Sulfur Adsorption at GaAs: Role of the Adsorbate Solvation and Reactivity in Modification of Semiconductor Surface Electronic Structure

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Density functional theory was used to calculate the global hardness and the local (condensed) softness of the free and monosolvated hydrosulfide-ion HS$^-$ in order to carry out an analysis of the solvation effect on the chemical reactivity of the ion and its interaction with GaAs surface. The solvents were water and different single-based alcohols. Sulfur atom in free and hydrated HS$^-$ ion is rather reactive toward both nucleophiles and electrophiles while water attached to the latter ion is inert. In contrast, sulfur atom in the ion solvated by an alcohol molecule is strongly nucleophilic whereas the solvent is strongly electrophilic. Besides, the nucleophility of sulfur atom in such an ion is the greater, the softer molecule solvates the ion. Accordingly, the adsorption of hydrated and solvated by alcohol molecule ions onto GaAs surface will proceed by fundamentally different mechanisms. This explains the previous experimental findings of the profound effect of the adsorbate solvation on the resulting semiconductor surface electronic structure.

1. Introduction

One of the main obstacles that hinders the development of GaAs based devices is poor electronic properties of GaAs surface. It is well-known[1] that a GaAs(100) surface has a high density of states that causes a high velocity of nonradiative surface recombination and pinning of the surface Fermi level near the middle of the band gap. The properties of these states are determined, in principle, by the semiconductor surface chemistry, and therefore, they can be affected to a great extent by a chemical treatment of the semiconductor. Among various chemical treatments suggested for surface modification of III−V compound semiconductors the adsorption of the ordered sulfur atoms layer from different sulfur-containing species has attracted considerable attention.[2−6] Sulfur adsorption was found to reduce the GaAs surface recombination velocity, which has been indicated by the enhancement of the photoluminescence yield[7] and by the variation of the surface band bending of the semiconductor.[8] Furthermore, the performance of the transistors[2] and lasers[9,10] made on the basis of GaAs and other III−V compound semiconductors can be improved considerably through the adsorption of sulfur.

Chemistry of the sulfur adsorption exerts crucial influence on the resulting surface electronic structure of the semiconductor. For example, the sulfur adsorption onto the GaAs(100) surface from an aqueous solution results in the increase of the photoluminescence intensity, but has no effect on the surface Fermi level position of the semiconductor.[7,11] Whereas the molecular sulfur adsorption in the ultrahigh vacuum causes the shift of the surface Fermi level on 0.2 eV toward the conduction band.[11] It should also be noted, that sulfur adsorption from the most of the sulfide solutions proceeds through the interaction of the solvated hydrosulfide ions HS$^-$ with the semiconductor surface and the increase of the reactivity of these ions under variation of the solute environment

stimulates the raise of the photoluminescence yield and simultaneous decrease of the surface depletion layer width of the sulfidized GaAs.[12]

One way to affect the chemical reactivity of atom or ion is the solvation, that is association with the number of the solvent molecules. The interaction with the solvent modifies the electronic shell of the solute[13] and therefore the adsorbate solvation can result in modification of its chemical properties. The most pronounced ionic solvation is observed in aqueous and alcoholic solutions, in which the formation of hydrogen bond network is possible.

In contrast to sulfur and hydrosulfide-ions adsorption from the aqueous solutions, their adsorption from the alcoholic ones modifies more effectively the electronic properties of GaAs as well as other III−V semiconductors. For instance, sulfur adsorption from the alcoholic solutions results in greater increase of the photoluminescence yield of GaAs[12] and GaN,[14] significant decrease of the surface depletion layer width of GaAs and InP,[12,15] and considerable (by 0.5−0.6 eV) shift of the GaAs surface Fermi level toward the conduction band.[16] Furthermore, the treatment with alcoholic sulfide solutions favors more efficient performance of semiconductor lasers.[17,18] These results attest that the ionic solvation of adsorbates opens the reasonable way for effective engineering of the electronic properties of the solid surfaces.

Despite substantial efforts undertaken to explain the mechanism of the modification of the semiconductor surface by sulfur atoms adsorption,[19−21] a comprehensive model capable of describing the response from the semiconductor surface electronic structure to the chemical interactions is still lacking.

This paper considers the effect of the solvation by different amphiprotic solvents on the reactivity of the hydrosulfide ion HS$^-$. The results obtained through the density functional calculations enable reasonable descriptions of the previous experimental results on the modification of the semiconductor surface electronic structure caused by the adsorption of the solvated hydrosulfide-ions.

