

Passivation of AlGaAs(100) surfaces with ammonium sulfide solutions

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X-ray photoelectron spectroscopy is used to study interaction of the native-oxide-covered Al_{0.3}Ga_{0.7}As(100) surfaces with different ammonium sulfide solutions. The most effective removal of the native oxide layer and chemical passivation is achieved after treatment with diluted aqueous ammonium sulfide solution with volume concentration of about ~4% prepared from the so-called aged ammonium sulfide. The treated surface contains tiny amount of elemental arsenic as well as residual gallium and aluminum oxides and is covered with the passivating layer consisting of arsenic sulfides. After treatment with the solution of the same concentration prepared from the freshly-opened ammonium sulfide the sulfur atoms are hardly adsorbed at the surface and arsenic sulfides are not formed. In addition, it is shown that after interaction of the concentrated (~44%) aged ammonium sulfide and ~4% solution of aged ammonium sulfide in 2-propyl alcohol, the surface alloy stoichiometry is disturbed due to removal of gallium atoms from the surface and the surface becomes covered with a relatively thick layer of aluminum oxide.

Keywords: AlGaAs, sulfur passivation, native oxide, X-ray photoelectron spectroscopy.

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1. Introduction

AlGaAs solid solutions are used frequently in modern nanoheterostructure devices (specifically, transistors, lasers, and solar cells) [1–6]. Direct-band-gap A^{III}B^V semiconductor layers with a band gap of 1.42–1.93 eV may be produced based on these solid solutions [7]. The lattice constants of AlGaAs compounds with an arbitrary aluminum content are close to the lattice constant of GaAs, which makes it possible to fabricate defect-free GaAs/AlGaAs heterostructures and superlattices with a thickness up to several micrometers with arbitrary profiles of variation of band potentials.

Various processes of epitaxial growth and post-growth processing are often combined in fabrication of modern semiconductor devices. In certain cases, one needs to perform epitaxial growth on structures produced by photolithography and subsequent chemical etching. Chemically active surfaces of A^{III}B^V semiconductors (especially those containing aluminum) get covered with a disordered native oxide layer after just a short-term contact with air, making subsequent epitaxial growth difficult. In this context, the development of methods for removing the native oxide layer from the surface of a semiconductor, which may be achieved by etching with acid solutions in an inert and oxygen-free atmosphere, is one of the pressing problems in semiconductor technology. However, chemical removal of oxide layers from the surface of aluminum-containing solid solutions is a significant challenge, since aluminum oxide is resistant to most chemical etchants used

in semiconductor processing [8,9]. It should be noted that various „dry“ etching techniques are, in most cases, not suitable for cleaning the surfaces of solid solutions, since they may alter the stoichiometry in the near-surface region [10,11].

Solutions of sodium sulfide Na₂S or ammonium sulfide (NH₄)₂S provide an opportunity to remove native oxide layers from semiconductor surfaces and are used extensively to modify the characteristics of devices based on A^{III}B^V semiconductors [12]. Although the mechanisms of interaction of sulfide solutions with the surfaces of binary A^{III}B^V semiconductors have been examined in sufficient detail [12], their interaction with the surfaces of aluminum-containing solid solutions of A^{III}B^V semiconductors (in particular, AlGaAs) remains virtually uninvestigated [13,14]. The interaction between Al_{0.3}Ga_{0.7}As(100) surfaces covered with a native oxide layer and an aqueous solution of sodium sulfide has been studied recently in [15]. However, it should be noted that different solutions of ammonium sulfide (NH₄)₂S [12] are the ones used most often for surface passivation of semiconductors and semiconductor devices. The aim of the present study is to determine the optimal conditions for passivation of the AlGaAs(100) surface with ammonium sulfide solutions with various concentrations and solvent types. X-ray photoelectron spectroscopy (XPS) was used to probe the evolution of chemical composition of the surface of *n*- and *p*-type Al_{0.3}Ga_{0.7}As(100) layers.

2. Experimental procedure

Molecular-beam epitaxy was used to grow *n*- and *p*-type layers of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}:\text{Si}$ and $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}:\text{Be}$ (100), respectively, with a thickness of $1\ \mu\text{m}$ and a doping level of $(1-3) \cdot 10^{17}\ \text{cm}^{-3}$ on *n*-GaAs(100) substrates. The samples were stored in air for several weeks to form a stable native oxide layer, and their surfaces were then treated with various solutions based on ammonium sulfide $(\text{NH}_4)_2\text{S}$.

Solutions were prepared with the use of two types of commercial $(\text{NH}_4)_2\text{S}$ (40–48 wt.% in H_2O) produced by Merck-Sigma-Aldrich: an „aged“ reagent [16], which was stored for several years in contact with atmospheric oxygen, and a „fresh“ one unsealed immediately before the experiment. Several solutions were used in experiments:

- concentrated commercial „aged“ solution, which is denoted below as $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (44%);
- dilute (4%) aqueous solution of „aged“ commercial $(\text{NH}_4)_2\text{S}$ (44%);
- dilute (4%) solution of „aged“ commercial $(\text{NH}_4)_2\text{S}$ (44%) in isopropyl alcohol (2PA);
- dilute (4%) aqueous solution of „fresh“ commercial $(\text{NH}_4)_2\text{S}$ (44%).

Following sulfide treatment, the samples were rinsed with water (or isopropyl alcohol) and introduced into the XPS chamber. The time of exposure of the samples to air was 30–90 min.

XPS studies were carried out using an Escalab 250Xi photoelectron spectrometer and an $\text{AlK}\alpha$ source with a photon energy of 1486.6 eV. The binding energy was measured from the Fermi level. The binding energy scale was calibrated by measuring the spectra of $\text{Au}\ 4f_{7/2}$ (84.0 eV) and $\text{Cu}\ 2p_{3/2}$ (932.7 eV) core levels on a special calibration sample. The vacuum level in the measurement chamber was $\leq 1 \cdot 10^{-9}$ mbar. The energy resolution of the spectra was no worse than 0.6 eV. The spectra of $\text{Al}\ 2p$, $\text{As}\ 3d$, and $\text{Ga}\ 3d$ core levels were decomposed with the use of Voigt functions. The parameters of these functions were presented in [15].

