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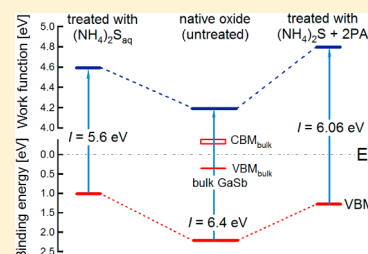
Sulfur Passivation of GaSb(100) Surfaces: Comparison of Aqueous and Alcoholic Sulfide Solutions Using Synchrotron Radiation Photoemission Spectroscopy

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ABSTRACT: In an attempt to rationalize empirically developed GaSb device optimization using alcoholic versus aqueous sulfide solutions, synchrotron radiation photoemission spectroscopy (SXPS) has been applied to study the chemical composition and the electronic properties of the GaSb(100) surface treated with ammonium sulfide dissolved in water versus 2-propanol. In addition the initial native oxide layer on GaSb(100) surface has been analyzed in detail. The variation of the solvent leads to variations in the chemical composition and electronic structure of the final sulfide layers. In the deeper parts of the passivation layers, the Ga/Sb atomic ratio is around 1 for 2-propanol and 2 for aqueous solution. Right at the surface it is 0.15 and 0.4, respectively. Valence band maximum and core levels of the sulfide layers are found at 0.26 and 0.4 eV higher binding energies using 2-propanol versus aqueous solution. Almost no oxygen is left on the surface treated using ammonium sulfide in 2-propanol, while with use of aqueous ammonium sulfide solution, inclusions of Ga₂O₃ are found. The carbon contamination is reduced 4 times using alcoholic, while it is increased by a factor of 1.25 with aqueous solution.



1. INTRODUCTION

GaSb is an important III–V semiconductor. Small effective electron and hole masses, high electrical conductivity, and ease of ohmic contact formation make it attractive for potential applications in quantum devices, e.g., tunnel field effect transistors (T-FETs).¹ In addition, GaSb is used as a substrate for epitaxial growth of various III–V ternary and quaternary compounds such as AlGa(In)As(Sb). The variations in band structures and band gaps make these compounds promising candidates for high-speed electronic and long-wavelength optical devices.^{1–4}

Like most III–V semiconductors, GaSb is chemically very active. The surface is easily oxidized and a several-nanometer-thick oxide layer is quickly formed upon exposure to air. The surface defects caused by modification of the surface roughness and stoichiometry lead to surface states, which can act as nonradiative recombination centers affecting detrimentally the device performance. Therefore, it is important to control the electronic structure and surface state density to optimize the performance and the reliability of GaSb devices. Various surface passivation methods, including wet and dry chemical processes,^{5–10} have been studied in efforts to improve the GaSb surface and interface characteristics. Unfortunately, most processing techniques are still water-based and leave some amount of residual oxides and degrade the structural quality of the surface.¹¹ Therefore, alternative, nonaqueous solutions capable of sulfidization are of particular interest for GaSb surface processing.¹²

In the case of the GaAs(100) surface it was demonstrated that compared to aqueous sulfide solutions, alcoholic sulfide solutions provide more effective electronic passivation and offer long-term stability of the sulfide coating in ambient atmosphere even under the influence of strong laser radiation.^{13,14} Treatment with alcoholic sulfide solutions was used to improve the performance of different light-emitting diodes, lasers and optical amplifiers,^{15–19} and solar cells.²⁰ Recently it was found that the treatment with alcoholic sulfide solution results in considerable improvement of the performance of GaSb (and also InAs) infrared photodiodes and that such passivation is more efficient than the passivation with aqueous sulfide solution.²¹

In this work the electronic structure and the chemistry of the GaSb(100) sulfur passivation achieved with aqueous and alcoholic sulfide solutions are analyzed by means of highly surface sensitive synchrotron radiation photoemission spectroscopy. Chemistry and electronic structure of the native oxide layer on GaSb(100) surface are investigated as well. The results rationalize the empirical finding of GaSb device optimization using alcoholic instead of aqueous ammonium sulfide solutions.

2. EXPERIMENTAL SECTION

The experiments have been performed at the undulator beamline U49/2 of the BESSY II storage ring, which provides

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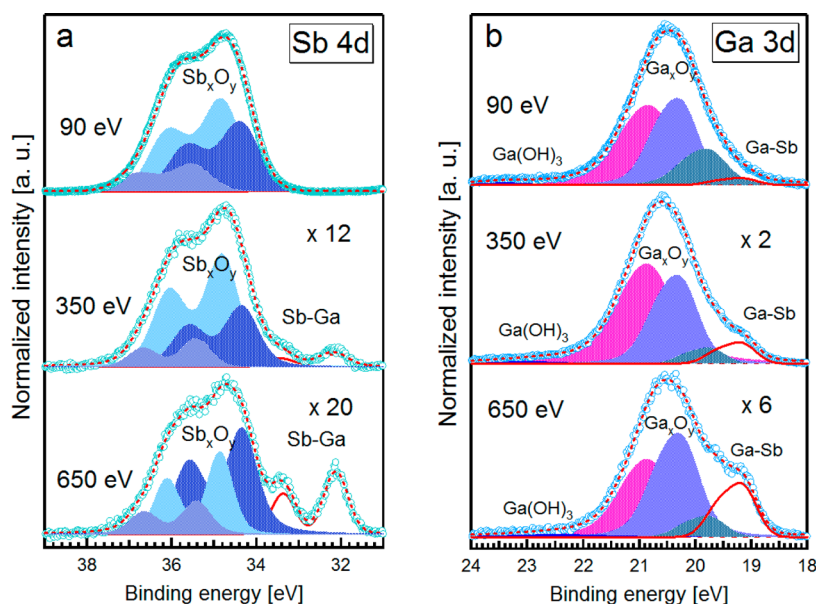