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2. Methodology of the Molecular Reactivity Account

Density functional theory[22] provides a very useful framework for understanding chemical reactivity. It states that all properties of atoms and molecules are entirely determined by the spatial distribution of the electron density. As one molecule approaches another—this takes place in the course of the chemical reaction—the electrons start to flow from the less electronegative reagent to the more electronegative one. Density functional theory assumes that the electronegativity is the negative electron chemical potential μ in the system that, after completion of the chemical reaction, should be constant everywhere within the product. The reactivity of the molecule can be characterized by the global hardness η (softness S).

$$\eta = \left(\frac{\partial \mu}{\partial N}\right)_v = \frac{1}{S} \tag{1}$$

where N is the number of electrons in the system and v is the external potential. The global hardness (softness) value constitutes the basis for the hard and soft acids and bases principle,[23] which proposes that reactions will occur most readily between species that are matching in hardness (softness). The soft reagents tend to form covalent bonds while the hard reagents tend to be involved into the ionic ones. The interaction energy then increases with the decrease of the hardness (the increase of the softness) of the reagents.

One way to evaluate the global hardness of molecules is the Koopmans' approximation

$$\eta = \frac{e_{LUMO} - e_{HOMO}}{2} \tag{2}$$

where e_{LUMO} and e_{HOMO} are the energies of the lowest unoccupied (LUMO) and the highest occupied (HOMO) molecular orbitals, respectively. This approach was also used to study the hardness of different closed-shell cations and anions.[24] In such an approximation, the global hardness of the semiconductor is equal to the half of its band gap or, speaking more strictly, to the half of its surface gap (the gap between filled and vacant surface states).

Considering the semiconductor surfaces, for which many nonequivalent adsorption sites are possible, as well as the complex nonmonoatomic adsorbates the problem of particular interest is the study of the local reactivity. For understanding the local reactivity, the corresponding local indexes are needed.[22] The Fukui function is introduced to be such an index

$$f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_v \tag{3}$$

which defines the response of the electron density $\rho(\vec{r})$ of the system on the change of the number of electrons at the constant external potential (the arrangement of nuclei). The other index is the local softness

$$s(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial \mu}\right)_v \tag{4}$$

It determines the response of the electron density $\rho(\vec{r})$ of the system on the change of the chemical potential at the constant external potential (the arrangement of nuclei).

The local softness is related to the Fukui function through the relationship

$$s(\vec{r}) = f(\vec{r})S \tag{5}$$

The integral of the Fukui function over the entire volume of the molecule is equal to unity, and accordingly, the integral of the local softness is equal to the global softness of the molecule.

The Fukui function indicates the propensity of the electron density to deform at a given position in order to donate or accept electrons. In other words, the larger Fukui function, the higher reactivity is at this position. The local softness contains the same information as the Fukui function plus additional information about the total molecular softness. Therefore, the local softness should be a better descriptor of the reactivity of different molecules toward semiconductor surface (or any other complex molecule) with a given hardness or softness.[25]

According to electronegativity difference between the reacting species, the chemical interaction occurs either between HOMO of the semiconductor and LUMO of the adsorbate (nucleophilic attack) or between LUMO of the semiconductor and HOMO of the adsorbate (electrophilic attack). Since for the systems with finite number of particles the left and right derivatives with respect to the number of particles are different, the Fukui function and the local softness are recognized for the nucleophilic $f^+(\vec{r})$ ($s^+(\vec{r})$), electrophilic $f^-(\vec{r})$ ($s^-(\vec{r})$), and radical (interaction between species with equal electronegativity) attack $f^0(\vec{r}) = {}^1/_2 [f^+(\vec{r}) + f^-(\vec{r})]$ ($s^0(\vec{r}) = {}^1/_2 [s^+(\vec{r}) + s^-(\vec{r})]$).

The hard and soft acids and bases principle is valid in local form as well,[26] namely, the interaction between molecules is favored when it occurs through sites matching in softness.

A reasonable method to assign a value of the Fukui function and the local softness is to condense their values around each atomic site into a single value that characterizes the atom in the molecule.[27] In the case of the Fukui function, this can be done assuming the electron density equal to the charge q_i of ith atoms in the molecule and differentiating it afterward with respect to the total number of electrons in the system. Thus, in a finite difference approximation,[27]

$$f_i^+ = q_i^{N+1} - q_i^N$$

$$f_i^- = q_i^N - q_i^{N-1}$$

$$f_i^0 = \frac{1}{2}(q_i^{N+1} - q_i^{N-1}) \tag{6}$$

The condensed local softnesses can be obtained according to eq 5 multiplying both sides of eqs 6 by the global softness value. The charges q_i^{N+1}, q_i^N, and q_i^{N-1} can be obtained by different quantum-chemical population analysis techniques for the systems with $N + 1$, N, and $N - 1$ electrons, respectively, all with the ground-state geometry of the N electrons system.

