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First-Principles Study of Adsorption Energetics of Alkanethiols on GaAs(001)

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ABSTRACT

Adsorption of alkanethiols on GaAs (001) surface under low coverage conditions was studied using density functional calculations in a periodic supercell approach. The study of physisorbed precursor and transition to chemisorption revealed that hydrogen atoms stay on the surface upon S-H bond cleavage and significantly affect desorption products and energies, in agreement with available experimental data. Binding of thiols to GaAs is found to be comparable or stronger than that of thiols to noble metals surfaces. Calculated thiolate-surface binding energies are found to be higher for Ga-rich than for As-rich surfaces, and are strongly dependent on surface reconstruction, adsorption site and coverage. This dependence is explained by the violation or fulfillment of electron counting rule, rehybridization of surface atom orbitals and strain relaxation upon addition of extra electrons brought by adsorption.

INTRODUCTION

In addition to widely used gold nanoparticles and thiolated gold substrates, semiconductors could offer potential benefits in using semiconductor-specific electronic properties for bio-sensing. For example, photoluminescence (PL) is expected to change upon adsorption of bioactive material on the surface and, thus, it can be used to monitor the event of adsorption. Development of new biosensors for in-vivo applications based on quantum dots (QDs) requires materials that would provide a PL signal in the wavelength region of the biological transparency window, i.e., around 1 μm. This opens the potential for the use of InAs QDs for biosensing. Consequently, passivation and biofunctionalization of GaAs surface becomes highly important as this is the material of choice for capping of InAs QDs. Self-assembled monolayers (SAMs) of thiols on GaAs can prevent degradation of the GaAs surface and enhance the performance of the device by protecting it from harmful exposure to oxygen. Thiols can also increase the PL signal from the substrate by removing the surface states which is important for a PL-based biosensor. At the same time, thiols with different endgroups can provide a link for the attachment of specific biomolecules. Thus, investigation of SAMs of alkanethiols on GaAs surface is interesting from both a fundamental perspective and for potential applications, including passivation of GaAs, creation of transition layers for Schottky diodes and nanolithography [1, 2].

Due to specific properties of semiconductors and the high sensitivity of thiol-surface bonding to the substrate properties, very little information from relatively well studied thiols on noble metals systems [3, 4] can be applied to thiols on GaAs. However, theoretical modeling of the semiconductor-thiol interface can be used as a supplementary characterization tool, which can help to verify the robustness of the GaAs-thiol interface and understand the atomic level processes of thiols adsorption and self-assembly. The modeling is expected to improve our understanding of the thiol deposition technique and to optimize a semiconductor-thiol interface addressing specific applications.

CALCULATION DETAILS

The calculations have been performed using a density functional theory (DFT) in a periodic supercell approach, based on pseudopotentials and numerical localized atomic orbitals as basis sets, as implemented in the SIESTA code [5]. The parameters, such as pseudopotentials, energy and k-grid cutoffs and basis sets can be found elsewhere [6]. Different surface reconstructions were studied and modeled using hydrogen terminated slabs of 7 to 10 atomic layers with surface unit cell sizes from (2×1) to (4×4).

All binding energies were calculated using the counterpoise method to avoid the basis set superposition error (BSSE) and including spin polarization. The reliability of our calculations was tested by comparison with published experimental and theoretical results of lattice constant, bulk modulus, band structure and density of states of bulk GaAs, structures and energetics of different GaAs surfaces, and energies of dissociation of different thiols and hydrogen molecules.

The structure of a chemisorbed monolayer film of thiol is determined by the sulphur-surface chemical bond and the intermolecular van der Waals forces between the hydrocarbon chains. Our calculations have shown that generalized gradients approximation (GGA) accurately reproduces bond strengths in organic molecules while unable to reproduce van der Waals attraction between thiols in SAM and between thiol and GaAs surface. Local density approximation (LDA) strongly overestimated the energetics of chemisorption, but van der Walls interactions were reproduced with results close to available experimental data.

RESULTS

Our previous study [6] addressed the bonding nature of thiolate to the surface. It revealed that thiolate adsorbs on the surface by saturating one of the surface dangling bonds. Thiolate tilt angle and tilt direction were found to be dictated by the direction of the dangling bond and unhybridized sulfur 3p orbital, and steric repulsion of the first CH_2 unit from the surface. Relatively short bond and small charge transfer between thiol and surface indicated a strong covalent bond with binding energy of 2.1 eV.