Figure 1. Native oxide covered GaSb(100). Excitation energy dependent Sb 4d (a) and Ga 3d (b) core-level photoemission spectra, surface sensitivity increasing from bottom to top. Dots are data points after background subtraction. Dashed red line is a fit with the indicated components. Spectra are normalized to maximum intensity. Scaling factors are given with respect to the intensities of the spectra measured with excitation energy of 90 eV.

photons in the energy range between $h\nu = 90$ eV and $h\nu = 1400$ eV. Valence band spectra have been taken using 90 eV photons. For highest surface sensitivity, Ga 3d and Sb 4d core levels were measured at 90 eV, S 2p and C 1s were measured at 350 eV, and Sb 3d and O 1s were measured at 650 eV photon energies. At the resulting kinetic energies the inelastic mean free path λ of the excited electrons is approximately 5 Å,²² implying that roughly 63% of the respective orbital emission stems from the first atomic layer, 23% from the second, and 9% from the third. In order to vary the information depth, Ga 3d and Sb 4d core levels were also measured at 220, 350, and 650 eV, resulting in mean free path λ of 12, 17, and 25 Å. All spectra were measured at normal emission. Core-level spectra were fitted with Voigt functions after Shirley background subtraction using IGOR Pro software (WaveMetrics, Inc.). For Sb 4d and Ga 3d similar parameters (Gaussian width for measurement uncertainty, Lorentzian width for lifetime broadening, spin–orbit splitting, branching ratio) as used in refs 23 and 24 were applied. The spectra were obtained using the Phoibos 150 (SPECS) energy analyzer of the experimental system “SoLiAS” (solid/liquid analysis system)²⁵ permanently operated at BESSY.

The work function of the samples is determined from the low kinetic energy cutoff of the secondary electron background (“secondary edge”) in the valence band spectra.²⁶ A bias of −4 V was applied to the sample during the work function measurements to distinguish between the analyzer and the sample cutoff and to efficiently collect the low energy electrons into the analyzer.

The GaSb(100) samples were cut from a Te-doped n-type wafer with carrier concentration of $(1-3) \times 10^{17} \text{ cm}^{-3}$. Commercial 40–48% ammonium sulfide $((\text{NH}_4)_2\text{S})$ aqueous solution was used as received. Such a high concentration of ammonium sulfide was used to minimize the amount of residual oxides on the surface left after treatment with aqueous ammonium sulfide solution, although roughening has to be expected.^{27,28} The aqueous solution was diluted by 2-propanol ($2\text{-C}_3\text{H}_7\text{OH}$) in the ratio of 1:10 to prepare the alcoholic

solution. The native oxide was measured on samples as received. Without preliminary chemical treatment the samples were treated for 30 min at room temperature ex situ (in air) either in the alcoholic or in the aqueous solution. Without rinsing, the samples were removed from the solution, dried for 5 min in air, loaded into an ultrahigh vacuum (UHV) buffer chamber that was rapidly evacuated, and transferred to the analysis chamber. Besides the difference of solvent, the same routine was used in the case of aqueous and 2-propanol solutions.

3. RESULTS

Prior to sulfur treatment the initial GaSb(100) surface is covered with a layer of antimony and gallium oxides and hydroxides. In Figure 1 spectra of Sb 4d and Ga 3d core levels are displayed, measured with increasing (bottom to top) surface sensitivity. The Sb 4d core level measured in the most surface-sensitive mode using 90 eV excitation energy can be fitted with three components corresponding to antimony oxide phases Sb_xO_y with different oxidation states. These components show chemical shifts from the Sb–Ga component of 2.2, 2.7, and 3.25 eV, respectively. The Sb–Ga component tentatively assigned to bulk emission appears in the spectra measured with higher excitation energies (350 eV and higher) at 32.2 eV. It was taken into account also in the fitting of the spectra measured at 90 and 220 eV excitation energies, where its intensity was much lower (2 orders of magnitude and by a factor of 25 and more, respectively) than the intensity of any antimony oxide component. The antimony oxide components with the chemical shifts of 2.7 and 3.25 eV can be assigned to Sb_2O_3 and Sb_2O_5 , respectively.²⁸ The component with the chemical shift of 2.2 eV can be associated with mixed oxides like GaSbO_4 . Assuming similar energy dependent mean free path λ in GaSb as in GaAs or InSb (~ 17 Å at 350 eV²²), the thickness of the native oxide layer can be estimated to be approximately $3\lambda_{350} \approx 50$ Å.

There are several other ways to estimate layer thickness from the photoemission data. In particular, the inelastic mean-free-path value not only can be obtained from optical data but can be calculated from the so-called TPP-2 formula.²² Also the effective attenuation length that accounts for the elastic scattering effects can be considered, although it is difficult to calculate it unambiguously.²⁹ These last two values are usually smaller than the inelastic mean free path value obtained from optical data that we used for thickness estimations. On the other hand, accurate determination of the native oxide layer thickness is hindered by its multiphase composition. Thus, in the sensitivity range obtained in our measurements, all absolute thickness values given have to be taken cum grano salis as good estimates, while the relative changes are precise.

