Synchrotron-Induced Photoemission of Emersed GaAs Electrodes after Electrochemical Etching in Br2/H2O Solutions

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Synchrotron-Induced Photoemission of Emersed GaAs Electrodes after Electrochemical Etching in Br$_2$/H$_2$O Solutions

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GaAs(110) surfaces have been studied after etching in Br$_2$/H$_2$O solutions and emersion from the electrolyte using high-resolution synchrotron-induced photoelectron spectroscopy. High-quality spectra of the core lines and the valence band region have been obtained by using a specifically developed transfer procedure, which allows synchrotron-induced XPS analysis after several transfers between the solution and vacuum. After treatment in Br$_2$/H$_2$O solutions, the surface of GaAs is covered by a mixture of mostly Ga$_2$O$_3$, Ga(OH)$_3$, As$_2$O$_3$, and As$_2$O$_5$. After rinsing in liquid H$_2$O, the arsenic oxides are dissolved leaving the GaAs surface covered with a layer of elementary arsenic and gallium oxides and hydroxides.

Introduction

The photoelectrochemistry of GaAs electrodes in aqueous electrolytes turns out to be rather complex because of the formation of surface states that result from the interaction of the electrode surface with electrolyte components[1]. Especially H$_2$O and oxygen are considered to be the main reactive species, and they can form several oxygen adsorption species, as well as bulklike oxides[2]. Several etching solutions have been suggested for the preparation of clean and oxygen-free surfaces[3], which can subsequently be used for epitaxial growth of heterojunctions or for the study of fundamental (photo)-electrochemical properties. To check for surface cleanliness and/or the composition of possibly formed surface layers, photoelectron spectroscopy (XPS or ESCA) with laboratory sources have often been used.[4−12] However, because of limited surface sensitivity and low energy resolution, only larger amounts of oxides are easily detected with this approach. So far, no systematic studies of emersed semiconductor electrodes have been performed using synchrotron-induced photoelectron spectroscopy, which has developed into a standard characterization technique for adsorbate-induced changes of semiconductor surfaces. Because of the increased surface sensitivity, reasonable results with synchrotron-induced XPS can only be expected when emersion and transfer of the electrodes is realized in a very controlled and perfectly clean procedure.

In this paper, we present our first results on the use of synchrotron-induced XPS for the characterization of GaAs(110) electrodes after treatment in wet etching solutions. For this study, Br$_2$/H$_2$O was used for etching as the involved chemical species can easily be identified with synchrotron-induced XPS by the available excitation energy. Br$_2$-containing solutions, usually with methanol as the solvent, belong to the standard etches for GaAs. For these first experiments, we selected the GaAs(110) cleavage plane instead of the technologically more important (100) surfaces because we wanted to start with the very defined surface conditions obtained after UHV cleavage. The surface composition that is obtained after different steps of etching is analyzed and compared to results from adsorption experiments containing the same species.[12−15]

Experimental Section

We used a specifically designed electrochemical chamber for the etching process and a special buffer chamber for the transfer of the samples into UHV. A schematic sketch of the setup is shown in Figure 1. The base pressure in the measurement chamber is about 1×10^{-10} mbar. After the electrode surface has been treated with wet etching solutions, it can (or cannot) be rinsed with deionized H$_2$O, and the remainders of the solutions are blown off the surface with clean and dry N$_2$. As etch solutions, Br$_2$/H$_2$O mixtures with a concentration ratio of about 10^{-3} have been used. All solutions and the electrochemistry chamber were kept in a N$_2$ atmosphere and were thus free of atmospheric O$_2$. After transfer into UHV (a pressure in the range of 10^{-9} mbar is usually reached within 20 min), the sample surface is characterized by photoelectron spectroscopy in the core and valence band regions with excitation energies in the minimum of the photoelectron escape curve. The spectra were recorded using an angle-resolving photoelectron spectrometer (VG ADES 500) in normal emission mode. All experiments were performed at the TGM7 monochromator of the BESSY storage ring, which provides photons in the energy range between 10 and 120 eV. The overall resolution in the presented experiments is set at 0.3 eV. To avoid problems in the setting of the binding energy scale, we present the chemical shifts of reacted species as relative shifts from the main lines of bulk GaAs. For the fitting of the core level lines, a mixed Gaussian−Lorentzian line shape was used,[16] and the experimental spectra were fit with the minimum number of components.