The local softness distribution at a GaAs surface was calculated in ref 28. Here it was shown that the softest places at the surface are the regions on top of the arsenic atoms, and the hardest places are the interatomic regions. At an ideal GaAs surface HOMO will be the filled dangling bonds localized at arsenic surface atoms (arsenic dimers) and at the LUMO will be the empty dangling bonds occurred at surface gallium atoms. At the real semiconductor surface, however, different irregularities exist, which can induce states in the band gap. They can be either LUMO (empty states) or HOMO (filled states) depending on their origin.

3. Computational Details

In this study we consider free hydrosulfide ion HS^- as well as HS^- ions associated with one solvent molecule. The solvent molecules were water (H_2O), methanol (CH_3OH), ethanol

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TABLE 1: Electronic Energy (*E*), Global Softness (*S*), and Dipole Moment (*D*) of the Free Solvent Molecules Calculated at the B3LYP/6-31+G(d,p) Level

solvent molecule	*E* (au)	*S* (1/eV)	*D* (debye)
vacuum		0	0
H_2O	−76.4	0.212	2.20
CH_3OH	−115.7	0.260	1.91
C_2H_5OH	−155.1	0.258	1.90
i-C_3H_7OH	−194.4	0.265	1.78
t-C_4H_9OH	−233.7	0.268	1.74

(C_2H_5OH), 2-propanol (i-C_3H_7OH), and *tert*-butyl alcohol (t-C_4H_9OH). The choice of the solvents was based on their previous use in the experiments on the modification of the semiconductor surfaces with the sulfide solutions.[12,14−18,29,30]

Quantum-chemical geometry optimization, frequency calculations and calculations of the reactivity indexes were performed with the GAUSSIAN-94 suite of programs.[31] The calculations were carried out within the framework of the density functional theory. Although the density functional calculation of the global hardness value in terms of the Koopmans' approximation is not straightforward, it must be considered as a most desirable bridge between the chemical reactivity study through the wave function theory and the chemical hardness (softness) concepts.[32] Becke's three-parameter functional[33] and Lee−Yang−Parr correlation functional[34] (B3LYP-method) with the 6-31+G(d,p) basis set were used throughout the calculations.

The calculation procedure was the following. Initially, the geometry of solvent molecules was optimized and the global hardness and softness for free solvent molecules was calculated by applying eqs 1 and 2. Thereupon the geometry optimization of the free ion and ion−solvent complexes was performed. The frequency calculations confirmed that each derived optimal structure corresponds to a minimum of energy (there were no imaginary frequency in the optimized geometry). Next, the complex global hardness and softness values were obtained using the eqs 1 and 2, and the charges q_i^N were taken from the Mulliken population analysis. Thereafter single point energy calculations of the complexes with the derived optimal geometry and with the ionic charges 0 and −2 were carried out to obtain charges q_i^{N-1} and q_i^{N+1}, respectively, which then were substituted into eq 6 to obtain the condensed Fukui functions. Finally, these condensed Fukui functions were multiplied by the global softness of the appropriate complex to obtain the condensed local softness values.

4. Reactivity of Solvated Hydrosulfide-Ions

In previous experimental study of sulfur adsorption at the semiconductor surface from different solutions,[15,17,29] the solvation effect was considered in relation to the static dielectric constant of the amphiprotic solvent. This study, however, considers the mono-solvated hydrosulfide-ions, thus, the static dielectric constant value can no longer be used for solvent classification. On the other hand, the static dielectric constant of the liquid is related to the static dipole polarizability of its molecule,[35] which in turn is related to the global softness.[36] So, in this study, the solvent was classified according to the global softness of its molecule to link the results with ones obtained previously in experiments. Calculated global softnesses as well as electronic energies and dipole moments of the considered solvent molecules are listed in Table 1.