The Ga 3d 90 eV core-level spectrum is somewhat less surface sensitive, and thus, a small Ga–Sb emission at 19.2 eV is visible, which can be tentatively assigned to bulk emission because it increases with increasing excitation energy. The energy difference between the Sb–Ga and Ga–Sb components is equal to 13.0 eV, which is consistent with literature data for energy difference between Sb and Ga bulk components in Sb 4d and Ga 3d core levels at the reconstructed GaSb(100) surfaces.^{23,24} The Ga 3d spectra can be fitted well with four additional components with chemical shifts to higher binding energy of +0.6, +1.1, +1.6, and +3.8 eV representing various gallium oxides and hydroxides. The assignment of the chemical shifts to gallium oxide species is quite controversial.^{30–32} The first can be assigned to gallium suboxide Ga_2O_x ($x = 1–2$)³³ or gallium hydroxide GaOH ,³² the second to gallium oxide Ga_2O_3 ,³⁰ the third also to gallium oxide Ga_2O_3 ,³² or to the mixed oxide $\text{Ga}(\text{SbO}_3)_3$,³⁰ and the fourth to higher gallium hydroxide $\text{Ga}(\text{OH})_3$ ³² or to the complex oxide GaSbO_4 .

Although we give assignments to stoichiometric compounds, we consider the native oxide as an amorphous layer containing local structures of gallium, antimony, and oxygen that correspond to the bonding situation in the assigned compounds. As the different assigned local bond structures appear with varying intensity ratios at different surface sensitivities, a three-dimensional amorphous mixture of oxides with gradually varying ratios of gallium, antimony, and oxygen is indicated rather than a layered structure.

Figure 2 (650 eV excitation) shows the spectral region where the Sb 3d core-level emission overlaps with the O 1s core level. The spectra have been normalized to the maximum intensity. Because of the lower kinetic energy of the photoelectrons emitted from the Sb 3d versus the 4d orbital, only a small bulk 3d emission is visible through the native oxide (compare Figure 1a bottom). The binding energies of Sb 3d_{5/2} bulk and oxide emissions are 527.3 and 530.2 eV, respectively. Sulfur treatment leads to a new Sb emission at 529.3 eV with a small width of the Gaussian broadening in the Voigt emission profile (fit not shown), indicating a more uniform chemical state compared to the oxide. The Sb intensity is reduced strongly (normalization factor 3.6) after treatment with aqueous solution and less so after treatment with alcoholic solution (normalization factor 1.5 in Figure 2). Obviously after treatment with aqueous ammonium sulfide solution the antimony oxides disappear completely while some O 1s photoemission is visible, which is probably due to gallium oxide residues that weakly appear in the Ga 3d emission (Figure 4b). On the other hand, after treatment with alcoholic solution, the O 1s core level is hardly visible at all, and accordingly, the Sb 3d line shape is perfectly fitted with a single Voigt function (not shown). So very

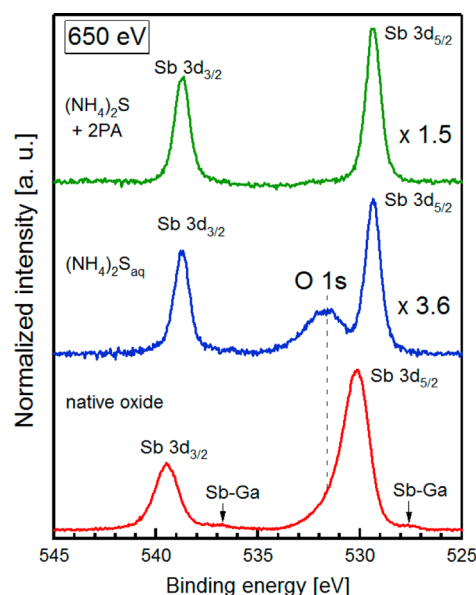


Figure 2. Photoemission spectra of the Sb 3d and O 1s core levels, collected from the native-oxide-covered GaSb(100) surface, as well as after treatment with aqueous ammonium sulfide solution $(\text{NH}_4)_2\text{S}_{\text{aq}}$ and with solution of ammonium sulfide in 2-propanol $[(\text{NH}_4)_2\text{S} + 2\text{PA}]$. The excitation energy was 650 eV. Spectra are normalized to maximum intensity. Scaling factors are given with respect to the intensity of the Sb 3d photoemission on the native-oxide-covered GaSb(100) surface.

different amounts of oxides are found after treatment using aqueous versus 2-propanol solution. As the exposure time to laboratory air was 5 min in both cases, we consider the oxide in the aqueous case to be a residuum of the native oxide or a byproduct of the etching process, although a higher resistance to oxidation of the sample treated with 2-propanol–ammonium sulfide solution cannot be excluded as well.

The survey spectra that include Sb 4d and Ga 3d core levels and the valence bands of the GaSb(100) surfaces treated with aqueous and alcoholic sulfide solutions taken at 90 eV excitation are shown in Figure 3. The emissions of oxide and hydroxide components of the nontreated sample (Figure 1) disappeared, and new emissions of sulfides appear. The positions of Sb 4d and Ga 3d emissions on the surfaces treated with aqueous and alcoholic sulfide solutions are different. In

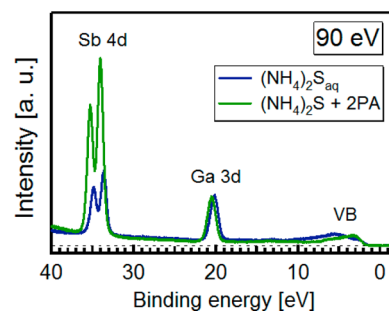


Figure 3. Survey photoemission spectra collected using 90 eV excitation energy from the GaSb(100) surface treated with aqueous ammonium sulfide solution $(\text{NH}_4)_2\text{S}_{\text{aq}}$ and with solution of ammonium sulfide in 2-propanol $[(\text{NH}_4)_2\text{S} + 2\text{PA}]$. A striking difference in Sb4d/Ga3d ratio is evident. Spectra are normalized to excitation intensity.