Physisorbed precursor

The calculated dissociation energy of S-H bond is 3.78 eV, in good agreement with experimental value of 3.75 eV. However, this bond can dissociate even at room temperatures when thiol is situated close to the surface. Two paths might be possible: one with H abstraction and the second with H adsorption on the surface. Molecular dynamics simulations of thiol approaching the surface with speeds corresponding to temperatures up to 1000 K show that hydrogen, which feels steric repulsion from the surface due to its lightness, easily rotates around S-C bond. Thus, hydrogen is always situated far from the surface at the moment when sulfur is close to the surface, providing the possibility for hydrogen abstraction. However, the H-S bond is stronger than S-As bond, which means that the total energy of free thiol near the surface will always be lower than that of chemisorbed thiol plus free hydrogen atom, thus, making hydrogen abstraction not possible. This would result in a lower sticking coefficient of thiol to GaAs at

higher temperatures, similar to what is observed for gold. It is generally accepted that adsorption of thiols on gold occurs via a physisorbed precursor [3]. Our calculations of the physisorption state of thiol on GaAs with sulfur situated on top of arsenic revealed that hydrogen also stays close to the surface. Physisorption energy calculated in LDA is found to be 1.1 eV for 5-carbons chain and depends on the chain length nonlinearly due to the fact that (001) surface is not atomically flat. This energy is about 2.5 times higher than interaction between free thiols, in agreement with experimental data [7]. This is explained by a twice as big atomic radius of Ga and As compared to that of C, resulting in higher polarizability and thus a stronger van der Waals interaction. If, due to thermal vibrations, two As atoms in adjacent dimers become close enough to each other, hydrogen vibrating with much higher frequency can appear closer to nearby arsenic than to sulfur, leading to a dissociation of the S-H bond and chemisorption of both thiolate and hydrogen. This process requires about 0.5 eV, which is much less than the dissociation energy of the S-H bond.

Recombinative desorption with hydrogen

Calculated energetics of thiol adsorption on (2×1) surface full of As dimers is shown in Fig.1. The energy gain due to chemisorption of thiolate and hydrogen is 1.25 eV (Fig.1d) and is comparable to that of physisorption (b). The energy required to cleave S-As bond and to desorb thiolate (d) is an already mentioned value of 2.1 eV which is a binding energy of thiolate to surface [6]. Desorption of hydrogen after desorption of a thiolate requires slightly higher energy (e) and results in total energy equal to that of direct S-H bond cleavage without participation of surface (a). However, since hydrogen stays adsorbed on the surface near the thiolate, the recombinative desorption process is possible, reverse to that of adsorption. This process (e) requires aforementioned 1.25 eV, i.e., much less energy than needed for thiolate desorption. Adsorbed hydrogen can also recombine with another hydrogen atom already present on the surface, desorbing as a hydrogen molecule (f). Formation of the H_2 molecule gives 2.28 eV gain per hydrogen atom and significantly reduces the energy required for desorption.

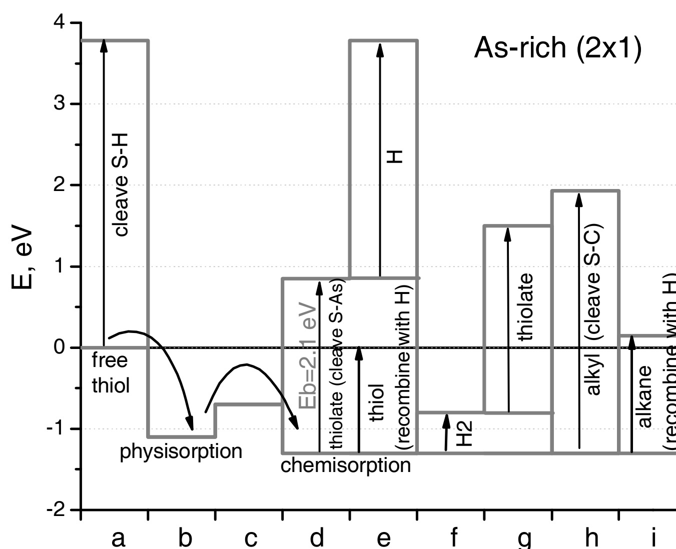

Figure 1. Adsorption-desorption paths and energetics on full As monolayer (2×1) reconstruction.