3. Results

Survey spectra of *n*- and *p*-AlGaAs(100) surfaces covered with a native oxide layer contain the photoemission peaks of Al, As, Ga, O, and C atoms. The typical $\text{As}\ 3d$, $\text{Ga}\ 3d$, and $\text{Al}\ 2p$ core level spectra of the initial *n*-AlGaAs(100) surface covered with a native oxide layer are shown in Figure 1. The spectra of the initial *p*-AlGaAs(100) surface are similar in shape, but are shifted toward lower binding energies due to the difference in the position of the surface Fermi level relative to the band gap edges. The spectrum of $\text{As}\ 3d$ core level may be decomposed into three components: bulk component As_{bulk} , elemental arsenic component As^0 shifted by 0.65 eV relative to the bulk one, and arsenic oxide component $\text{As}-\text{O}$ with a chemical shift of 3.1 eV (Figure 1, *a*).

The spectra of $\text{Ga}\ 3d$ core level of the initial AlGaAs(100) surfaces may be decomposed into bulk component $\text{Ga}-\text{As}$ and component $\text{Ga}-\text{O}$ induced by gallium oxides, which is shifted by 1.0 eV relative to the bulk component (Figure 1, *b*).

The spectra of $\text{Al}\ 2p$ core level of the initial AlGaAs(100) surfaces may also be decomposed into two components (Figure 1, *c*): bulk component $\text{Al}-\text{As}$ and a component with a chemical shift of 0.75 eV, which should correspond to aluminum oxides $\text{Al}-\text{O}$.

When the *n*- $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ (100) surface was treated with the „aged“ $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (44%) solution for 2 min, the intensity of the $\text{O}\ 1s$ core level photoemission decreased (Figure 2, *a*) and the photoemission of $\text{S}\ 2p$ core level emerged (Figure 2, *b*). It should be noted that the $\text{S}\ 2p$ core level photoemission in gallium-containing compounds overlaps with the photoemission of $\text{Ga}\ 3s$ core level. Therefore, the $\text{Ga}\ 3s$ core level spectrum measured on the initial untreated surface was subtracted from the spectrum of the treated surface to obtain a pure $\text{S}\ 2p$ photoemission signal (shown in the upper part of Figure 2, *b*) [17].

The spectra of $\text{As}\ 3d$, $\text{Ga}\ 3d$, and $\text{Al}\ 2p$ core levels changed significantly after treatment with the „aged“ $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (44%) solution (see Figure 1). Specifically, the component induced by arsenic oxides vanished from the $\text{As}\ 3d$ spectrum, of $\text{As}\ 3d$, and the component associated with elemental arsenic also became significantly weaker (Figure 1, *a*). At the same time, a small new component with a chemical shift of approximately 1.8 eV was formed. This component can be associated with $\text{As}-\text{S}$ bonds [17], since the sulfur $\text{S}\ 2p$ photoemission appeared simultaneously (Figure 2, *b*).

In addition, the component attributed to gallium oxides became less pronounced (Figure 1, *b*). The chemical shift of this component decreased to ~ 0.75 eV, which suggests the possible presence of a contribution from $\text{Ga}-\text{S}$ and $\text{Ga}-\text{O}$ chemical bonds in it. At the same time, the component induced by aluminum oxides $\text{Al}-\text{O}$ in the $\text{Al}\ 2p$ spectrum became significantly more pronounced after treatment with the „aged“ $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (44%) solution (Figure 1, *c*). This behavior of $\text{Al}-\text{O}$ component (Figure 1, *c*) correlates with changes in the spectrum of core level $\text{O}\ 1s$ (Figure 2, *a*). Following treatment with the „aged“ $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (44%) solution for 2 min, the $\text{O}\ 1s$ photoemission intensity did indeed decrease in accordance with the observed removal of arsenic oxides (Figure 1, *a*) and suppression of gallium oxides (Figure 1, *b*). When the surface was processed for a longer time (6 min), the $\text{O}\ 1s$ photoemission intensity increased significantly (Figure 2, *a*).

The coating thicknesses for each surface component were estimated using the following formula [18]:

$$d = \lambda \ln((I_S/I_B) + 1), \quad (1)$$

where I_S is the intensity of the surface component in the core level spectrum, I_B is the intensity of the bulk component in the spectrum of the corresponding core level, and