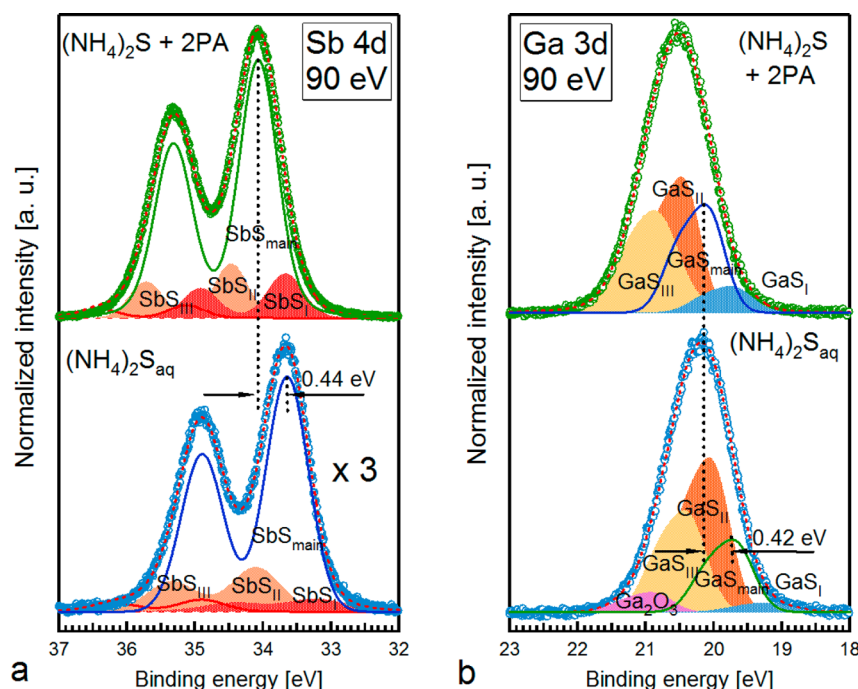


Figure 4. Deconvolution of 90 eV excited Sb 4d (a) and Ga 3d (b) core-level spectra from GaSb(100) after aqueous ammonium sulfide $(\text{NH}_4)_2\text{S}_{\text{aq}}$ passivation and ammonium sulfide in 2-propanol $(\text{NH}_4)_2\text{S} + 2\text{PA}$ passivation. Dots are data points after background subtraction. Dashed red line is a fit with the indicated components. Spectra are normalized to maximum intensity. The intensity of the Sb 4d spectrum on the surface treated with alcoholic sulfide solution is 3 times higher than on the surface treated with aqueous ammonium sulfide solution.

particular, on the surface treated with the solution of ammonium sulfide in 2-propanol the Sb 4d and Ga 3d peaks are shifted to higher binding energies by +0.45 and +0.35 eV, respectively, from the peaks measured on the surface treated with aqueous ammonium sulfide solution (Figure 3). Most strikingly, the Sb 4d emission intensity is 3 times stronger on the surface treated with alcoholic compared to aqueous solution, while the intensity of the Ga 3d emission is the same in both cases. Taking into account the cross-section corrections for the intensities of the corresponding core-level emissions at 90 eV excitation,³⁴ the Ga to Sb atomic ratio right at the surface is 0.15 after alcoholic and 0.4 after aqueous solution treatment.

The sulfur-treated surfaces have also been measured at 220, 350, and 650 eV excitation energy (not displayed). As there is no indication of bulk emission even in the spectra measured using 650 eV excitation, a lower estimate of the passivation layer thickness is $3\lambda_{650} \approx 75$ Å, but the thickness is presumably much higher, as 140 Å was measured using transmission electron microscopy after treatment for only 5 min using only 21% aqueous ammonium sulfide solution.³⁵ The Ga 3d and Sb 4d sulfide spectra show a 14.0 eV difference in binding energy, while this difference is 13.0 eV for the Ga–Sb and Sb–Ga emissions (Figure 1), in accord with published values of 12.9–13.0 eV,^{23,24} and for the emissions from the native oxide it is about 14.5 eV. As the Allred–Rochow electronegativities of Ga and Sb have the same value (of 1.8), this points to the fact that the binding energy of the Sb 4d orbital changes more easily with partial charge transfer than that of the Ga 3d orbital.