The optimal structure of the complexes consisted of the hydrosulfide-ion HS^- with different solvent molecules attached is shown in Figure 1. The optimal internal coordinates of all complexes are listed in Table 2.
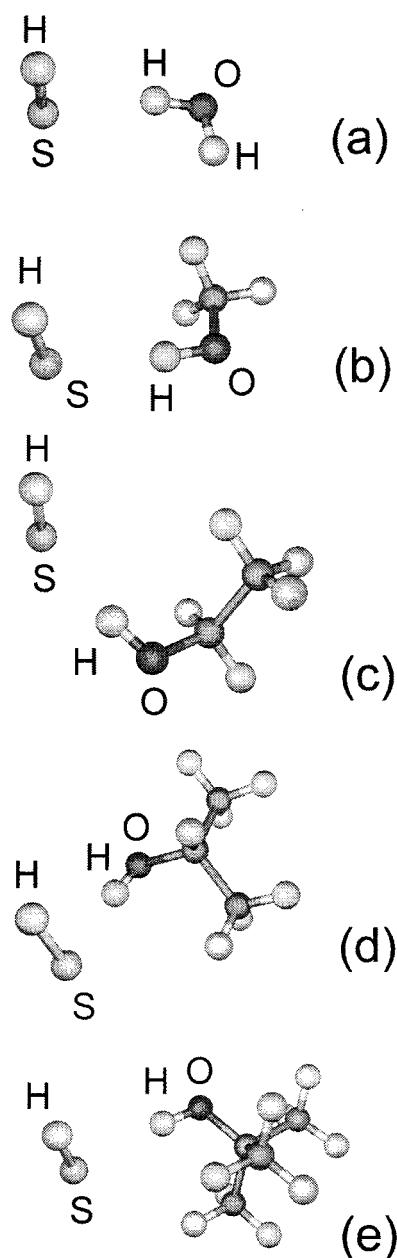
Figure 1. Optimal structures for the minimum states of the complexes consisted of the hydrosulfide-ion HS^- associated with water (a), methanol (b), ethanol (c), 2-propanol (d), and *tert*-butyl alcohol (e) molecules.

Solvation affects considerably the global hardness of the ion (Figure 2a). Solvation by the relatively hard water molecule results in the minor increase of the complex global hardness in comparison with the hardness of free ion. Solvation by more soft alcohol molecules causes the decrease of the global hardness of the complexes. The solvation causes the borrowing of the ionic charge by the solvent molecule (that is, the hydrogen bond is formed), which is stronger when the ion is solvated by an alcohol molecule (Figure 2b).

To study the local reactivity of different sites in the solvated complexes the condensed softness of the constituent atoms and fragments was calculated. The effect of the solvation on the condensed softness of the sulfur atom in the hydrosulfide-ion is shown in Figure 3a. Hydration (that is the solvation by water molecule) decreases slightly the condensed softness of sulfur atom for nucleophilic, electrophilic, and radical attacks leaving

TABLE 2: Optimal Internal Coordinates for Complexes and Free Solvent Molecules (in Parantheses) Calculated at the B3LYP/6-31+G(d,p) Level

complex	R_{S-H}, Å (ion bond length)	R_{S-H}, Å (hydrogen bond length)	R_{O-H}, Å	$R_{O-alkyl}$,[a] Å	R_{O-S}, Å	H−O−alkyl angle[b], deg	S−(H−O)[c] angle, deg
free HS$^-$	1.356						
HS$^-$ + H$_2$O	1.354	2.264	0.997 (0.965)	0.965 (0.965)	3.235	101.3 (105.7)	164.3
HS$^-$ + CH$_3$OH	1.354	2.212	1.001 (0.965)	1.408 (1.425)	3.206	107.4 (109.1)	171.8
HS$^-$ + C$_2$H$_5$OH	1.354	2.215	1.001 (0.966)	1.412 (1.430)	3.205	107.4 (108.8)	170.1
HS$^-$ + i-C$_3$H$_7$OH	1.353	2.216	1.001 (0.966)	1.416 (1.437)	3.210	107.9 (108.9)	172.0
HS$^-$ + t-C$_4$H$_9$OH	1.353	2.253	1.000 (0.967)	1.424 (1.444)	3.250	109.2 (108.7)	175.0

