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Structure, Bonding Nature, and Binding Energy of Alkanethiolate on As-Rich GaAs (001) Surface: A Density Functional Theory Study

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Chemisorption of alkanethiols on As-rich GaAs (001) surface under a low coverage condition was studied using first principles density functional calculations in a periodic supercell approach. The thiolate adsorption site, tilt angle and its direction are dictated by the high directionality of As dangling bond and sulfur 3p orbital participating in bonding and steric repulsion of the first three CH_2 units from the surface. Small charge transfer between thiolate and surface, strong dependence of total energy on tilt angle, and a relatively short length of 2.28 Å of the S−As bond indicate the highly covalent nature of the bonding. Calculated binding energy of 2.1 eV is consistent with the available experimental data.

Self-assembled monolayers (SAMs) of organosulfur compounds on solid surfaces have attracted a great deal of interest from both a fundamental perspective and due to potential applications. While SAMs on noble metals have been extensively studied,[1−3] relatively limited data has been available concerning monolayers of thiols on semiconductor surfaces. The formation of SAMs of alkanethiols on oxide-free GaAs (001) surface, together with the potential of this approach for efficient surface passivation of this material, has been demonstrated some time ago.[4,5] Among other potential applications of SAMs on semiconductor surfaces and particularly on GaAs are the development of precursors for the growth of II−VI materials[6] and creation of transition layers for ohmic contacts and Schottky diodes.[7] Long-chain SAMs have been applied for speciality masks used in nanolithography.[8] There has also been observed a steady growing interest in developing GaAs-thiol interfaces for chemical sensing[9] and biosensing applications.[10,11] The structure of a chemisorbed monolayer film of thiol is determined by the surface chemical bond and the intermolecular van der Waals forces between the hydrocarbon chains. Theoretical modeling of the semiconductor−thiol interface can provide information valuable for understanding the bonding nature of such a material system and, ultimately, it would help to design and optimize a semiconductor−thiol interface addressing a specific application. Modeling of the GaAs−thiol interface deserves separate attention as the to date available theoretical calculations of metal−thiol interfaces show markedly different results, even for very similar surfaces such as gold, silver, and copper.[12−16] Clearly, the adsorption of a thiol is strongly influenced by the material's overall chemical reactivity, lattice constant, crystallographic orientation, etc. Therefore, a little information available from the well-studied SAMs of thiols on noble metals can be applied to GaAs. In contrast to alkanethiols on gold, which are considered a prototype example of SAMs, theoretical studies of thiols on GaAs appear to be missing in the literature. In this work, we report the results of ab initio calculations of alkanethiols adsorption on GaAs (001) under low surface coverage conditions.

The calculations have been performed using a density functional theory (DFT) approach based on pseudopotentials and numerical localized atomic orbitals as basis sets, as implemented in the SIESTA code.[17] We have used the generalized gradient approximation (GGA) with the Perdew−Burke−Ernzerhof exchange-correlation functional (PBE),[18] which was reported[19] to reproduce organic molecules properties with the quality comparable to the results obtained with the Becke−Lee−Yang−Parr functional (BLYP).[20,21] The PBE also provides better accuracy than local density approximation in description of polar surfaces,[22] such as GaAs (001). We used scalar relativistic Troullier−Martins pseudopotentials with nonlinear core corrections (NLCC), not including 3d electrons in valence configuration for Ga and As. Double ζ plus polarization orbital (DZP) bases were used for Ga and As, and triple ζ plus polarization (TZP) for H, C, S, and As in the topmost layer, with the cutoff radii optimized variationally using a simplex method.[23] The method of Monkhorst and Pack was used for Brillouin zone sampling at accuracy equivalent to that obtained with an 12 Å radius supercell.[24] The Hartree and exchange-correlation potentials were evaluated on a real space mesh with a 350 Ry equivalent plane wave energy cutoff providing convergence of binding energies to the 5 meV level.

The periodic supercell approach was employed to model GaAs (001) surface. Surface reconstruction with full monolayer of As was used throughout the work, as it has been shown that standard etching procedures used for thiols deposition on GaAs result in an excess of As on surface and XPS shows that sulfur binds to As rather than to Ga.[25,26] The slab consisted of eight atomic layers, with thiol placed on one side and the rear surface saturated with H atoms. A distance of 12 Å from the topmost atom of thiol to the rear side of the next slab in the *z*-direction was used to avoid spurious interactions between slabs. The bottommost layer of Ga atoms along with H-layer was fixed

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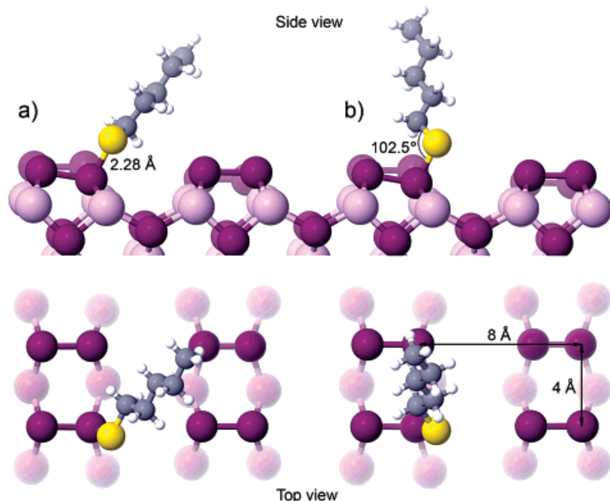

Figure 1. Optimized geometries of pentanethiol on As-rich GaAs (001) surface obtained from relaxation of thiolate lying flat to the surface (a) and standing upright (b).