In an attempt to specify the composition of the passivation layers after treatment with aqueous and alcoholic sulfide solution, we performed fitting of the energy dependent Sb 4d and Ga 3d spectra. The most consistent fits with the least number of species over both treatments and all excitation

energies are displayed in Figure 4 for the 90 eV spectra. The Sb 4d core level on the surface treated with aqueous and alcoholic sulfide solution exhibits a narrow main component at 33.6 and 34.1 eV, respectively (Figure 3). For a good fit, three additional components of much lower intensity, shifted from the respective main one by -0.4 (SbS_I), $+0.4$ (SbS_{II}), and around $+1.1$ eV (SbS_{III}), have to be introduced (Figure 4a). A fit of the Ga 3d emission is shown in Figure 4b. The sulfur related Ga 3d component at 19.65 (aqueous) and 20.07 eV (alcoholic) (Figure 4b) becomes dominant at higher excitation energies. For both treatments three similarly shifted additional sulfur related components are resolved by fitting the energy dependent spectra. The shifts are -0.4 and -0.5 eV for alcoholic and aqueous, respectively (GaS_I in Figure 4b), and $+0.35$ (GaS_{II}) and $+0.7$ eV (GaS_{III}) for both solutions. In the aqueous case a component at 20.8 eV can be assigned to gallium oxide Ga₂O₃,³⁰ in accord with the remnant oxygen 1s emission (Figure 2). In the energy dependent spectra, this emission shows constant intensity, indicating the presence of Ga₂O₃ throughout the passivation layer.

Although we do not assume extended crystalline structures in the passivation layer, in the following, a formal tentative assignment is given, relating the binding energies of the Sb and Ga spectral components in the fit to expected partial charge in stoichiometric compounds. Sb can adopt various formal oxidation states as in Sb₂S₃, Sb₂S₄, and Sb₂S₅. Possible formal assignments therefore are the SbS_{main} component to Sb₂S₃, the SbS_{II} component to Sb₂S₄, the SbS_{III} component to Sb₂S₅, and the SbS_I component to a single Sb–S bond where Sb may be back-bonded to Ga. Ga usually adopts the formal oxidation state 3, but the oxidation state 1 is also possible as in Ga₂S. Different chemical shifted components may appear because of varying numbers of bonds to other Ga, Sb, and S atoms. Well-known binary compounds are Ga₂S₃ and GaS, but also ternary

phases such as GaSbS_4 and GaSbS may be considered. Tentative assignments are the GaS_{III} component with the strongest sulfur related chemical shift to Ga_2S_3 , the GaS_{II} component to GaS , the main component to GaSbS_4 , and the GaS_{I} component to GaSbS . As the peak labeled GaS_{I} does not change its relative intensity at higher excitation energy, it is not bulk related. Note that the antimony-related components SbS_{II} and SbS_{I} can have contributions from GaSbS_4 and GaSbS phases as well.

At 350 eV excitation, the intensity of the sulfur S 2p emission is 1.4 times larger on the $\text{GaSb}(100)$ surface treated with alcoholic ammonium sulfide solution than on the surface treated with aqueous solution and the emission is shifted to higher binding energy by 0.27 eV (Figure 5). As the Sb 4d and

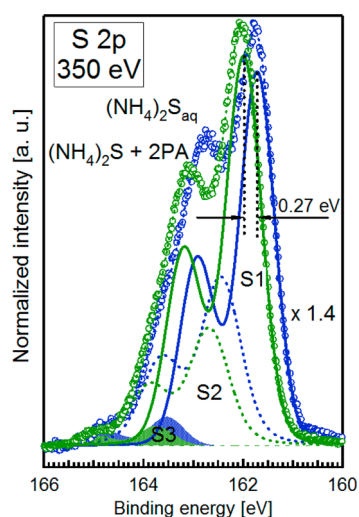


Figure 5. 350 eV excited S 2p core-level spectra from the $\text{GaSb}(100)$ surface after aqueous ammonium sulfide $(\text{NH}_4)_2\text{S}_{\text{aq}}$ passivation and ammonium sulfide in 2-propanol $(\text{NH}_4)_2\text{S} + 2\text{PA}$ passivation. After 2-propanol treatment the intensity is stronger by a factor of 1.4. Dots are data points after background subtraction. Fitting components S1, S2, S3 are represented by solid lines, dashed lines, and filled curves, respectively. Spectra are normalized to maximum intensity.

Ga 3d core levels are also shifted to higher binding energies after 2-propanol versus aqueous ammonium sulfide solution (Figures 3 and 4), an overall shift of the spectra due to a different surface Fermi level position in the energy gap is indicated. As the shift of the Sb 4d and Ga 3d core levels is 0.43 eV, chemical shifts also have to be considered, indicating a higher negative partial charge of the S atoms after treatment in 2-propanol solution, which may also vary over the passivation layer depth.

The S 2p core-level spectra can be fitted with three different components. Besides the main components S1 at 161.7 eV (aqueous) and 162.0 eV (alcoholic), two additional components shifted by +0.7 eV (S2) and +1.8 eV (S3) are needed for a good fit. The ratios of the areas of S 2p core-level components S1:S2:S3 are equal to 1.00:0.55:0.07 and 1.00:0.35:0.05 for the $\text{GaSb}(100)$ surfaces treated with aqueous and alcoholic solution, respectively. So on the surface treated with the solution of ammonium sulfide in 2-propanol, the component S1 is much stronger than the second component S2 compared to the surface treated with aqueous ammonium sulfide solution. As the antimony content is higher after the treatment with alcoholic ammonium sulfide solution (Figure 3), the S1

component of the S 2p core level can be assigned to sulfur bonded to antimony atoms. The component S2 can be associated with the Ga–S bonds, while the small component S3 with the chemical shift of 1.8 eV indicates excess elemental sulfur that occurs in addition.

After treatment of the $\text{GaSb}(100)$ surface with aqueous ammonium sulfide solution the carbon contamination increases by a factor of 1.25, whereas after treatment with solution of ammonium sulfide in 2-propanol it decreases considerably (4 times) (Figure 6). The C 1s core levels show a high binding energy shoulder that may be related to oxygen bonded carbon species.