[a] For the water molecule, it is the distance between O atom and H atom not involved to the hydrogen bond. [b] For the water molecule, it is the H−O−H angle. [c] Angle between sulfur atom of the ion and hydrogen and oxygen atoms of the solvent's OH group.
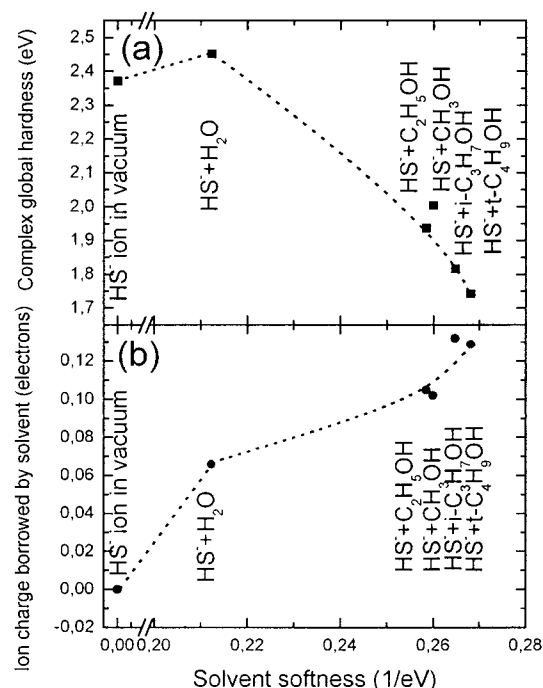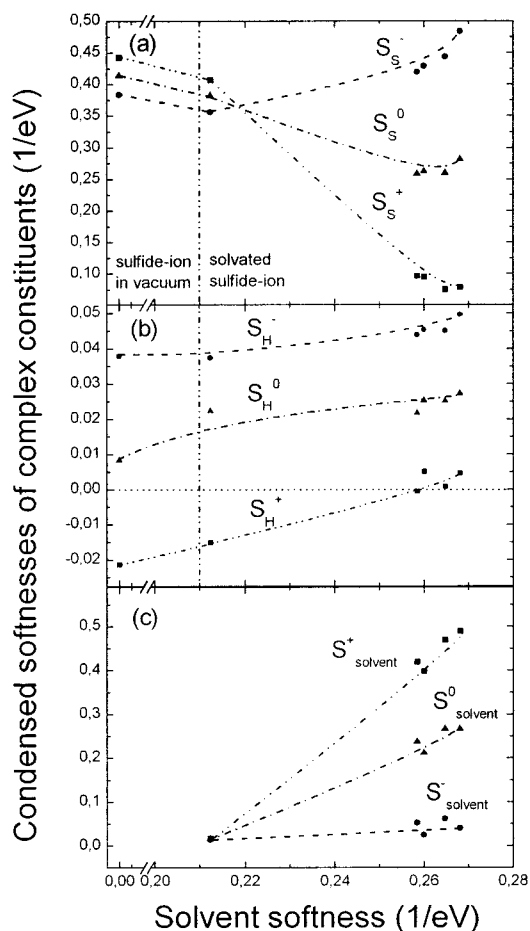

Figure 2. Calculated values of the global hardness of the complexes (a) and of the charge borrowed by the solvent molecule from the hydrosulfide-ion (b), as a function of the global softness of free solvent molecule. Results are depicted by dots with lines given as a guide to the eye.

Figure 3. Condensed softnesses for the nucleophilic s_i^+, electrophilic s_i^-, and radical s_i^0 attacks of the sulfur atom (a), hydrogen atom built in the hydrosulfide-ion (b), and of the solvent molecule solvating the hydrosulfide-ion (c), as a function of the global softness of free solvent molecule. Results are depicted by dots with lines given as a guide to the eye.

the relationship between them almost the same as for free hydrosulfide ion. In contrast, the solvation by the alcohol molecules results in the increase in the condensed softness for the electrophilic attack s_S^- and in a drastic decrease in the condensed softness for the nucleophilic attack s_S^+: these features are more essential when the softer solvent molecule solvates the ion. The condensed softness for the radical attack s_S^0 for the complexes with the alcohol solvent molecules is lower than that for the hydrated complex and free ion, but it increases slightly with the increase in the softness of the alcohol molecule solvating the ion.

The condensed softness of the hydrogen atom built in the HS$^-$ ion is shown in Figure 3b. Evidently in all cases considered this hydrogen atom is very hard with respect to any attack (its condensed softness is more than in order of magnitude lower than the appropriate condensed softness of the sulfur atom and in certain cases it is even negative).

The condensed softness of the attached solvent molecule is displayed in Figure 3c. Evidently water solvating the hydrosulfide ion is very hard toward any direction of the charge transfer, while the softness of alcohol molecules for nucleophilic and radical attacks is fairly high. The most reactive site in an alcohol molecule hydrogen bonded to the ion is the alkyl group

(Table 3). In water molecule that hydrated the ion it is the hydrogen atom not involved into the hydrogen bond although its reactivity is rather low.