Experimental Results and Discussion

The photoemission spectra of GaAs(110) surfaces after cleavage in UHV and after treatment in the Br$_2$/H$_2$O etching solution for different exposure times and subsequent rinsing in water are shown in Figures 2 and 3 for the core lines and Figure 4 for the valence band spectra. All spectra have been measured

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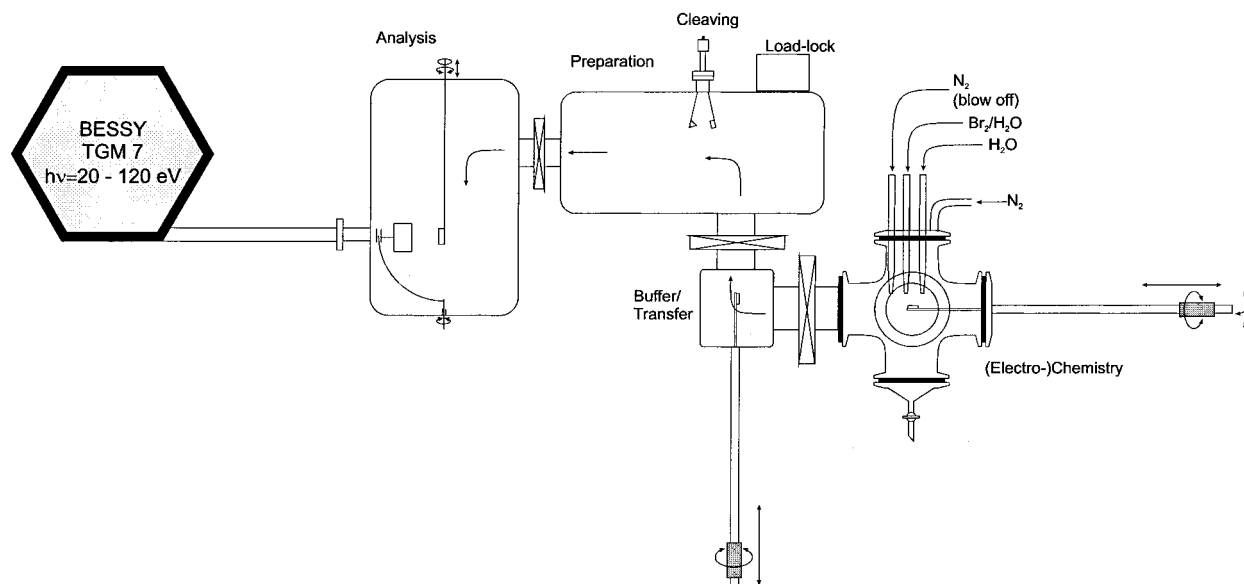
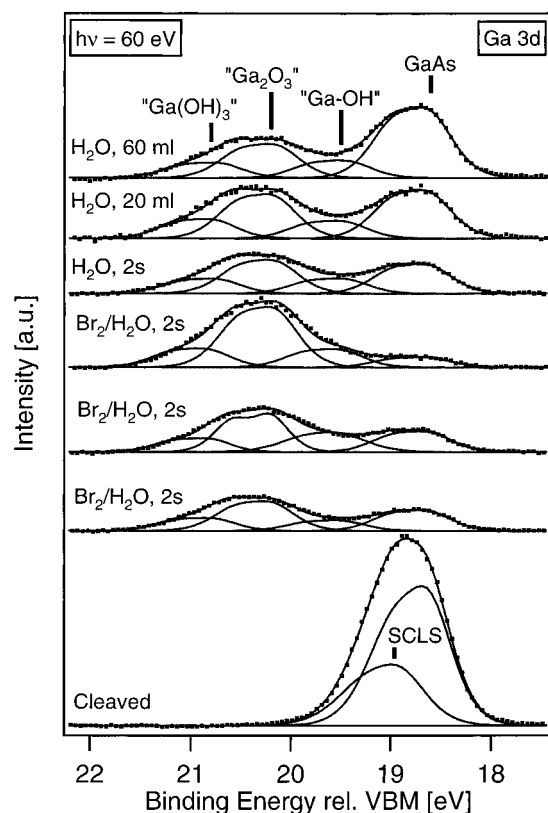**Figure 1.** Principle sketch of the experimental setup used for the emersion experiments (unscaled).