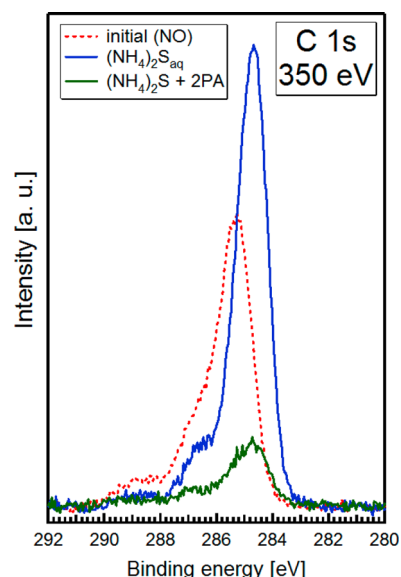


Figure 6. Photoemission spectra of C 1s core level collected from the native-oxide-covered $\text{GaSb}(100)$ surface and after treatment with aqueous ammonium sulfide solution $(\text{NH}_4)_2\text{S}_{\text{aq}}$ and with solution of ammonium sulfide in 2-propanol $(\text{NH}_4)_2\text{S} + 2\text{PA}$. The excitation energy was 350 eV. Spectra are normalized to excitation intensity.

The valence band edge of the native-oxide-covered $\text{GaSb}(100)$ surface contains a clear onset at about 2.2 eV below the Fermi level (Figure 7a). On the other hand, about 0.35 eV below the surface Fermi level there is an onset of a very weak emission (Figure 7b), which corresponds to the position of the valence band maximum of the $\text{GaSb}(100)$ bulk at its interface with the native oxide. So the Fermi level of the n- $\text{GaSb}(100)$ surface covered with native oxide is pinned near the mid-gap energy position. The valence band spectra of the $\text{GaSb}(100)$ surfaces treated with aqueous and alcoholic sulfide solutions contain similar sulfur related features but with different intensities (Figure 7c). The valence states onset of the surface treated with alcoholic solution is 260 meV lower compared to the surface treated with aqueous ammonium sulfide solution on which the onset of the valence states starts at 1.00 eV (Figure 7d). A similar shift to higher binding energy after treatment with the solution of ammonium sulfide in 2-propanol is observed in the Sb 4d and Ga 3d emissions measured at 90 eV excitation energy (Figures 3 and 4).

The work function as derived from the secondary electron emission edge of the valence band spectra (not shown) is 4.2 eV for the untreated native-oxide-covered $\text{GaSb}(100)$ surface. With alcoholic sulfide solution passivation the work function

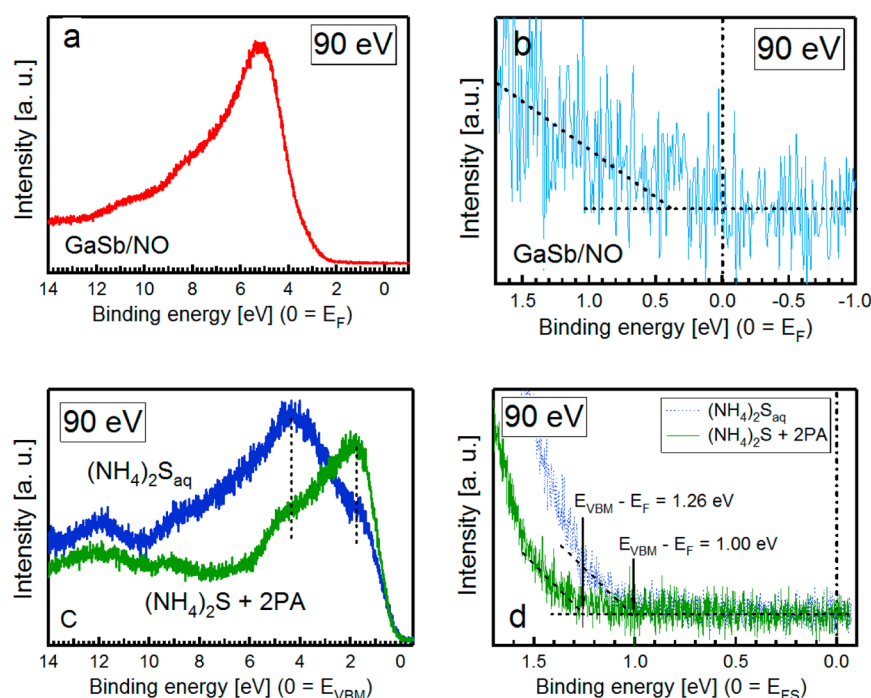


Figure 7. (a) Valence band spectrum of the native-oxide-covered GaSb(100) surface. (b) Valence band photoemission from the GaSb(100)/native oxide interface. (c) Valence band photoemission after treatment with aqueous ammonium sulfide solution $(\text{NH}_4)_2\text{S}_{\text{aq}}$ and with solution of ammonium sulfide in 2-propanol $[(\text{NH}_4)_2\text{S} + 2\text{PA}]$. (d) Close-up of the valence band edges. The excitation energy was 90 eV.

increases to 4.8 versus 4.6 eV in the case of aqueous solution passivation.

4. DISCUSSION

Treatment of the n-GaSb(100) surface with aqueous and 2-propanol–ammonium sulfide solution leads to the formation of GaSb–sulfide passivation layers of different composition.