Two conclusions about the influence of the solvation on the reactivity of the hydrosulfide-ion can be made from the obtained results. The first one can be illustrated from the consideration of the relative nucleophility[37] of sulfur atom in the ion (that is the ratio s_S^-/s_S^+). The dependence of the relative nucleophility of sulfur atom in the ions on the solvent molecule is shown in Figure 4. Evidently the relative nucleophility of sulfur in hydrated and free ions is close to unity and therefore the sulfur atom has almost equal (rather high) probability to donate and accept electrons. On the contrary, sulfur in the ion solvated by any alcohol molecule being considered has rather high relative

TABLE 3: Condensed Softnesses s_i^+ toward Electrophilic Attack for Different Parts of the Solvent Molecules Calculated at the B3LYP/6-31+G(d,p) Level

solvent molecule	condensed softness (1/eV)		
	H atom	O atom	alkyl group[a]
H_2O	8.3×10^{-4}	5.8×10^{-4}	0.015
CH_3OH	-9.5×10^{-4}	-4.7×10^{-2}	0.45
C_2H_5OH	-2.1×10^{-3}	-4.9×10^{-3}	0.43
i-C_3H_7OH	2.0×10^{-3}	-1.3×10^{-2}	0.48
t-C_4H_9OH	1.6×10^{-3}	-8.6×10^{-2}	0.50

[a] For water molecules, it is the hydrogen atom not involved in the hydrogen bond.
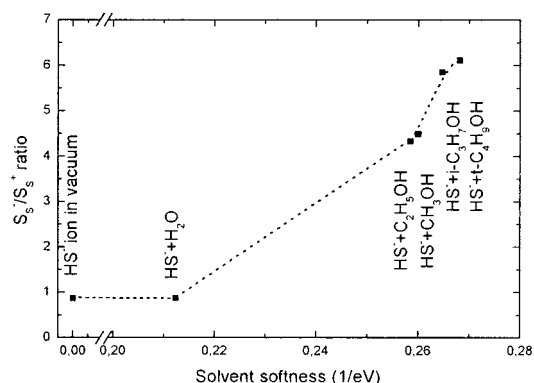
Figure 4. The relative nucleophility of the sulfur atom in the solvated hydrosulfide ion (s_S^-/s_S^+ ratio), as a function of the global softness of free solvent molecule. Results are depicted by dots with lines given as a guide to the eye.

nucleophility and therefore this sulfur atom can readily donate electrons but can hardly accept them.

The second conclusion can be made on the basis of the consideration of the local softness of the molecule solvating the ion. Water in the hydrated ion is almost inert with respect to any direction of charge transfer. By contrast, an alcohol molecule solvating the ion can readily accept electrons, but unable to donate them as well.

Thus, depending on the ion's environment the reactions in which the solvated HS^- ion can participate will be fundamentally different. Free and hydrated hydrosulfide-ions can readily react both with nucleophiles and electrophiles through the sulfur atom. In contrast, sulfur atom in HS^- ion solvated by an alcohol molecule can be attacked by electrophiles only while the reaction with the nucleophiles can proceed mainly through the alkyl group of the solvent.

5. Reactivity of the Solvated Hydrosulfide-Ion toward the GaAs(100) Surface

Study of the charge transfer processes proceeding at the surface in the course of the adsorption is important to understand the attendant modification of the semiconductor surface electronic structure. It has been found experimentally that the hydrosulfide-ions in solutions interact both with arsenic and with gallium atoms at the GaAs(100) surface.[3,4,11,29] The occupied dangling bonds, which occur at surface arsenic atoms, will be nucleophiles for the solvated hydrosulfide ions. Accordingly, the vacant dangling bonds, which are localized at the surface gallium atoms, will be the electrophiles. Therefore, the reactivity of the sulfur atom with respect to the surface arsenic and gallium atoms can be determined by the condensed softness s_S^+ and s_S^-, respectively. Moreover, the high density of the surface states inherent to GaAs permits the adsorbates reaction with the surface states, which will be an essential channel of the chemical interaction modifying surface electronic structure of GaAs. According to the obtained dependencies of the condensed softness of the ions' constituents (Figure 3) and of the relative nucleophility of the sulfur atom in the solvated hydrosulfide ions (Figure 4), the following scenario of the interaction of the solvated ions with the GaAs(100) surface can be considered.

5.1. Interaction with Surface Atoms. The slightly electrophilic sulfur atom in free and hydrated hydrosulfide ion has nevertheless rather high s_S^+ as well as s_S^- condensed softness (Figure 3a), so it is susceptible to interaction with both nucleophiles and electrophiles. Accordingly it can form strong covalent bonds both with the surface arsenic atom (soft nucleophile site[28]) and with the surface gallium atom (soft electrophile site[28]). Its interaction with arsenic atom will shift the level of the surface arsenic occupied orbital deeper to the valence band while the interaction with gallium atom will shift the level of the surface gallium unoccupied orbital higher to the conduction band. Obviously the adsorption of hydrated and free hydrosulfide ions should cause the intrinsic surface gap of the semiconductor to be increased. This conclusion is consistent with the results of ab initio cluster calculations of the GaAs surface covered by sulfur.[38] However, since the gallium unoccupied and arsenic occupied levels are shifting apart, it is evident that such an interaction can result in no or minor variation of the surface Fermi level position with reference to the semiconductor bands. Indeed the adsorption of hydrosulfide ions from an aqueous solution had minor influence on the surface band bending of GaAs(100).[11,12]

