Modification of the GaSb(100) surface in ammonium sulfide solutions - morphology and stoichiometry

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Abstract. The changes in the stoichiometry and morphology of the GaSb(100) surface in the process of sulfide passivation with aqueous and alcoholic ammonium sulfide solutions were studied by AFM and XPS. It was found that after sulfide treatment the Ga/Sb ratio can vary in the range from 0.13 to 3, while the surface roughness can be changed from 1.1 to 5.5, depending on the concentration of the (NH₄)₂S solution, solvent and passivation time.

1. Introduction
Gallium antimonide (GaSb) is widely used in infrared optoelectronic devices, as well as in high-frequency field-effect transistors [1–3]. It is known that the gallium antimonide surface is extremely chemically active. Thus, even after short air exposure, an oxide layer several nanometers thick consisting of a mixture of different antimony and gallium oxides is formed on the surface of GaSb deteriorating its morphology and creating surface traps for charge carriers. Moreover, the chemical composition and thickness of this oxide layer depend on environmental conditions and time of air exposure. The key problem in the development of devices based on GaSb is the removal of these oxides providing flatness and stoichiometry of the surface.

A promising technique for removing oxides from the surface of III–V semiconductors is chemical passivation, which results in the removal of oxides, and formation of chemically inert protecting layer on the surface. One of such approaches is sulfide passivation with ammonium sulfide (NH₄)₂S solutions. These solutions are also used to modify the surface of GaSb(100), as well as its interfaces with subsequently grown insulator layers for various metal–insulator–semiconductor structure applications [4]. In the process of sulfide chemical passivation, several different chemical processes take place simultaneously on the semiconductor surface, which results in change of both stoichiometry and surface roughness.

Today it is clear that surface roughness and deviations from stoichiometry are essential in establishing band alignment at semiconductor/insulator interfaces and related electrical characteristics of the devices involving such interfaces [4–6].

However, the data on the results of sulfide passivation of the GaSb(100) surface in ammonium sulfide solutions is still scattered and contradictory. Depending on the composition of the ammonium sulfide solution the morphology [6], as well as surface stoichiometry [7] of the passivated GaSb(100) surface, can vary in a great extent.

The aim of this work is to understand systematically how the morphology and stoichiometry of the GaSb(100) surface is affected by the composition of the ammonium sulfide solution and the duration of the treatment.
2. Experimental

In this work, n-GaSb(100) samples with a concentration of $2 \times 10^{17}$ cm$^{-3}$ were studied. Chemical treatment was carried out with ammonium sulfide (NH$_4$)$_2$S solutions either in water or in isopropanol (2-C$_3$H$_7$OH) of various concentrations. Prior to chemical treatment, the samples were cleaned ultrasonically in acetone for 5 min at room temperature. Three groups of samples were prepared. In order to identify the effect of sulfur concentration in an aqueous solution of ammonium sulfide, one group was treated with a commercial aqueous solution of ammonium sulfide (NH$_4$)$_2$S with a concentration of 40–42%. For samples of the second group, this solution was diluted with water in a ratio of 1:9 so that the concentration of the solution was 4%. To clarify the role of the ammonium sulfide solvent (NH$_4$)$_2$S in the third group of samples, isopropyl alcohol (2-C$_3$H$_7$OH) was chosen as the solvent. The sulfur concentration in this solution was also 4%.

The surface roughness of the samples was analyzed from surface morphology, measured by the atomic force microscopy (AFM) in air employing an NTegra-Aura atomic-force microscope (NT-MDT, Russia), operating in semicontact mode using an NSG11 probe with a stiffness coefficient of 5 N/m and a probe tip curvature of 10 nm. The root-mean-square deviation of height (RMS) over an area of 3x3 $\mu$m was chosen as a quantitative value of roughness.

Surface stoichiometry (Ga/Sb ratio) was estimated from X-ray photoelectron spectroscopy (XPS) spectra of the Ga 3$d$ and Sb 4$d$ core levels. The XPS spectra were measured using an X-ray photoemission spectrometer (SPECS, Germany) using a MgK$\alpha$ source ($h\nu = 1253.6$ eV). All spectra were measured at normal emission. The binding energies of the core levels were referred to the Fermi level determined on an argon-sputtered Au sample. The energy scale of the spectrometer was calibrated by the gold line Au 4$f_{7/2}$, which binding energy was accepted to be 84.0 eV.

3. Results

The AFM study of the initial GaSb(100) surface showed that the surface roughness (RMS) of the crystals under study can vary essentially from one sample to another within the same wafer. Nevertheless, the average roughness among these samples was 1.18 nm. This value was chosen as the value of the roughness of the samples before treatment. Figure 1 shows a typical AFM image of a 1x1 $\mu$m area of the initial GaSb surface. Due to deviation of initial value of RMS, the initial roughness was measured and averaged for all samples subjected to sulfide treatments and roughness after treatment was normalized to this averaged value.