Figure 2. Synchrotron-induced XP spectra of the Ga 3d core level after subsequent surface treatments (of the same sample): "Br$_2$/H$_2$O, 2s" etch with Br$_2$/H$_2$O solution for 2 s; "H$_2$O, 2s" exposure to liquid H$_2$O for 2 s; and "H$_2$O, 20 mL" rinsing with 20 mL of liquid H$_2$O within 40 s.

Figure 3. Synchrotron-induced XP spectra of the As 3d core level after subsequent surface treatments (of the same sample): "Br$_2$/H$_2$O, 2s" etch with Br$_2$/H$_2$O solution for 2 s; "H$_2$O, 2s" exposure to liquid H$_2$O for 2 s; and "H$_2$O, 20 mL" rinsing with 20 mL of liquid H$_2$O within 40 s.

using excitation energies that produce photoelectrons in the minimum of the photoelectron escape curve around 40 eV. Thus, the surface sensitivity of the spectral information is around 0.6 nm (inelastic mean free path). After cleavage of the sample, the spectral shapes of the Ga and As 3d emissions show the well-known asymmetry due to surface core level shifts (SCLS).[17] After exposure to the etching solution, the Ga 3d spectrum is evidently composed of at least three different Ga oxidation components, which follow from the application of the peak fitting routine (Table 1). The relative amounts of these oxides
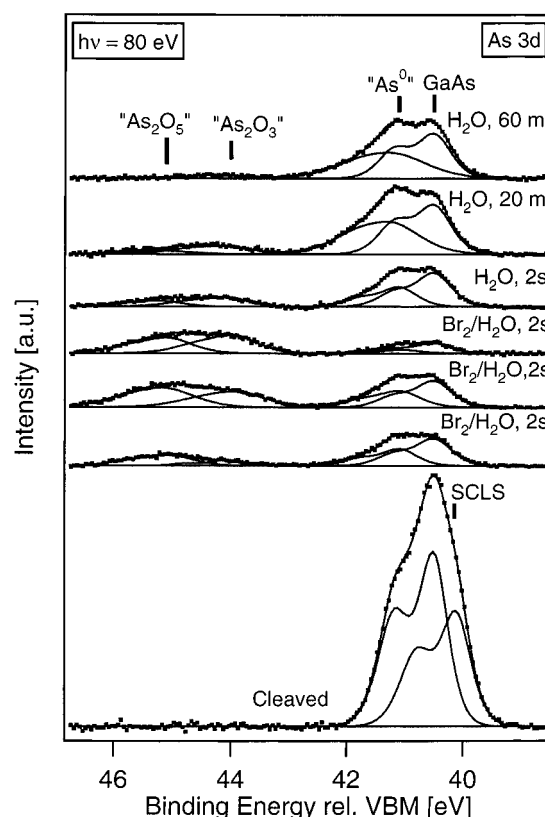
do not change very much for different etching times and also not for subsequent H$_2$O rinsing steps, which were used to dissolve soluble reaction products. In addition to the GaAs bulk component, the main oxide species with $\Delta E = 1.3$ eV is "Ga$_2$O$_3$", which should indicate Ga^{3+} oxidation states in an oxygen coordination sphere. This assignment is in good agreement with previously obtained data of thicker oxides formed on GaAs.[18,19] However, for oxides formed in the monolayer regime by exposure to O$_2$ in UHV, lower binding energy shifts of $\Delta E = 1.0$ eV have been found.[20] In addition, small amounts
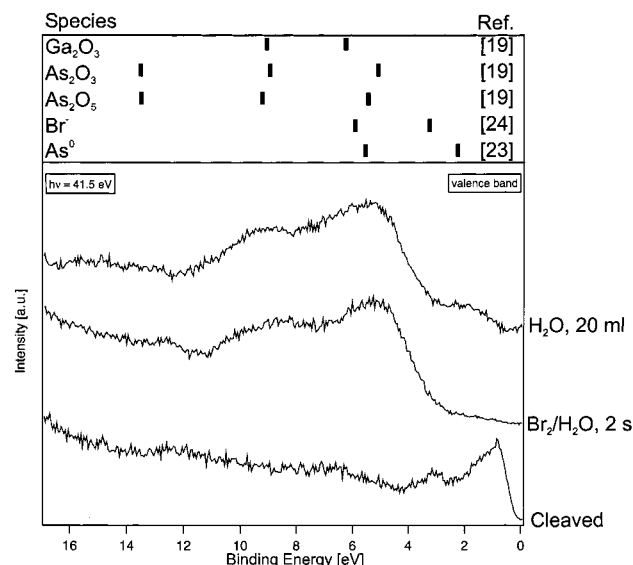
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Figure 4. Valence band spectra of GaAs(110) after subsequent surface treatments (of the same sample): "Br$_2$/H$_2$O, 2s" etch with Br$_2$/H$_2$O solution for 2 s; "H$_2$O, 2s" exposure to liquid H$_2$O for 2 s; and "H$_2$O, 20 mL" rinsing with 20 mL of liquid H$_2$O.