The sulfur atom of the ions solvated by an alcohol molecule has rather high s_S^- softness but its s_S^+ softness is about order of magnitude lower (Figure 3a). Accordingly sulfur in such an ion is susceptible to reaction with electrophiles (Figure 4) while it is very hard toward nucleophiles. So, at the GaAs(100) surface it can readily react with the surface gallium atoms and such a reaction will result in the shift of the level of the gallium unoccupied orbital higher to the conduction band. Whereas, due to the local hard and soft acids and bases principle,[26] it is difficult for sulfur atom in such ions to form covalent bond with the surface arsenic atom. However, the interaction is also possible in this case if the alcohol molecule attached to the ion, which has a high condensed softness s_{solv}^+ (Figure 3c), will participate in the reaction between the solvated ion and surface arsenic atom. Although the alcohol molecule cannot be chemisorbed at the surface (at least at room and elevated temperatures), it, nevertheless, can split the alkyl group that can react with the arsenic atoms. The products of such a reaction are soluble in corresponding alcohol, therefore, the surface after sulfidizing in alcoholic solutions should be depleted of arsenic. The depletion of the GaAs(100) surface in arsenic was clearly observed by X-ray photoelectron spectroscopy after the treatment with the alcoholic sulfide solutions.[29]

On the other hand, because of low s_S^+ softness the sulfur atom in principle can be adsorbed at the hard region of the surface, which, according to ref 28, is the region between atoms. Such an interaction should result in no essential shear of the electronic shells and hence the adsorption bond will be mostly ionic. In this case the surface should possess a high dipole moment. Both shift of the gallium unoccupied orbital and the formation of the dipole moment at the surface in this case should result in the essential shift of the surface Fermi level toward the conduction band of the semiconductor. The shift of the surface Fermi level by 0.5−0.6 eV was observed experimentally as the GaAs(100) surface was treated with the ammonium sulfide solution in 2-propanol.[16,30] It was also confirmed that

this surface dipole moment stems from the interaction of the surface arsenic with sulfur atoms.[30]

It should be mentioned that the value of the global hardness of the solvated ion represents the overall reactivity of the ion, particularly, the reactivity is smaller, the greater the hardness value. Just the same order of reactivity of hydrosulfide-ions in different environment toward GaAs(100) and InP(100) surfaces as presented in Figure 2a was observed experimentally.[12,15,29]

5.2. Interaction with Surface States. The Fermi level at the bare GaAs(100) surface grown by the molecular beam epitaxy as well as covered by the native oxide layer is pinned mainly by the acceptor-type surface states.[1] These states capture electrons from the near-surface semiconductor bulk causing it to be depleted. So at the surface the band bending exists (upward at n-GaAs surface and downward at p-GaAs one). Since the density of states at the GaAs(100) surface is rather high, the chemical softness of the surface states is fairly high as well.[39]

Acceptor states at the GaAs(100) surface are occupied by the electrons captured from the semiconductor bulk. On one hand, these states are soft acid sites (capable of trapping electrons), while on the other hand, they are soft HOMO (nucleophiles). As a result, sulfur adsorption from the hydrosulfide ions at the surface state would be determined by the condensed softness s_S^+.

Sulfur in free and hydrated ions has fairly high condensed softness s_S^+ (Figure 3a). Therefore, the acceptor surface states can readily react with the sulfur atom that constituent such an ion. In these cases the strong covalent bond will be formed, and the binding energy shifts the surface state level from the middle of the band gap toward the valence band of the semiconductor. However, the charge localized at this state remains intact because the solvent molecule (water) cannot accept it (the condensed softness of the water molecule associated with the ion is fairly low (Figure 3c)). Hence, the depletion layer width and the surface Fermi level position of the semiconductor remains essentially unchanged after such an interaction. On the other hand, the shift of the state from the middle of the band gap causes the nonradiative surface recombination velocity to be reduced. Decrease of the surface recombination velocity occurred, and yet no noticeable change in the surface Fermi level position and depletion layer width was seen repeatedly in experiments while the GaAs(100) surface was treated with aqueous sulfide solutions.[7,11,12,15]

