

Role of Solvent in Adsorption at Semiconductor/Electrolyte Interface: Effect on Surface Chemistry and Electronic Properties

M.V. Lebedev,* Th. Mayer, and W. Jaegermann
 TU-Darmstadt, FB Material- und Geowissenschaften,
 FG Oberflächenforschung, Petersenstraße 23, 64287
 Darmstadt, Germany

*e-mail: mleb@triad.iffpe.rssi.ru

The vast majority of chemical processes at semiconductor surfaces proceed at the interface between the solid and solutions. It is well-known that solvation of ions and molecules is able to profoundly alter chemical processes, since intermolecular interactions in solutions may affect the molecular valence shell. The objective of this study is to understand the role of the solvent in adsorbate interaction with semiconductor surfaces, as well as the solvation effect on the atomic and electronic structure of the formed surface.

Ab initio calculations have shown that hydrated hydrosulfide ion can donate and accept electrons, whereas the ion solvated by alcohol molecules can only donate electrons, but cannot accept them in a chemical reaction.¹ Accordingly, the interaction of such ions with the semiconductor surface will proceed by different mechanisms. On interaction of hydrated ion with GaAs(100) surface, the charge localized in surface states remains unchanged and the formed As-S bonds should be covalent. By contrast, the interaction of the ion solvated by alcohol molecules should reduce the charge localized in surface states, while the formed As-S bonds should have higher ionicity.

Experimental results support this model. It was shown by Raman scattering that the charge remaining on the GaAs(100) surface states remains intact after treatment with aqueous hydrosulfide-ions-containing solutions, which manifests as no change in surface depletion layer width (Fig.1). By contrast, treatment in solutions of ammonium sulfide in different alcohols results in considerable decrease of the depletion layer width and, therefore, of the charge localized in surface states. The charge localized in surface states decreases, and the intensity of photoluminescence increase with the decrease of the dielectric constant of the solvent (Fig.1). A similar dependence was obtained for InP(100) surfaces.² Thus, electronic properties of the surface covered by adsorbed hydrosulfide-ions depend on the solvent.

XPS shows that the ionicity of As-S chemical bonds depend on the solvent used for the hydrosulfide-ions adsorption (Fig.2). With the decrease of the dielectric constant of the solvent, the chemical shift of the As-S component in As-related core-level spectra increases and the ionization energy of the surface increases as well (Fig.3). So, the atomic structure of the surface covered by adsorbed hydrosulfide-ions depends on the solvent.

Thus, modification of chemical properties of the adsorbate through its solvation by various solvents can affect adsorbate interaction with III-V semiconductor surfaces. Atomic and electronic structure of adsorbate-covered surface can “remember” the solvent from which the adsorption was performed.

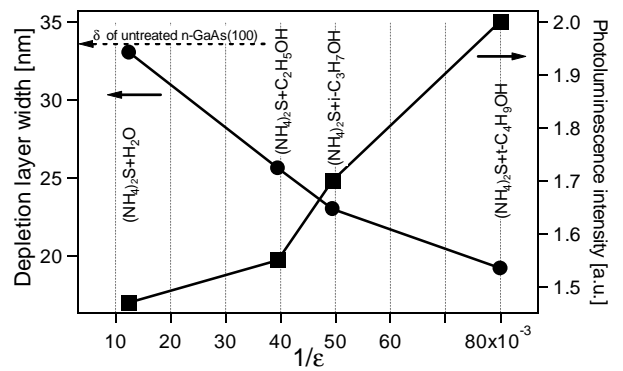


Fig. 1. Dependence of the surface depletion layer width (circles) and of the photoluminescence intensity relative to the untreated sample (squares) for n-GaAs ($N_D = 10^{18} \text{ cm}^{-3}$) treated with different hydrosulfide-ions-containing solutions on the reciprocal dielectric constant of the solvent.

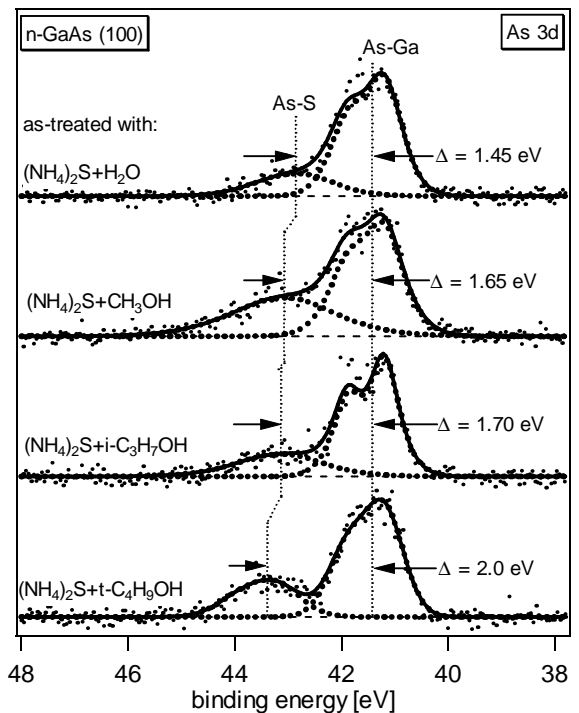


Fig. 2. As 3p core level spectra for different as-treated surfaces as a function of solution.

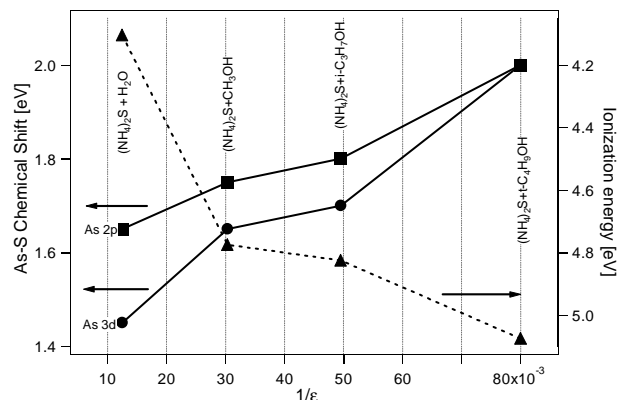


Fig. 3. The chemical shift of As-S component in As 3d (circles) and As 2p (squares) core level spectra and ionization energy (triangles) of as-treated surfaces as a function of the reciprocal dielectric constant of the solvent where the adsorption of sulfur was proceeded.

¹ M.V. Lebedev, *J. Phys. Chem B* **105**, 5427 (2001).

² V.N. Bessolov, E.V. Konenkova, M.V. Lebedev, and D.R.T. Zahn, *Phys. Solid State* **41**, 793 (1999).