![AFM image of the initial GaSb(100) surface](image)

**Figure 1.** AFM image of the initial GaSb(100) surface (a) and the corresponding profile along white line (b).

For all samples under study, XPS spectra of Ga 3$d$ and Sb 4$d$ core levels were recorded. Figure 2 shows examples of XPS spectra of GaSb(100) surfaces treated for 13 minutes in aqueous (NH$_4$)$_2$S solutions of different concentrations to indicate the effect of ammonium sulfide concentration in aqueous solution on surface stoichiometry. To determine surface stoichiometry, the integral intensities...
of each core level spectra were calculated, taking into account the corresponding photoionization cross sections [8]. In particular, the ratio of integral intensities of Sb 4$d$ and Ga 3$d$ core level spectra shown on figure 2a is about 3.6. As for excitation energy of 1253.6 eV the photoionization cross section of Sb 4$d$ core level is 3 times higher than that for the Ga 3$d$ core level, the resulting Ga/Sb ratio can be estimated as about 1.2. As one can see, in the spectrum of the GaSb(100) surface treated in more concentrated aqueous ammonium sulfide solution (figure 2b) the relative intensity of Sb 4$d$ peak is much less, so the Ga/Sb ratio increases to 2.8, in a good agreement to the value obtained in [7] after treatment of GaSb(100) surface in a similar solution.

![Figure 2](image_url)  
**Figure 2.** XPS spectra of Ga 3$d$ and Sb 4$d$ core levels for GaSb(100) surfaces treated for 13 min in aqueous (NH$_4$)$_2$S solution with concentration of 4% (a) or 40% (b).

In aqueous ammonium sulfide solutions the surface roughness starts to increase from the beginning of the treatment process. This is probably due to the fact that at the initial stage of passivation, the etching of gallium and antimony oxides is the dominant process. As the rates of these reactions are not the same, the surface is etched non-uniformly and an increase in the surface roughness is observed. It should be noted that the etching of the GaSb crystal itself does not occur, since the Ga/Sb ratio remained intact at this stage.

The surface of samples treated with 4% aqueous solution of (NH$_4$)$_2$S becomes smoother as the time of treatment increases. Thus, during treatment for 30 minutes, the RMS of the surface was reduced to ~ 0.85 nm (70% of the initial RMS). However, surface stoichiometry substantially changes in this case and the Ga/Sb ratio exceeds the value of 2. All the data obtained for this solution are summarized in the diagram in figure 3.

![Figure 3](image_url)  
**Figure 3.** The dependence of the surface RMS (red-black bars) and the Ga/Sb ratio (white-black bars) on the treatment time in a dilute (4%) aqueous solution of ammonium sulfide.
Similar changes in stoichiometry are observed in the case of a more concentrated aqueous ammonium sulfide solution (see figure 4). After half an hour of the treatment with the concentrated (40%) aqueous ammonium sulfide solution the Ga/Sb ratio increases more than by a factor of 3 relative to the initial value. In addition, the surface roughness in this case increases essentially with time of treatment in the solution. One of the possible explanations is the formation of the protective layer several tens of nanometers thick with a non-uniform chemical composition [9].

Replacing the solvent in an ammonium sulfide solution from water to 2-propanol maintaining a low concentration (4%) leads to unexpected results (see figure 5). For short passivation times (less than 4–5 minutes), the surface roughness changes very little. Taking into account the above-mentioned variation in the RMS value over the sample surface, the recorded changes can be considered as the experimental error. On the other hand, the change in surface stoichiometry suggests that the process of interaction of the passivating solution with the surface is quite active. This interaction becomes especially noticeable after treating for more than 5 minutes. In this case, the surface roughness begins to increase sharply, and the content of Ga on the surface, on the contrary, decreases. After the treatment for 30 min, the surface is enriched in antimony (the Ga/Sb ratio is 0.13) and covered with objects with a characteristic size of ~ 0.5 microns.

4. Conclusion
The changes in the stoichiometry and morphology of the GaSb(100) surface in the process of sulfide passivation with ammonium sulfide solutions were studied by AFM and XPS. It was found that after sulfide treatment the Ga/Sb ratio can vary in the range from 0.13 to 3, while the surface roughness can
be changed from 1.1 to 5.5, depending on the concentration of the (NH₄)₂S solution, solvent and time of treatment. The obtained results should be taken into account because stoichiometry and morphology have a significant impact on the interface electronic structure and transport properties.

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