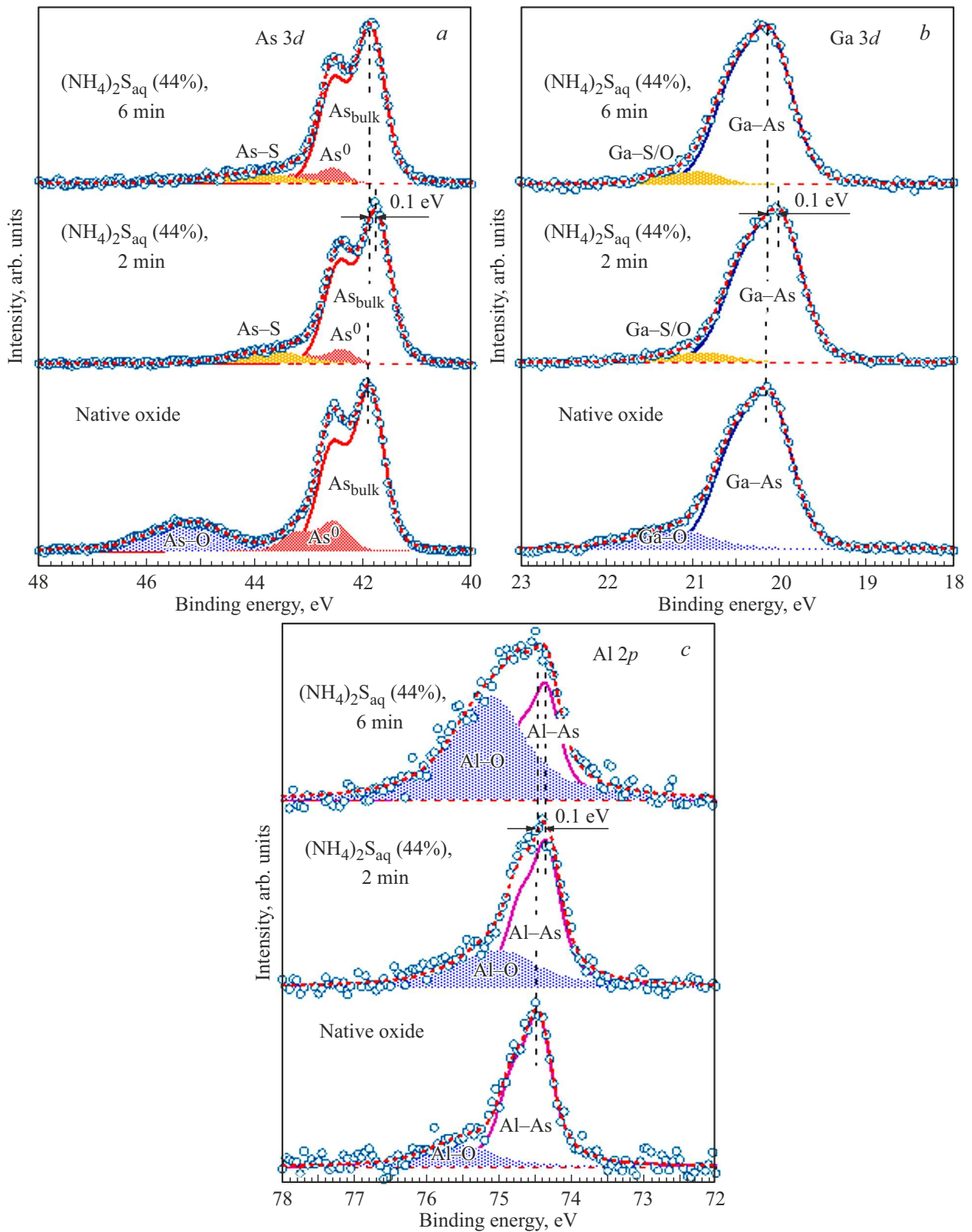


Figure 1. Decomposition of the As 3d (a), Ga 3d (b), and Al 2p (c) core level spectra measured on the n -Al_{0.3}Ga_{0.7}As(100) surface covered with a native oxide layer before and after treatment with an „aged“ (NH₄)₂S_{aq} (44%) solution for 2 and 6 min.

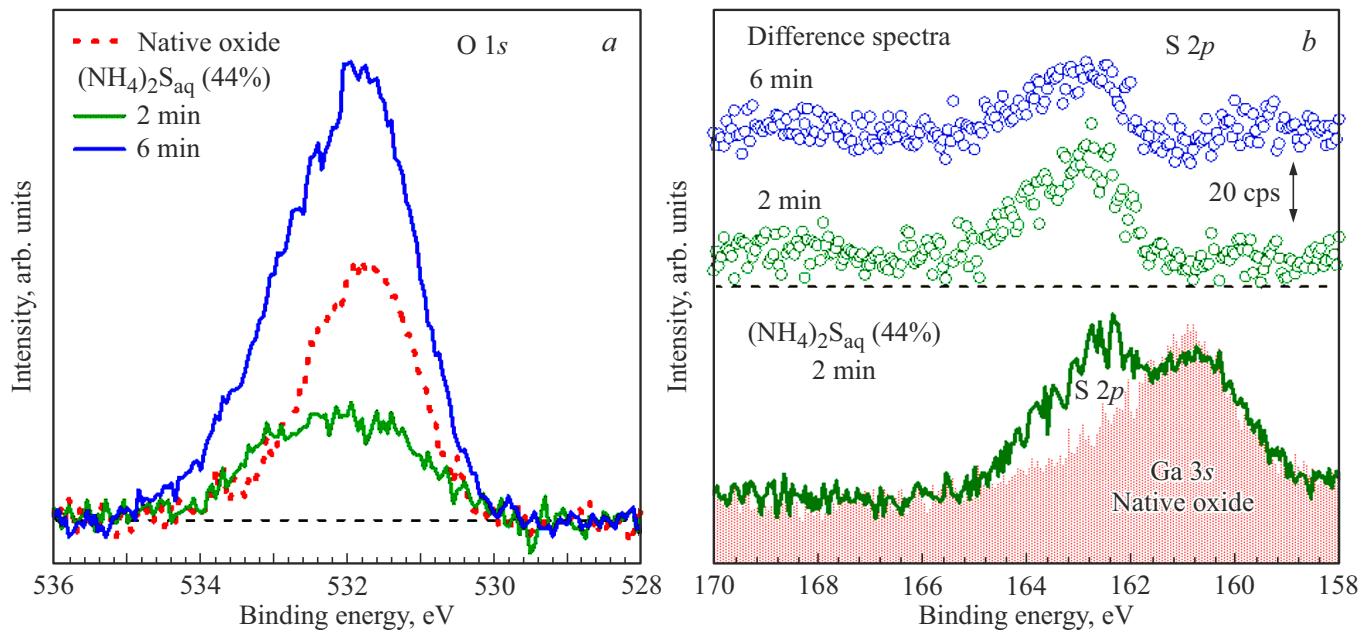


Figure 2. *a* — Spectra of O $1s$ core level measured on the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface covered with a native oxide layer before and after treatment with an „aged“ $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (44%) solution for 2 and 6 min. *b* — Lower part: spectra of the region of binding energies of level S $2p$ measured on the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface covered with an oxide layer before and after treatment with an „aged“ $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (44%) solution for 2 min. The spectrum measured prior to treatment contains only the Ga $3s$ level photoemission (shaded red). Upper part: difference spectra of level S $2p$ obtained by subtracting the spectrum of Ga $3s$ photoemission of the initial $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface covered with an oxide layer from the spectra measured after the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface was treated with an „aged“ $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (44%) solution for 2 and 6 min. (A color version of the figure is provided in the online version of the paper).