TABLE 1: Binding Energy Shifts of Surface Species Formed on GaAs(110) after Etching in Br$_2$/H$_2$O

species	ΔBE/eV
Ga (3d)	
"SCLS"	0.3
"Ga-OH"	0.9
"Ga$_2$O$_3$"	1.6
"Ga(OH)$_3$"	2.2
As (3d)	
"SCLS"	−0.4
As^0	0.6
"As$_2$O$_3$"	3.5
"As$_2$O$_5$"	4.6

of "Ga$_2$O/GaOH" can be detected at $\Delta E = 0.9$ eV. Furthermore, a strongly shifted emission line at $\Delta E = 2.2$ eV is evident in the spectra. On the basis of the binding energy difference, this can be assigned to the formation of GaAsO$_4$, as also suggested for O$_2$-treated surfaces.[19] However, we prefer to assume the formation of "Ga(OH)$_3$" species, which have been previously detected on GaAs electrodes after treatment in H$_2$O,[22] as this component of the spectrum shows a dependence on H$_2$O rinsing that is completely different from that of the arsenic oxides detected on the surface (see below). The spectral changes of the As 3d spectra show increased amounts of "As$_2$O$_3$"/"As$_2$O$_5$" mixtures formed on the surface after increased Br$_2$/H$_2$O exposure times (Figure 3). Because the possible surface oxides such as "As$_2$O$_3$" and "As$_2$O$_5$" are soluble in H$_2$O, they are subsequently completely dissolved by rinsing with water. The As 3d spectrum indicates the existence of elementary As covering the surface. The As layer is already formed before the arsenic oxides are removed by water rinsing, as is evidenced by the increasing spectral contribution from the As layer with reduced oxide thickness, while simultaneously, the ratio of As^0 to the bulk As component is almost unchanged. The preferential removal of arsenic oxides with water rinsing was also observed by Woodall et al.[11] It cannot be decided from the spectral results whether As is directly formed by reaction with the etching solution or whether previously formed arsenic oxide reacts with GaAs to form the thermodynamically more stable combination Ga$_2$O$_3$ and As at the GaAs/oxide phase boundary. We can definitely

exclude GaBr$_x$ and AsBr$_x$ species from being present on the surface as they show different core level shifts.[12−15]

