situ. Detailed information about elementary reaction processes in the presence of all relevant species may be obtained. In future experiments the pump–freeze procedure will be further optimized to minimize unintended condensation of water from the  $\text{N}_2$  vented buffer chamber.

**Acknowledgment.** The experimental station SoLiAS is financed by the German Ministry of Education and Research under Contract No. BMBF 05 KS1RD/0. Financial support of BESSY beam time by the German Ministry of Education and Research (BMBF) under Contract No. 05ES3XBA/5 is gratefully acknowledged. M.V.L. is grateful to Alexander von Humboldt Foundation for a Research Fellowship.

## References and Notes

- (1) Memming, R. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1979; Vol. 11.
- (2) Jaegermann, W. The semiconductor/electrolyte interface: A surface science approach. In *Modern Aspects of Electrochemistry*; White, R. E., Ed.; Plenum Press: New York, 1996; Vol. 30.
- (3) Beerbom, M.; Mayer, Th.; Jaegermann, W. *J. Phys. Chem. B* **2000**, *104*, 8503.
- (4) Beerbom, M.; Henrion, O.; Klein, A.; Mayer, T.; Jaegermann, W. *Electrochim. Acta* **2000**, *45*, 4663.
- (5) Saito, J.; Kondo, K. *J. Appl. Phys.* **1990**, *67*, 6274.
- (6) Nooney, M.; Liberman, V.; Xu, M.; Ludviksson, A.; Martin, R. M. *Surf. Sci.* **1994**, *302*, 192.
- (7) Su, C.; Dai, Z. G.; Luo, W.; Sun, D. H.; Vernon, M. F.; Bent, B. E.; *Surf. Sci.* **1994**, *312*, 181.
- (8) Senga, T.; Matsumi, Y.; Kawasaki, M. *J. Vac. Sci. Technol. B* **1996**, *14*, 3230.
- (9) Hung, W. H.; Wu, S. L.; Chang, C. C. *J. Phys. Chem. B* **1998**, *102*, 1141.
- (10) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.
- (11) Lebedev, M. V. *Prog. Surf. Sci.* **2002**, *70*, 153.
- (12) Tereshchenko, O. E.; Chikichev, S. I.; Terekhov, A. S. *J. Vac. Sci. Technol. A* **1999**, *17*, 2655.
- (13) Tereshchenko, O. E.; Paget, D.; Chiaradia, P.; Bonnet, J. E.; Wiame, F.; Taleb-Ibrahimi, A. *Appl. Phys. Lett.* **2003**, *82*, 4280.
- (14) Laukkanen, P.; Kuzmin, M.; Perälä, R. E.; Vaara, R. L.; Väyrynen, I. *J. Appl. Surf. Sci.* **2003**, *206*, 2.
- (15) Akita, K.; Taneya, M.; Sugimoto, Y.; Hidaka, H. *J. Electrochem. Soc.* **1990**, *137*, 2081.
- (16) Lu, Z. H.; Chatenoud, F.; Dion, M. M.; Graham, M. J.; Ruda, H. E.; Koutzarov, I.; Liu, Q.; Mitchell, C. E. J.; Hill, I. G.; McLean, M. B. *Appl. Phys. Lett.* **1995**, *67*, 670.
- (17) Ishikawa, Y.; Ishii, H.; Hasegawa, H.; Fukui, T. *J. Vac. Sci. Technol. B* **1994**, *12*, 2711.
- (18) Mayer, T.; Jaegermann, W. In *Synchrotron Techniques in Interfacial Electrochemistry*; Melendres, C. A., Tadjeddine, A., Eds.; 1994, p 451.
- (19) Ensling, D.; Hunger, R.; Kraft, D.; Mayer, Th.; Jaegermann, W.; Rodrigues-Girones, M.; Ichizli, V.; Hartnagel, H. L. *Nucl. Instrum. Methods B* **2003**, *200*, 432.
- (20) Mayer, Th.; Lebedev, M.; Hunger, R.; Jaegermann, W. *Appl. Surf. Sci.* **2005**, *252*, 31.
- (21) Osakabe, S.; Adachi, S. *Jpn. J. Appl. Phys.* **1997**, *36*, 7119.
- (22) Thiel, P. A.; Madey, P. E. *Surf. Sci. Rep.* **1987**, *7*, 211.
- (23) Jaegermann, W.; Mayer, T.  $\text{H}_2\text{O}$  and OH on Semiconductors. In *Physics of Covered Solid Surfaces. LANDOLT-BÖRNSTEIN III/42 A4*; Bonzel, H. P., Ed.; Springer: in press.
- (24) Tanuma, S.; Powell, C. J.; Penn, D. R. *Surf. Interface Anal.* **1991**, *17*, 927.
- (25) Henderson, M. A. *Surf. Sci. Rep.* **2002**, *46*, 1.
- (26) Ludviksson, A.; Xu, M.; Martin, R. *Surf. Sci.* **1992**, *277*, 282.
- (27) Le Lay, G.; Mao, D.; Kahn, A.; Hwu, Y.; Margaritondo, G. *Phys. Rev. B* **1991**, *43*, 14301.
- (28) Yeh, J. J.; Lindau, I. *At. Data Nucl. Data Tables* **1985**, *32*, 1.
- (29) Simpson, W. C.; Shuh, D. K.; Hung, W. H.; Håkansson, M. C.; Kanski, J.; Karlsson, U. O.; Yarmoff, J. A. *J. Vac. Sci. Technol. A* **1996**, *14*, 1815.
- (30) Stepniak, F.; Rioux, D.; Weaver, J. H. *Phys. Rev. B* **1994**, *50*, 1929.
- (31) Frese, K. W.; Morrison, S. R. *Appl. Surf. Sci.* **1981**, *8*, 266.
- (32) Lebedev, M. V.; Ensling, D.; Hunger, R.; Mayer, T.; Jaegermann, W. *Appl. Surf. Sci.* **2004**, *229*, 226.
- (33) Erné, B. H.; Stchakovsky, M.; Ozanam, F.; Chazalviel, J.-N. *J. Electrochem. Soc.* **1998**, *145*, 447.
- (34) Hollinger, G.; Skheyta-Kabbani, R.; Gendry, M. *Phys. Rev. B* **1994**, *49*, 11159.
- (35) Liberman, V.; Haase, G.; Osgood, R. M., Jr. *J. Chem. Phys.* **1992**, *96*, 1590.
- (36) Bond, P.; Brier, P. N.; Fletcher, J.; Jia, W. J.; Price, H.; Gorry, P. A. *Surf. Sci.* **1998**, *418*, 181.
- (37) French, C. L.; Balch, W. S.; Foord, J. S. *J. Phys.: Condens. Matter* **1991**, *3*, S351.
- (38) Jenichen, A.; Engler, C. *J. Phys. Chem. B* **2000**, *104*, 8210.