λ is the depth of emission of photoelectrons from a given core level, which is equal to their mean free path without inelastic scattering for normally emitted photoelectrons [19]. The value of λ for photoelectrons of Al $2p$, As $3d$, and Ga $3d$ core levels with a kinetic energy of 1410–1465 eV was set to $\sim 30 \text{ \AA}$ (i. e., ~ 10.6 monolayers) [20].

Figure 3 presents the thicknesses of coverages for various components located on the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface before and after treatment with the „aged“ $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (44%) solution that were estimated by formula (1). It is evident that the treatment of $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ with $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (44%) leads to the removal of arsenic oxides, a reduction in the amount of gallium oxide on the surface, and a certain reduction in the amount of elemental arsenic, which gets converted into arsenic sulfide. In contrast, the amount of aluminum oxides increases considerably.

A similar pattern was observed in the interaction of the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface with the dilute $(\text{NH}_4)_2\text{S}+2\text{PA}$ (4%) alcohol solution prepared from „aged“ ammonium sulfide. Specifically, complete removal of arsenic oxides and accumulation of aluminum oxides with simultaneous formation of arsenic sulfides from elemental arsenic were also noted (Figure 4).

At the same time, complete removal of arsenic oxides (Figure 5, *a*) and a significant reduction in the amount of elemental arsenic (Figure 5, *a*), gallium oxide (Figure 5, *b*), and aluminum oxide (Figure 5, *c*) were observed after the

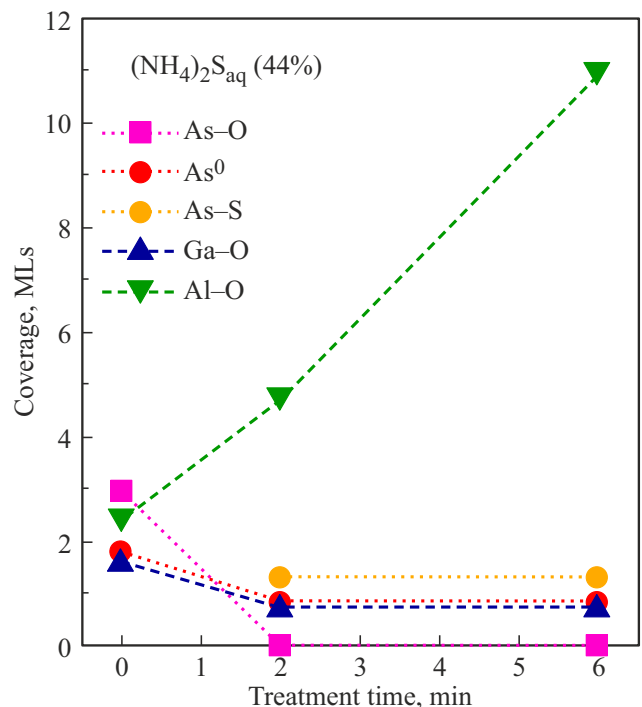


Figure 3. Variation of thickness of coverages for different components on the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface treated with the „aged“ $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (44%) solution.

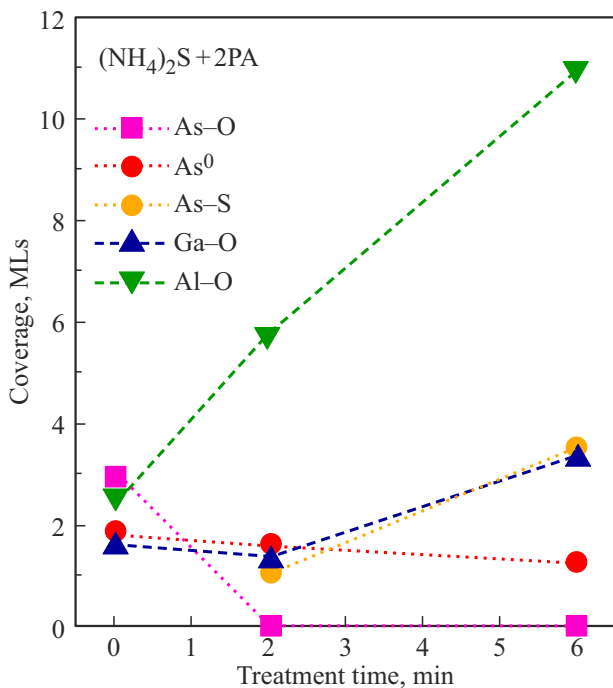


Figure 4. Variation of thickness of coverages for different components on the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface treated with the $(\text{NH}_4)_2\text{S}+2\text{PA}$ alcohol solution prepared from „aged“ $(\text{NH}_4)_2\text{S}$.

$n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface was treated with the dilute $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%) solution prepared from „aged“ ammonium sulfide. The oxygen O 1s photoemission intensity decreased approximately by a factor of 3 (Figure 6, a) after short-term processing (2 min). However, the intensity of the oxygen photoemission signal did not decrease further (Figure 6, a) when the treatment time was extended to 6 min. That said, a peak of sulfur S 2p photoemission emerged after treatment (Figure 6, b). It should be noted that the shift of the maximum of oxygen O 1s photoemission toward higher binding energies after treatment (Figure 6, a) indicates that a significant fraction of residual adsorbed oxygen on the surface is in the form of hydroxyl groups OH^- [21]. These groups may be included into soluble complexes $\text{NH}_4\text{Ga}(\text{OH})_4$ (and/or $\text{NH}_4\text{Al}(\text{OH})_4$) forming in the interaction of gallium/aluminum oxides with $(\text{NH}_4)^+$ ions [22]. It is difficult to examine the nitrogen N 1s peak in detail, since the relatively weak photoemission signal of N 1s will overlap with intense Auger peaks of gallium in spectra excited by the AlK_α source.

Figure 7 presents the thicknesses of coverages for various components located on the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface before and after treatment with the $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%) solution prepared from „aged“ ammonium sulfide that were estimated by formula (1). It can be seen that approximately one monolayer of gallium and aluminum oxides remains on the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface after 6 min of treatment. Note that these oxides could form as a result of short-term

(~ 1 h) exposure of the surface to air after processing before the introduction into the vacuum chamber of the XPS setup.