It is reasonable to expect that mechanism of the interaction of the hydrosulfide-ion solvated by the alcohol molecule with the acceptor surface state of the semiconductor will be different. In this case the softness s_S^+ is small, so it is difficult for the sulfur atom to interact with the occupied surface state. However, the solvent molecule has high softness for the nucleophilic attack s_{solv}^+ (Figure 3c) and it can readily interact with this state. As a result, the electron from the surface state is captured by the alkyl group of the alcohol molecule (the most reactive part according to the distribution of the local softness s_i^+ in the alcohol molecules [Table 3]) and goes away from the surface through the solution to the gas phase. Furthermore, the surface state can capture another electron from the semiconductor bulk, but this process is hampered due to the occurrence of the surface depletion layer. On the other hand, this vacant acceptor surface state can now be subjected to the interaction with the sulfur atom, which softness s_S^- is rather high. Accordingly, the hydrosulfide ion will be adsorbed at this surface state. In this case, the level of the acceptor state (LUMO) noticeably shifts toward the conduction band. This may cause two effects. The first is the decrease of the nonradiative recombination velocity

as in the cases of free and hydrated ions adsorption. The second is the reduction of the charge localization at surface states and, therefore, the decrease of the width of the surface depletion layer.

These effects were really observed in experiments. It was found that the treatment of the GaAs(100) surface with the solutions of ammonium or sodium sulfide in various single-based alcohols results in the decrease of the surface recombination velocity and that this decrease occurs with the substantial decrease of the depletion layer width of the semiconductor.[12,15,16,29] The decrease of both surface recombination velocity and surface depletion layer width was dependent on the solvent used for the preparation of the solution.[12,15,29] It can be explained assuming that the higher nucleophility of the sulfur atom in the ion permits more intensive charge release from the acceptor surface states and therefore the more effective modification of the surface electronic structure can be achieved. The order of sulfur relative nucleophility in the solvated hydrosulfide-ions as the solvent is varied is shown in Figure 4. This order agrees satisfactorily with the experimentally obtained corresponding sequences of the photoluminescence intensity and depletion layer width values.[12,15,29] For example, sulfur in the hydrated ion has the lowest relative nucleophility (about unity), and experimentally for the GaAs(100) surface treated with an aqueous sulfide solution the photoluminescence intensity enhancement with no decrease of the width of the surface depletion layer was observed. Sulfur in the ion solvated by ethanol has intermediate relative nucleophility (about 4). Accordingly the GaAs(100) surface treated with the sulfide solution in ethanol possessed the higher photoluminescence intensity than the surface treated with an aqueous solution with the noticeable decrease of the depletion layer depth. Finally, sulfur in the ion solvated by *tert*-butyl alcohol has the maximal value of the relative nucleophility obtained (about 6). Correspondingly the GaAs(100) surface treated with the sulfide solution in *tert*-butyl alcohol has the highest photoluminescence intensity (which corresponds to the lowest surface recombination velocity) and the lowest width of the surface depletion layer. Similar dependencies were experimentally obtained for InP[14] as well as for GaN[14] surfaces treated with different sulfide solutions.

It should be noted that the ion solvation is possible not only in the liquid phase, but in the gas phase as well. The latter case called microsolvation[40−43] permits the construction of the solvation shell of the ion in a desired manner. The obtained results testify that the adsorption at the GaAs(100) surface of the microsolvated clusters consisted of the ion HS⁻ associated with at least one solvent molecule holds great promise for the GaAs surface modification, which enables fine-tuning the desired surface electronic properties. Such a technique combines the possibility to control the adsorbate properties before adsorption by the solvation with the advantages of the gas-phase adsorption processes.

6. Conclusions

Density functional calculations of the global hardness and the local (condensed) softness has been used to study the solvation effect on the reactivity of the hydrosulfide-ion HS⁻. Free and monosolvated by water and different single-based alcohols ions have been considered. Solvation by alcohol molecules results in the increase of the global reactivity of the hydrosulfide ion while the hydration decreases slightly the global reactivity in comparison with the reactivity of free hydrosulfide-ion. The study of the local reactivity of the ions' constituents has enabled the ions considered to be divided into two groups.

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One group involves free and hydrated HS$^-$ ions, which sulfur atom is rather reactive toward both nucleophiles and electrophiles while the solvent molecule (if any) is inert. The other group contains ions solvated by the alcohol molecules. In these ions, the sulfur atom is strongly nucleophilic whereas the solvent molecule is strongly electrophilic. Accordingly, the adsorption of these ions onto GaAs surface will proceed by a fundamentally different mechanism and therefore it will result in a different modification of the semiconductor's surface electronic structure. The obtained results and the proposed mechanisms for such adsorption processes make possible the reasonable explanation of the previously obtained experimental results related to the adsorbate solvation influence on the electronic structure of the semiconductor surface treated with different sulfide solutions. The present findings show great promise of the gas-phase adsorption of the microsolvated ions for semiconductor surface modification.

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