It was possible to measure reasonable valence band spectra of the reacted GaAs surfaces also after wet Br$_2$/H$_2$O etching and subsequent water rinsing that were not dominated by contaminations due to C$_x$H$_y$ layers. As expected from the core level results, the spectrum after Br$_2$/H$_2$O etch is dominated by strong emission between 4 and 11 eV binding energy, which can be assigned to contributions from the O 2p levels of different oxides and/or hydroxides. The expectation values for the emission lines of the different species are indicated in the inset of the spectrum. It is interesting to note that the emission features that can be assigned to elementary As can be detected only after removal of the arsenic oxides by water rinsing. Furthermore, it is quite clear that no contributions from bromides are found in the surface reaction layer on GaAs, as follows from the comparison of the experimental data to reference values (for typical emission lines of bromides, see Figure 4 and ref 14). This is also in good agreement with Br 3d core level spectra, which indicate that some contributions from Br that can be found on the surface after emersion and transfer are composed of molecular species and are evidently due to reminiscents from the etching solutions.

In summary, our spectral results show that the wet chemical etch of the GaAs(110) surface with Br$_2$/H$_2$O solutions leads to the formation of a surface reaction layer containing a mixture of different gallium oxides and arsenic oxides. The reaction is not restricted to the topmost surface layer but proceeds into the bulk of the sample. We, therefore, can assume that Br$_2$ is involved in the oxidative breaking of the GaAs surface bonds and back-bonds forming gallium bromide and arsenic bromide species in the first step. Subsequently, the bromides are readily hydrolyzed to form the respective oxides. This is also supported by the fact that GaAs(110) surfaces exposed to liquid H$_2$O even for extended times do not show the formation of oxides.[23] Furthermore, model experiments of GaAs etching in which Br$_2$/H$_2$O adsorbate mixtures are adsorbed step-by-step onto GaAs surfaces clearly indicate the formation of GaBr$_3$, AsBr$_3$, and AsBr$_5$ species as the initial step, which subsequently react to oxides/hydroxides with coadsorbed H$_2$O. Water rinsing leads to the preferential dissolution of the formed arsenic oxides, leaving the gallium oxide mixtures nearly unchanged and elementary As on the surface, both of which are hardly soluble in H$_2$O.[23,24] The final composition of the surface is thus determined by many parameters, such as etching concentrations, etching time, subsequent rinsing, etc. that can be analyzed in a very controlled manner and with high spectral resolution, as we have shown in this paper.

Conclusions

We have shown in this paper that wet chemical etching processes can be analyzed with high surface sensitivity and high energy resolution using synchrotron-induced photoelectron spectroscopy. It was shown that much more detailed information is directly available by using the given advancement in the spectral performance. Thus, such complex wet chemical etches as given by Br$_2$/H$_2$O mixtures can readily be analyzed with respect to their reactivity and the step-by-step semiconductor surface composition using variations in the treatment procedure. In principle, the applied technique also allows for the investigation of surface potentials such as band bending, work function, Fermi level pinning, surface photovoltages, etc.[1] Therefore, we expect that through the use of optimized emersion and transfer conditions in combination with model experiments, complex

electrochemical etching processes can be approached at a level of detail similar to that applied to surface reactions by adsorbates. Furthermore, we plan to extend our studies of using synchrotron-induced XPS for ex situ analysis of electrochemical reactions of semiconductor samples also to electrodes to which potentials and (photo)currents have been applied.

References and Notes

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