The effect of surface treatment on the elemental composition of the solid solution was studied in order to analyze the mechanisms of interaction of various ammonium sulfide solutions with the $\text{AlGaAs}(100)$ surface (Figure 8). The ratios of integrated intensities of the Al 2p, Ga 3d, and As 3d core level spectra (with their photoionization cross sections taken into account) were used to determine the Al/Ga and (Ga+Al)/As ratios of atomic concentrations [23]. It should be noted that changes in the Al/Ga and (Ga+Al)/As atomic concentrations ratios after chemical treatment characterize modifications of the near-surface chemical composition with surface oxides/sulfides instead of compositional variations of the solid solution in the bulk.

It is evident that treatment with the „aged“ $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (44%) solution for 6 min led to a significant change in the composition of the near-surface AlGaAs region due to the fact that Ga and As atoms pass into the solution (Figure 8). The surface became enriched with aluminum, which oxidizes rapidly in air. However, the possibility of surface oxidation in the solution cannot be excluded. This may explain the increase in intensity of oxygen O 1s photoemission (Figure 2, a) and the aluminum oxide component in the spectrum of Al 2p core level (Figures 1, c and 3) after treatment with the „aged“ $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (44%) solution for 6 min. The thickness of the aluminum oxide layer estimated using formula (1) was close to 11 monolayers (i. e., $\sim 30 \text{ \AA}$ see Figure 3).

The dilute $(\text{NH}_4)_2\text{S}+2\text{PA}$ (4%) alcohol solution prepared from „aged“ ammonium sulfide did also remove arsenic and gallium atoms from the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface, although in a lesser degree than the $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (44%) solution (Figure 8). The estimated thickness of the aluminum oxide coating on this surface was also approximately equal to 11 monolayers (Figure 4).

At the same time, the Al/Ga ratio remained virtually unchanged (decreased slightly) after the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface was treated with the dilute $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%) solution prepared from „aged“ ammonium sulfide, although a certain amount of arsenic was removed from the surface (Figure 8). The amount of residual gallium and aluminum oxides decreased with treatment time to a level on the order of a monolayer (Figure 7). The binding energies of bulk components in the decompositions of As 3d, Ga 3d, and Al 2p core level spectra remained unchanged after the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface was treated with the $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%) solution prepared from „aged“ ammonium sulfide (Figure 7), which suggests that this treatment has no effect on band bending of the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface.

It should be noted that the dilute $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%) solution prepared from „fresh“ ammonium sulfide was less efficient in removing the native oxide layer from the surface of n - and $p\text{-AlGaAs}(100)$ (Figure 9, a) than the aqueous solution of the same concentration prepared from „aged“ ammonium sulfide (Figure 5, a). In addition, only trace amounts of sulfur were detected on the surface

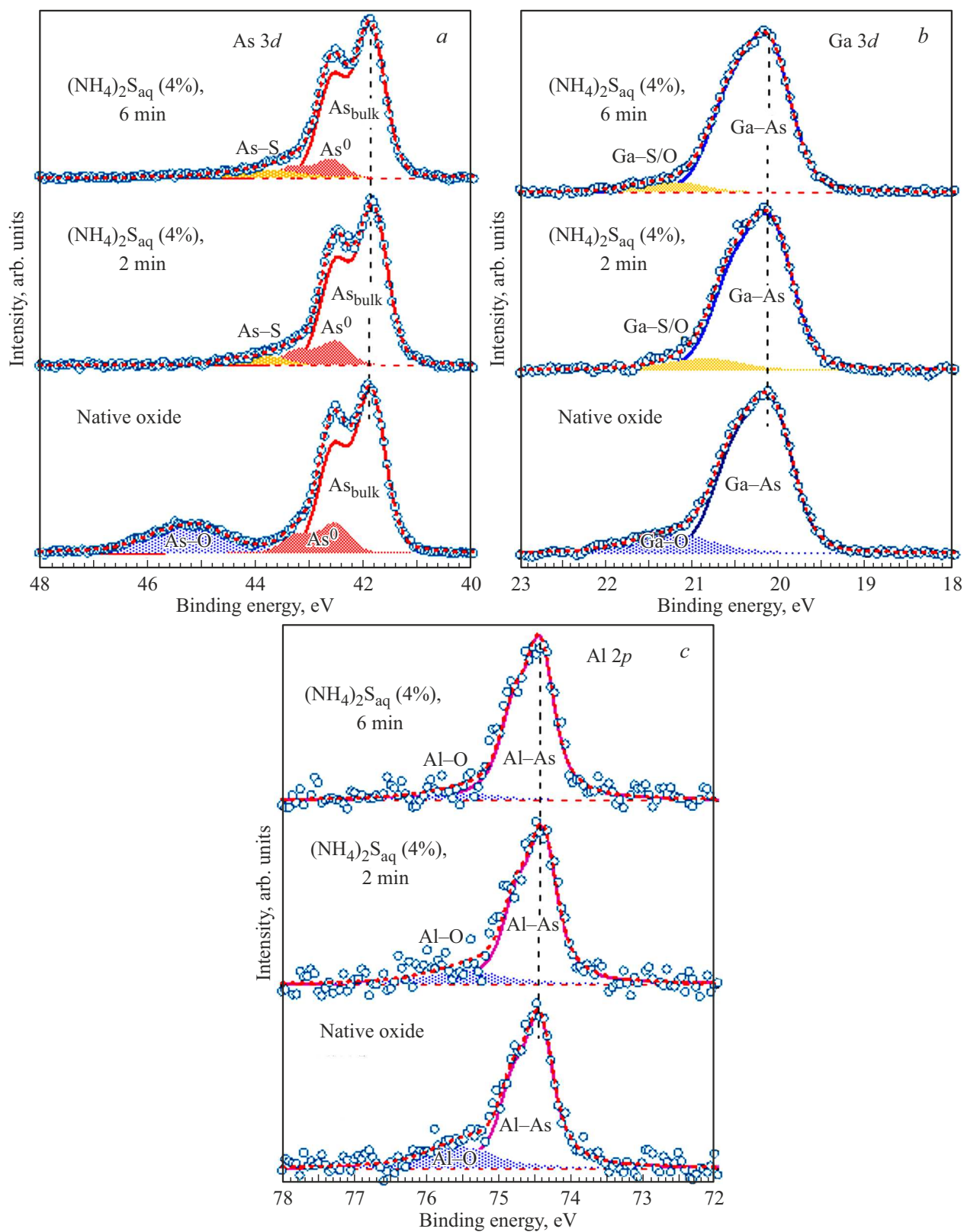


Figure 5. Decomposition of the As 3d (a), Ga 3d (b), and Al 2p (c) core level spectra measured on the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface covered with a native oxide layer before and after 2 and 6 min of treatment with the $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%) solution prepared from „aged“ ammonium sulfide.