Both solutions efficiently remove the native oxide layer (Figure 3), but the 2-propanol solution removes oxygen almost completely, whereas the aqueous solution leaves some oxygen in the passivating layer (Figure 2). In addition the 2-propanol solution reduces the carbon contamination considerably, whereas the aqueous solution increases the carbon contamination (Figure 6). A similar lack of carbon contamination reduction after treatment of the GaSb(100) surface with aqueous ammonium sulfide solution was observed before.³⁶ Rinsing with 2-propanol of the GaAs(100) surface etched with ammonium hydroxide solution caused more effective removal of carbon contamination than rinsing with water.³⁷

The dependence of the Ga/Sb atomic concentration ratios on the excitation energy and thereby the information depth is shown in Figure 8. These ratios were obtained as the ratios of integrated Ga 3d and Sb 4d emissions corrected by the corresponding cross sections of atomic orbitals. The orbital cross sections $\sigma_{\text{Ga}3d}$ and $\sigma_{\text{Sb}4d}$ taken from ref 34 are given in Table 1. The cross-section-corrected ratios of Ga–Sb and Sb–Ga components in the spectra of the native-oxide-covered GaSb(100) surface measured at different excitation energies (Figure 1) are also indicated in Table 1. Note that these ratios differ from 1, which would be expected assuming that Ga–Sb and Sb–Ga components stem solely from bulk photoemission of the native-oxide-covered GaSb(100) surface. In particular, in the spectra measured with 90, 220, and 350 eV the Ga–Sb/Sb–Ga ratio is much larger than 1, which means that the bulk photoemission in the Ga 3d spectra is overestimated by the

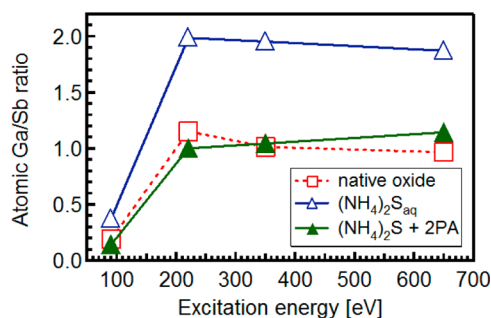


Figure 8. Total atomic Ga/Sb ratios of the native-oxide-covered GaSb(100) surface at different excitation energies, as well as from that surface treated with aqueous ammonium sulfide solution $[(\text{NH}_4)_2\text{S}_{\text{aq}}]$ and with solution of ammonium sulfide in 2-propanol $[(\text{NH}_4)_2\text{S} + 2\text{PA}]$. The ratios are derived from the overall integral Ga 3d and Sb 4d emission intensities, including all components.

Table 1. Orbital Cross Sections $\sigma_{\text{Ga}3d}$ and $\sigma_{\text{Sb}4d}$ (Taken from Ref 34) and Cross-Section-Corrected Ratios of Ga–Sb and Sb–Ga Photoemission Components in the Ga 3d and Sb 4d Spectra of the Native-Oxide-Covered GaSb(100) Surface Measured at Different Excitation Energies

excitation energy, eV	orbital cross sections (ref 34)		Ga–Sb(3d)/Sb–Ga(4d) ratio, corrected using orbital cross sections
	$\sigma_{\text{Ga}3d}$	$\sigma_{\text{Sb}4d}$	
90	9.0	6.5	2.3
220	3.5	0.8	4.15
350	1.2	0.7	1.45
650	0.25	0.3	0.9

component labeled Ga–Sb. We tentatively explain this deviation assuming a Ga suboxide or surface species with the

same binding energy as bulk Ga–Sb, which may be present in the gallium oxide phase at the given information depth of the multiphase native oxide layer. On the other hand, in the spectra measured with 650 eV the Ga–Sb/Sb–Ga ratio is 0.9 indicating that the bulk photoemission in the Sb 4d spectrum is somewhat overestimated by the component labeled Sb–Ga in this case. So there may be some additional Sb species with similar binding energy as the bulk emission. Possibly right at the oxide/bulk interface elemental antimony is present (with a chemical shift of 0.2 eV from the bulk emission¹²), similar to elemental As found at the GaAs (100) oxide/bulk interface.³⁰ For the oxide as well as for the sulfur-passivated layers, the Ga/Sb ratio strongly decreases toward the very surface, indicating Sb segregation (Figure 8). In the interior of the native oxide layer and of the sulfide layer obtained using the solution of ammonium sulfide in 2-propanol, the Ga/Sb ratio is very close to 1, in accord with the stoichiometric bulk value. In the interior of the sulfide layer formed after treatment with aqueous sulfide solution, a gallium enriched sulfide layer with a Ga/Sb ratio of about 2 has formed.

Thus, the aqueous and alcoholic ammonium sulfide solutions interact with the semiconductor surface atoms in different manner. In particular, after etching off the native oxide layer, aqueous ammonium sulfide solution affects mostly antimony sites and the reaction products are dissolved in the solution, whereas the alcoholic solution interacts with both the gallium and antimony sites at the surface and leaves the Ga/Sb ratio in accord with the stoichiometric bulk value. The solutions of sodium sulfide in different solvents affected the GaSb(100) surface in a different way too.¹² In particular, after the treatment with the aqueous solution of sodium sulfide, the Ga/Sb ratio decreased, whereas after the treatment with the nonaqueous solution (solution of Na₂S in benzene with addition of cation complexing agent 15-crown-5 and oxidant), the Ga/Sb ratio increased.¹²

The electronic surface conditions concerning valence states onset and work function are summarized in Figure 9, illustrating the increase of the work function with both sulfur passivation treatments but more so for the 2-propanol than for the aqueous solution. Also, the ionization potential of the GaSb(100) surface is higher by 0.46 eV when treated with 2-propanol instead of aqueous ammonium sulfide solution.