Similar to cleavage of S-As bond, cleavage of S-C bond requires quite high energy of 3.2 eV (h). However, recombination of the alkyl part of the thiol with surface hydrogen and desorption as alkane, leaving sulfur on the surface, requires smaller energy of only 1.35 eV (i). The calculated energy diagram is in good agreement with experimental temperature programmed desorption data [7], suggesting desorption of molecular hydrogen, intact thiol, and alkane, along with the absence of thiolate desorption peaks in spectra.

Effect of surface reconstruction

Intuitively, one can expect different binding energies of thiolate depending on surface termination, i.e., depending on whether S-As or S-Ga bond is formed. Our calculations indeed confirmed the difference of binding energies depending on surface termination, however, surface reconstruction was found to play a much more important role.

Calculated energy diagrams of thiol adsorption on the most stable Ga- and As-rich reconstructions are shown on Fig.2. The most prominent difference between the two reconstructions is that thiol adsorption on As-rich β2(2×4) surface is not energetically favorable at all. This is not due to impossibility of binding sulfur to arsenic; since it was already shown above that thiolate adsorption is favorable on another As-rich reconstruction. The difference in binding energies of thiolate to clean surface is also significant: 2.8 eV for Ga-rich surface and 1.1 eV for As-rich β2 surface, compared to 2.1 eV for As-rich (2×1) reconstruction.

One can also note that while on As-rich (2×1) and Ga-rich (4×2) surfaces thiolate and hydrogen binding energies are quite similar, on As-rich β2(2×4) surface thiolate binding energy is about two times higher than that of hydrogen. Such a difference could be expected for different adsorption sites of thiolate and hydrogen, however in these examples adsorption sites were chosen to be identical – on adjacent surface dimers (see also Fig.3). To understand the observed differences we also calculated desorption energies for different desorption order of the parts, i.e., when hydrogen desorbs after thiolate and vice versa. The difference is the most visible for As-rich β2(2×4) reconstruction, where desorption of the second part (not important thiolate or hydrogen) is much easier than that of the first part. At the same time, desorption energies of

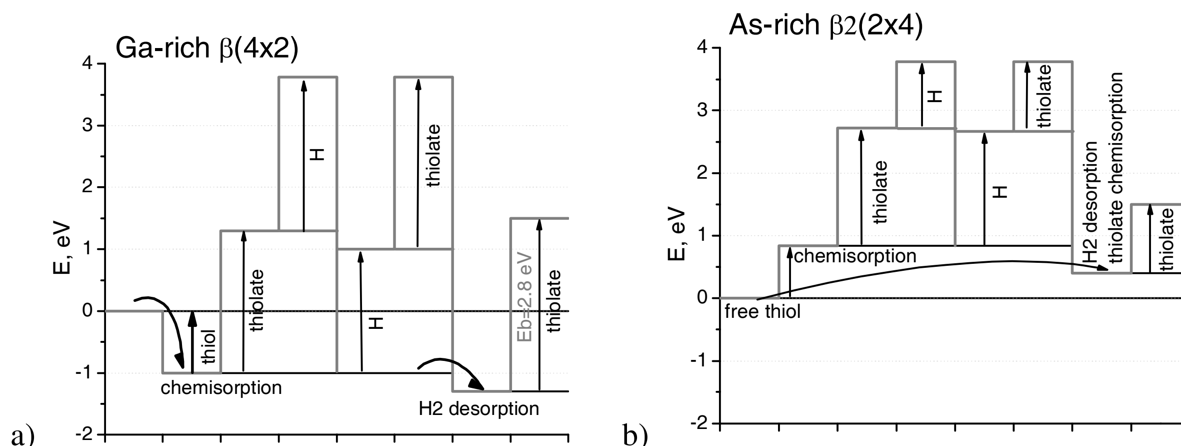

Figure 2. Adsorption energetics on Ga-rich β(4×2) (a) and As-rich β2(2×4) (b) reconstructions.

thiolate and hydrogen under the same conditions become very similar, in agreement with the two mentioned cases of As-rich (2×1) and Ga-rich surfaces.

Investigation of surface relaxation upon adsorption and shapes of the molecular orbitals (Fig.3) can explain the observed differences in binding energies. The electron counting rule [8] plays a crucial role in defining whether adsorption of thiol would be favorable. According to electron counting model, each As atom provides 5/4 electrons per bond to Ga, whereas Ga provides 3/4 electrons per bond to As, while each atom provides 1 electron per bond to the atom of the same sort. The dangling bonds can be either empty or fully occupied. i.e., contain 2 electrons.