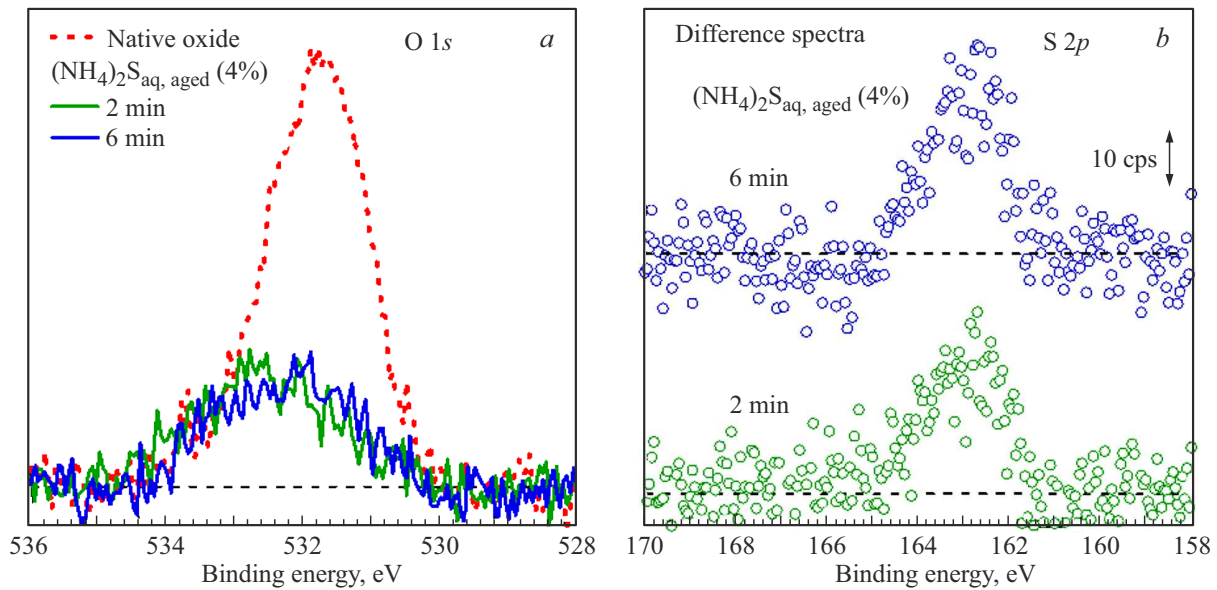


Figure 6. *a* — Spectra of O 1s core level measured on the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface before and after 2 and 6 min of treatment with the $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%) solution prepared from „aged“ ammonium sulfide. *b* — Difference S 2p spectra obtained as the ones in Figure 2, *b* for the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface treated for 2 and 6 min with the $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%) solution prepared from „aged“ ammonium sulfide.

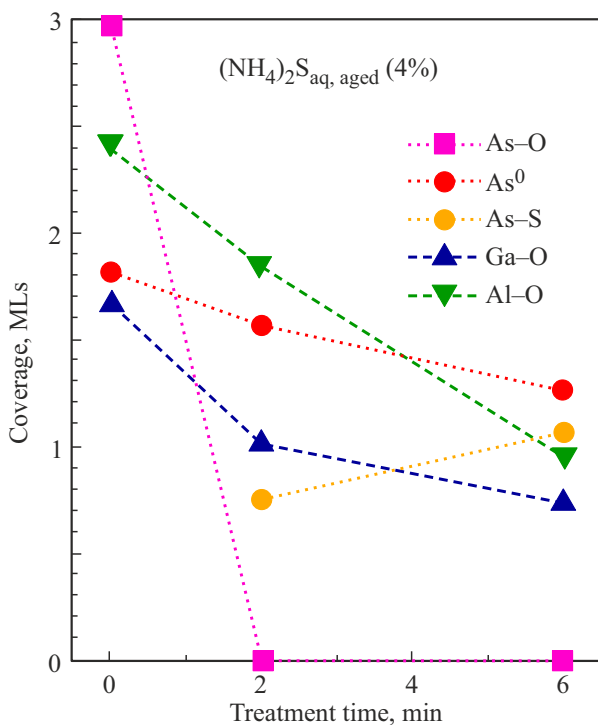


Figure 7. Variation of thickness of coverages for different components on the $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface treated with the $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%) solution prepared from „aged“ $(\text{NH}_4)_2\text{S}$.

spectra, although certain amounts of arsenic oxides and/or hydroxides did remain on the surface (Figure 10, *a*). This may be indicative of incomplete etching of the native oxide layer in the solution or oxidation of the surface as a result of subsequent exposure to air.