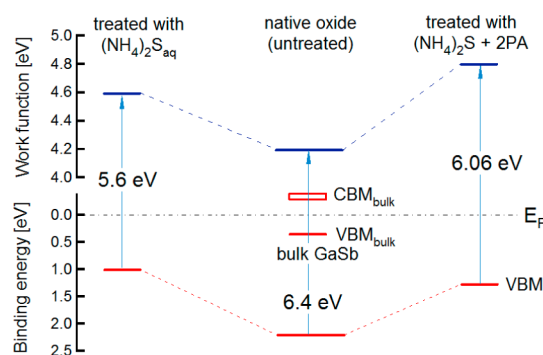


Figure 9. Binding energies of the valence band onsets and work function values obtained from the native-oxide-covered GaSb(100) surface and after treatment with aqueous ammonium sulfide solution $(\text{NH}_4)_2\text{S}_{\text{aq}}$ and with solution of ammonium sulfide in 2-propanol $[(\text{NH}_4)_2\text{S} + 2\text{PA}]$. The values of ionization energy are shown as well. Also, the valence and conduction band edges are indicated for GaSb(100) at the interface with its native oxide layer.

The valence band spectra of both sulfur-treated GaSb(100) surfaces (Figure 7d) clearly indicate the formation of wide band gap passivation layers, and in addition to the Ga enrichment, the sulfide layer formed in aqueous solution also contains inclusions of gallium oxide. So the GaSb(100) surface treated with ammonium sulfide in 2-propanol is in short notation a GaSb/GaSbS_x heterojunction, while the GaSb(100) surface treated with aqueous ammonium sulfide solution is a GaSb/GaSb_{0.5}S_y:Ga₂O₃ heterojunction (with the colon indicating inclusions). The S/Ga atomic ratios determined on the basis of S 2p and Ga 3d spectra measured using excitation energies of 350 and 650 eV are given in Table 2. Obviously the sulfide layer

Table 2. Total Atomic S/Ga Ratios Obtained at Different Excitation Energies on the GaSb(100) Surface Treated with Aqueous Ammonium Sulfide Solution $[(\text{NH}_4)_2\text{S}_{\text{aq}}]$ and Solution of Ammonium Sulfide in 2-Propanol $[(\text{NH}_4)_2\text{S} + 2\text{PA}]^a$

excitation energy, eV	atomic S/Ga ratio measured on the GaSb(100) surface	
	treated with $(\text{NH}_4)_2\text{S}_{\text{aq}}$	treated with $(\text{NH}_4)_2\text{S} + 2\text{PA}$
350	2	3.6
650	4	3.6

^aThe ratios are derived from the overall intensities of integral S 2p and Ga 3d emissions measured at a given excitation energy and corrected using orbital cross sections.³⁴

formed after treatment of the GaSb(100) surface with the solution of ammonium sulfide in 2-propanol has uniform concentration of sulfur throughout the probed passivating layer, whereas on the GaSb(100) surface treated with aqueous ammonium sulfide solution the sulfur content decreases toward the surface. The increased work function by 0.4 and 0.6 eV for aqueous versus alcoholic treatment compared to the native-oxide-covered surface may be related to stronger chemical stability (chemical passivation). The deeper valence band maximum (and core-level states) of the GaSbS_x layer formed after treatment with alcoholic solution compared to the GaSb_{0.5}S_y:Ga₂O₃ layer formed from aqueous solution causes stronger confinement of carriers in the semiconductor, i.e., better electronic passivation.

5. SUMMARY AND CONCLUSION

Excitation energy dependent synchrotron radiation photoemission spectroscopy has been used to study the chemical composition and the electronic properties of the GaSb(100) surface after sulfur passivation using aqueous versus 2-propanol–ammonium sulfide solution. In addition the native oxide layer has been characterized. Throughout the native oxide film, the Ga/Sb ratio is about 1 and its thickness is about 50 Å. The valence states maximum of the native oxide is found 2.2 eV below the Fermi level, and its work function is 4.2 eV. A low emission of the bulk valence band is detected with its onset energy at 0.35 eV. With both sulfide solutions the native oxide layer is removed from the GaSb(100) surface and wide band gap sulfide passivation layers form with thickness of >75 Å. The composition of the passivation layer depends on the solvent used: after treatment with the solution of ammonium sulfide in 2-propanol this layer consists of gallium and antimony sulfides with a Ga/Sb ratio of around 1. After treatment with aqueous ammonium sulfide solution the passivation layer consists of gallium and antimony sulfides and inclusions of gallium oxide. This layer is strongly gallium enriched with Ga/Sb ratio equal

to 2. Right at the surfaces both passivation layers are enriched with antimony sulfide. Also, the surface electronic structure becomes dependent on the solution used. After treatment with aqueous and alcoholic sulfide solutions the work function values are 4.6 and 4.8 eV, respectively. The photoemission onset of the sulfide layer on the GaSb(100) surface treated with aqueous and alcoholic ammonium sulfide solution is, respectively, 1.0 and 1.26 eV below the surface Fermi level position, leading to ionization potentials of 5.6 and 6.06 eV, respectively. The carbon contamination is reduced 4 times using alcoholic, while it is increased by a factor of 1.25 with aqueous solution.

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Notes

The authors declare no competing financial interest.

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