

Solvent-Affected Chemistry at GaAs/Sulfide Solution Interface

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Chemical treatment of GaAs(100) surface can modify its electronic structure. For instance, adsorption of sulfur atoms from sulfide solutions results in considerable reduction in surface recombination velocity, which makes possible the improvement of the performance of many electronic devices, such as lasers, transistors, solar cells. It was found that the electronic structure of the sulfur-treated surface depends considerably on the solvent used for sulfur adsorption.¹ Particularly, using the alcohols with low dielectric constant value instead of water enables the surface recombination velocity and surface states density to be reduced dramatically. The goal of this work is to study the surface chemistry of sulfur adsorption from solutions depending on the solvent.

GaAs(100) sulfur-treated surfaces were studied by XPS and UPS. Prior to sulfur treatment the surface was cleaned by Ar-sputtering and annealing, so, the treatment was carried out on the oxide-free surface. The sulfur treatment was carried out in inert N₂ atmosphere and transfer of the sample to this atmosphere and back to UHV was accomplished without any contact with ambient air. Solutions of (NH₄)₂S in water and different alcohols were used for the surface treatment. After the treatment the solution was removed from the surface before sample transfer to UHV.

It was found that the character of the formed As-S bonds essentially depend on solvent. In aqueous sulfide solution the bond has lower ionicity (it has minimal chemical shift). The treatment with alcoholic sulfide solution results in the formation of As-S bonds with increased ionicity, as evidenced by increased chemical shifts, as well as by increased ionization energy of the semiconductor.

Successive annealing of the surface results in breaking of As-S bonds and formation of Ga-S bonds. This process also depends on the prehistory of the sample, e.g., in which solution it was treated. Treatment in aqueous solution results in As-S bond breaking at relatively low temperature, and the formation of elemental As accompanies the Ga-S bonds formation. By contrast, after annealing of the surfaces treated with solutions in isopropanol or tert-butanol, Ga-S bonds are formed accompanied first by a decrease in As-S bonds ionicity. The As-S bonds disappear completely at higher temperature compared to the surface treated with aqueous solution, and As-As surface dimers appear instead. The Ga-S component in core-level spectra is independent on the solvent. However, the valence-band spectra contain features related to Ga-S bonds (Fig. 1) and their binding energy increase with the decrease in the dielectric constant of the solvent (Fig. 2).

This solvent-affected chemistry is related to variations in sulfide-ions reactivity due to the different influence of the solvate shell in different solutions.

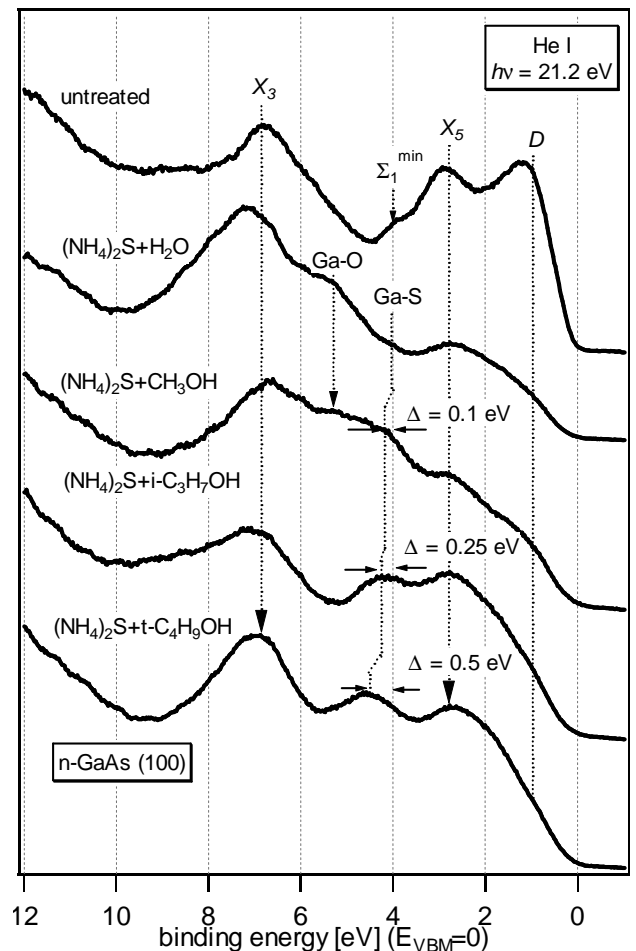


Fig. 1. Normal emission valence band photoemission spectrum of bare n-GaAs(100) surface (upper curve) and spectra of such a surface treated with different sulfide solutions and annealed at 400 °C.

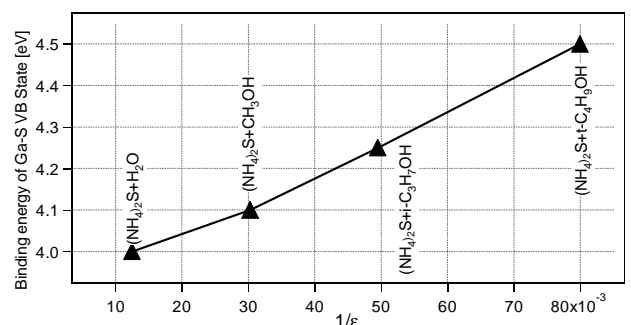


Fig. 2. Binding energy of the Ga-S related valence band state as a function of the reciprocal dielectric constant of the solvent where the adsorption of sulfur was proceeded.

¹ V.N. Bessolov and M.V. Lebedev, *Semiconductors*, **32**, 1141 (1998).