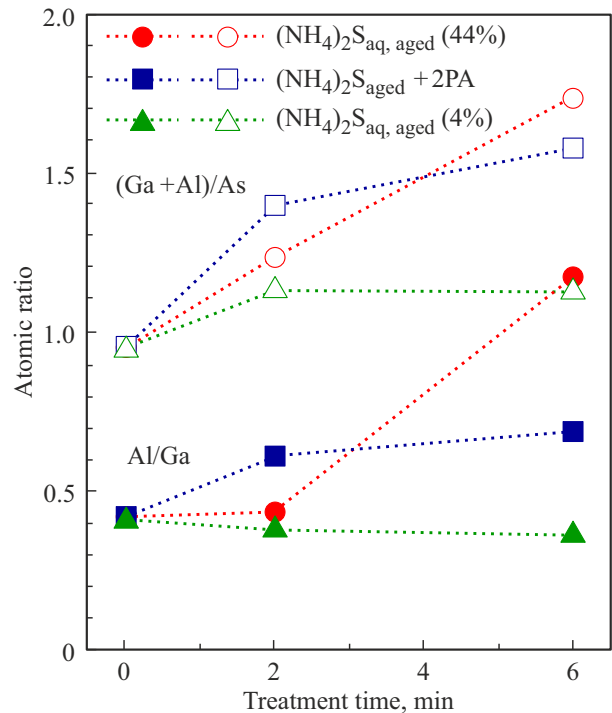


Figure 8. Variation of Al/Ga and (Ga+Al)/As atomic concentration ratios after treatment of the oxide-covered $n\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface with various sulfide solutions prepared from „aged“ ammonium sulfide.

after treatment with the solution prepared from „fresh“ ammonium sulfide (Figure 9, *b*). It should also be noted that the component associated with arsenic sulfides was lacking almost completely in the decomposition of As 3d core level

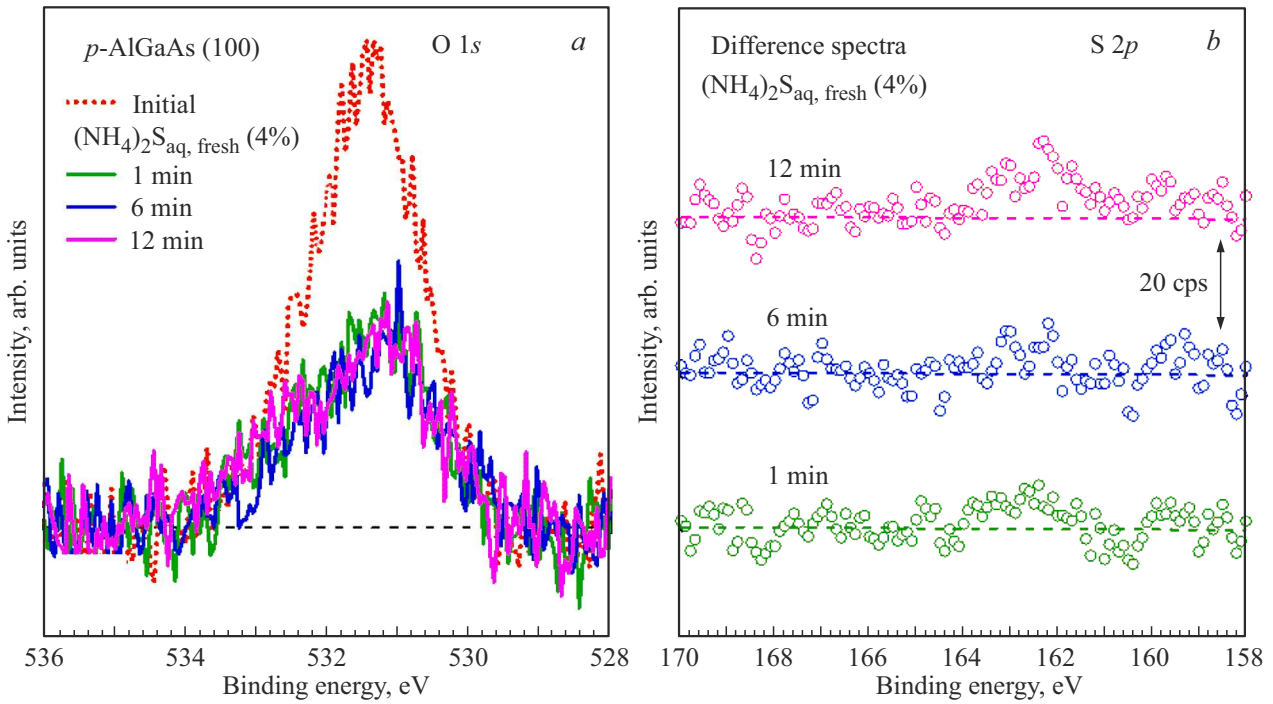


Figure 9. *a* — Spectra of O 1s core level measured on the $p\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface covered with a native oxide layer before and after 1, 6, and 12 min of treatment with the $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%) solution prepared from „fresh“ ammonium sulfide. *b* — Difference S 2p spectra obtained as the ones in Figure 2, *b* for the $p\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface treated for 1, 6, and 12 min with the $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%) solution prepared from „fresh“ ammonium sulfide.

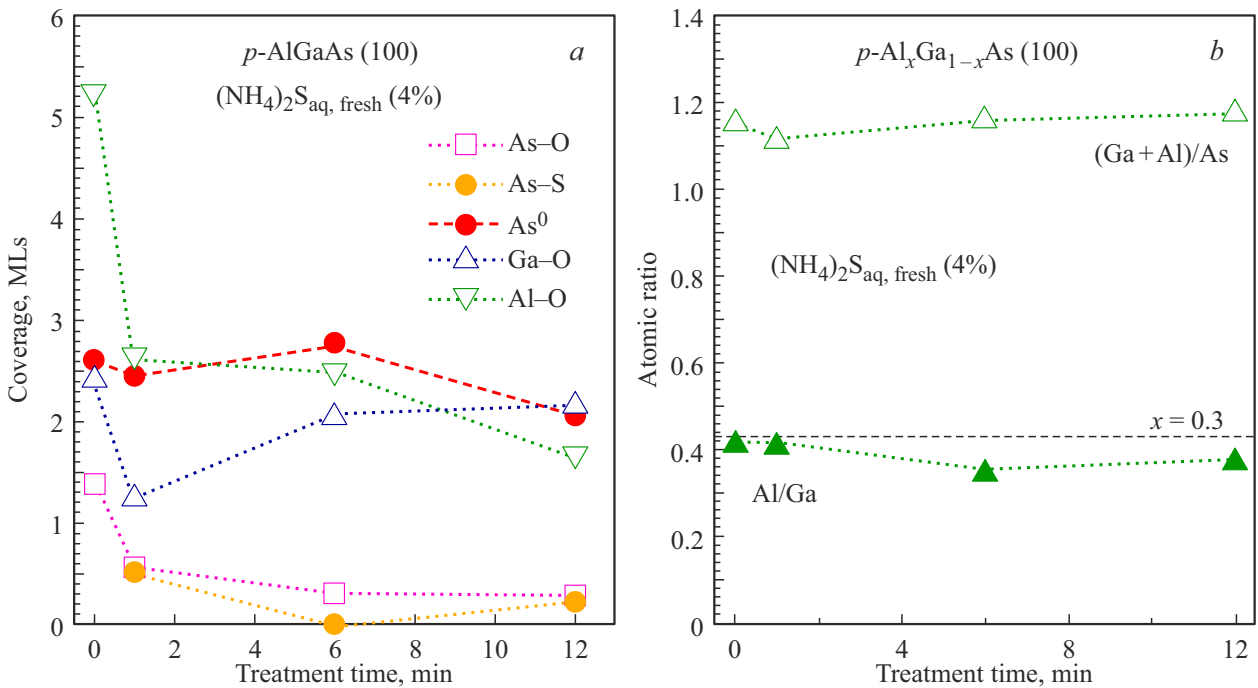
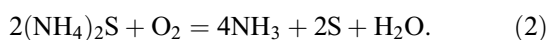