On As-rich β2(2×4) reconstructions, the electron counting rule is satisfied by the formation of three As dimers and transfer of electrons from four Ga dangling bonds to six As dangling bonds. Adsorption of thiolate and hydrogen on As dangling bonds leads to the excess of two electrons in the unit cell. To satisfy the electron counting rule, the surface relaxes by breaking the As dimer, 2 electrons from As-As bond now form second dangling bond on the first As atom, and excess 2 electrons due to thiol adsorption form a dangling bond on the second As (Fig.3a). Since dangling bonds have higher energy than dimer bond and two new dangling bonds were created, such a surface reconstruction has much higher energy than the free surface. Thus, thiol adsorption becomes unfavorable. However, cleavage of As-S or As-H still requires some amount of energy, since unsaturated S or H have much higher total energy.

The energy of the surface after hydrogen desorption becomes even higher, since now there is an excess of only one electron and the electron counting rule cannot be satisfied even after surface relaxation. This results in a much smaller energy needed to desorb the thiolate and return the surface to its ideal state.

Similar considerations are applicable for other surface reconstructions. For As-rich (2×1) reconstruction, which does not satisfy the electron counting rule, thiol adsorption brings extra electrons that help fulfill the rule, resulting in favorable adsorption of thiol.

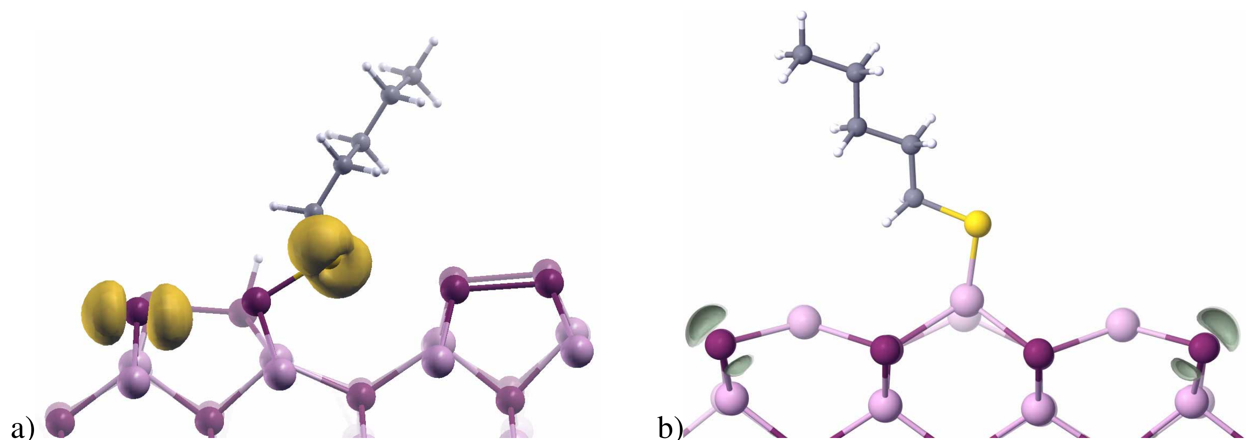

Figure 3. Surface relaxation upon thiolate and hydrogen adsorption. Highest occupied orbitals of As-rich β2(2×4) surface (a) and partially empty As dangling bond on Ga-rich β(4×2) surface (b).

For Ga-rich β(4×2) reconstruction, adsorption of thiolate and hydrogen on empty Ga dangling bonds leads to a deficiency of 2 electrons, since now previously empty bonds should contain 2 electrons. These electrons are taken partially from As dangling bonds (not changing their hybridization) (Fig.3b) and partially from the thiolate itself. Now Ga atoms change their hybridization from sp2 to sp3, which lowers their energy and also helps to reduce strain caused by sp2 hybridization, also lowering the total energy of the system. All in all, the energy gain due to the formation of the Ga-H and Ga-S bonds, rehybridization and strain relaxation becomes greater than the loss due to partial emptying of As dangling bonds, thus resulting in favorable thiol adsorption.

CONCLUSIONS

Our theoretical study of alkanethiols adsorption on GaAs (001) have shown that, upon transition from physisorbed to chemisorbed state, hydrogen atom stays on surface significantly affecting desorption products and energies, in agreement with available experimental data. Strong dependence of adsorption energetics on surface reconstruction emphasizes the importance of the right choice of surface treatment before thiolation. A simple electron counting rule can be used to predict the possibility of thiol adsorption on other semiconductor surface reconstructions.

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