Figure 10. *a* — Variation of thickness of coverages for different components on the $p\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface in the course of treatment of the $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%) solution prepared from „fresh“ ammonium sulfide. *b* — Variation of Al/Ga and (Ga+Al)/As atomic concentration ratios in the course of treatment of the $p\text{-Al}_{0.3}\text{Ga}_{0.7}\text{As}(100)$ surface with the $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%) solution prepared from „fresh“ ammonium sulfide.

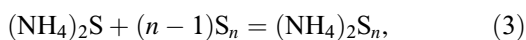
The $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%) solution prepared from „fresh“ ammonium sulfide removed aluminum oxides slightly faster than gallium oxides, while the $(\text{Ga}+\text{Al})/\text{As}$ atomic concentrations ratio remained virtually unchanged (Figure 10, *b*). Approximately 2–2.5 monolayers of gallium and aluminum oxides remained on the *p*-AlGaAs(100) surface covered with a native oxide layer after its interaction with this solution (Figure 10, *a*). The amount of residual oxides on the *n*-Al_{0.3}Ga_{0.7}As(100) surface treated with the same solution was approximately the same.

4. Discussion

As was mentioned earlier, the so-called „aged“ solution formed naturally during several years of storage of a commercial concentrated ammonium sulfide solution in air in an unsealed factory container. Under such storage conditions, the solution interacts with atmospheric oxygen each time the container is opened. This leads to the formation of elemental sulfur that floats on the surface:



In addition, prolonged exposure of the ammonium sulfide solution to air may lead to the formation of polysulfides [24] due to the interaction of the concentrated basic solution with formed sulfur molecules:



where *n* may assume a value of 2 or higher. Exhibiting both oxidizing and reducing properties, sulfur enables the formation of arsenic sulfides when its oxides are removed in all the used solutions prepared from „aged“ ammonium sulfide, regardless of their concentration and solvent type (see Figures 3, 4, 7). At the same time, when Al_{0.3}Ga_{0.7}As(100) is treated (Figure 9, *b*) with the $(\text{NH}_4)_2\text{S}_{\text{aq}}$ (4%) aqueous solution prepared from „fresh“ ammonium sulfide, a sulfide layer virtually does not form; i.e., chemical passivation of the surface is not achieved. A similar effect was observed when InGaAsP comb structures were treated with „aged“ ammonium sulfide, which induced a stronger reduction of the surface recombination rate than a „fresh“ solution [16].

The process of removal of oxides of group III elements (gallium and aluminum) from the surface of a semiconductor depends strongly on the solution concentration and the solvent type (Figure 8). The interaction with a concentrated „aged“ solution alters the stoichiometric composition in the near-surface region due to the removal of more electronegative gallium atoms. Gallium oxides are etched much faster than aluminum oxides in the concentrated „aged“ $(\text{NH}_4)_2\text{S}$ (~ 44%) solution and the dilute solution of „aged“ $(\text{NH}_4)_2\text{S}$ in isopropyl alcohol, while the rates of etching of these group III oxides in the dilute aqueous solution of „aged“ ammonium sulfide are practically the same. A small amount of gallium and aluminum oxides remains on the surface, which is attributable to oxidation of the treated surface that

is exposed to air during the transfer of samples into the XPS chamber. Thus, the examination of several ammonium sulfide solutions revealed that the dilute aqueous solution of $(\text{NH}_4)_2\text{S}$ with a concentration of ~ 4% prepared from an „aged“ commercial ammonium sulfide solution is the most efficient of them in removing the native oxide layer and passivating the Al_{0.3}Ga_{0.7}As(100) surface.

5. Conclusion

The interaction of a native-oxide-covered Al_{0.3}Ga_{0.7}As(100) surface with various ammonium sulfide solutions was studied by X-ray photoelectron spectroscopy. It was demonstrated that the highest efficiency of etching of the native oxide layer and chemical passivation is achieved by treating the surface with an aqueous solution of ammonium sulfide with a concentration of ~ 4% prepared from a commercial reagent „aged“ over the course of several years by storing it in air in a factory container that is opened repeatedly. This solution ensures almost complete removal of oxides from the semiconductor surface and induces the formation of a thin (approximately one monolayer) passivating layer consisting of arsenic sulfides. The stoichiometry of the surface remains undisturbed in the process. A similar solution prepared from „fresh“ ammonium sulfide does also remove oxides from the surface, but a sulfide passivating layer does not form. When the surface is treated with a concentrated (44%) aqueous solution of „aged“ ammonium sulfide or a dilute alcohol solution of „aged“ ammonium sulfide, gallium atoms from the surface pass into the solution, and the stoichiometry of the surface layer is disturbed. In this case, the surface gets covered with a relatively thick aluminum oxide layer.

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Conflict of interest

The authors declare that they have no conflict of interest.

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