during geometry optimization, while the rest of the atoms were allowed to relax. The use of hydrogen termination is necessary due to the polar nature of the (001) surface. Binding energies were calculated as a difference between total energy of the slab−adsorbate system and the energies of bare surface and adsorbate molecule in gas phase, using the counterpoise method to avoid the basis set superposition error (BSSE).[27] Spin polarization was included in all binding energy calculations. 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,[28] structures and energetics of different GaAs surfaces,[22] and energies of dissociation of thiol and hydrogen molecules.[12−14,16] The calculated GaAs lattice constant is 5.756 Å (experimental value 5.65 Å), H−H bond strength in hydrogen molecule 4.57 eV and S−H bond in thiol 3.78 eV, as compared to experimental values of 4.75 (with zero-point energy removed for direct comparison to calculations) and 3.73 eV, respectively. The observed overestimation of lattice constant and deviations of binding energies are common for all GGA calculations.

We studied the structure of the thiolate adsorbed on GaAs (001) surface by using (2 × 4) surface unit cell (8 × 16 Å^2), which corresponds to a low coverage limit. This avoided interaction between thiols on the surface and potential calculation errors, as it is known that current DFT functionals do not describe the van der Waals interactions correctly. Dimerization of top arsenic atoms was found to stabilize the system by 1.36 eV in comparison with the unreconstructed surface. It has been reported that short-chain thiols (with 1 or 2 carbon atoms) adopt different equilibrium geometries and have different binding energies than longer chain molecules.[12,16,29] Since we are interested in chemisorption of thiol on the surface as a stage preceding the formation of SAMs, we have carried out calculations for pentanethiol, a relatively long chain thiol that would not require excessive computation time.

The equilibrium geometries obtained from molecular dynamics simulations and subsequent conjugate gradient geometry optimizations starting from a thiolate lying parallel to the surface and from a thiolate standing upright are shown in Figure 1a and 1b, respectively. Both geometries have practically identical energy and simulations starting from different initial conditions end up in one of them. The sulfur atom is situated almost on top of arsenic, while structures with sulfur in bridge or hollow site positions were found to be 1 eV higher in energy.

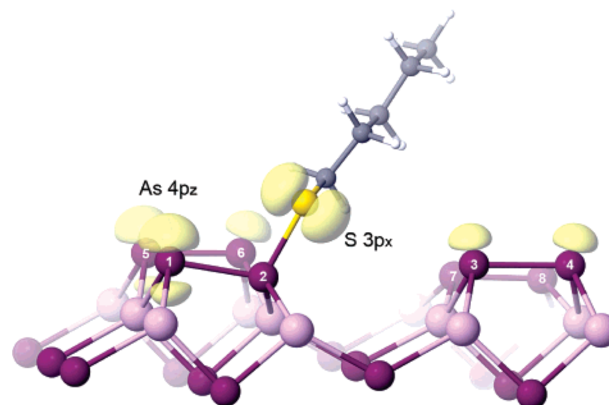

Figure 2. High lying molecular orbitals of thiolate chemisorbed on (001) GaAs surface. Isodensity surfaces correspond to 0.02 a.u.

The structure in Figure 1a has a tilt angle of 44° from surface normal with the S−C−C plane tilt of 35° (which is sometimes called "lean") and S−C bond lying almost parallel to the surface. The thiol is tilted diagonally, in the direction of the second nearest neighbor As dimer. In the second structure thiol is tilted 30° from normal in the direction of the farther arsenic of the adjacent As dimer, with 20° lean and S−C bond is 55° from surface normal. There are numerous similarities between these two geometries. In both of them the As−S bond lies along the arsenic dangling bond and the As−S−C angle is close to the value of H−S−C angle in free thiol. Geometries with As, S, and C lying in one line are found to be up to 0.5 eV higher in energy than the optimal configurations, similar to reported values for thiols on gold.[12] Such a preference for the bond directionality from both surface and thiol indicates a high covalency and thus strength of the bond. The length of As−S bond is 2.28 Å, which is shorter than 2.5 Å for Au−S[12,15,16] and 2.35 Å for Cu−S,[12,30] suggesting stronger binding of thiol to GaAs than to Au surface.

The value of the As−S−C angle is 106° and 102.5° for the structures in Figure 1a and 1b, respectively. This is closer to the ideal tetrahedral angle of 109.5°, rather than to 96° H−S−C angle in free thiol, suggesting that sulfur s states could hybridize with p states, similar to the hybridization reported for methylthiol on gold and silver in the on-top positions[15] and for phenylthiol on gold.[31] However, closer examination of the density of states and shapes of high-lying molecular orbitals for the thiol−GaAs case does not support this suggestion. Figure 2 shows the molecular orbitals lying in the 1 eV energy window below the Fermi level. This is the highest occupied molecular orbital (HOMO) of the thiol and it coincides in energy with the dangling bonds of arsenic. The molecular orbital on sulfur has a pronounced p_x character, similar to that in free thiol, thus, the bonds to carbon and to arsenic (or hydrogen) which are formed by the remaining p_y and p_z orbitals should tend to be at right angle. The deviation to higher angle values can be explained by steric repulsion between hydrogen atoms in the first CH_2 unit and arsenic in adjacent dimers. In both configurations the distance from H to the nearest As is about 3.3 Å, which is comparable to the sum of van der Waals radii of H (1.2 Å) and As (2 Å). This also explains the tilt direction of the thiol; it rotates to accommodate the first CH_2 unit in the hollow between As dimers. Other tilt directions are less favorable since one of the first three CH_2 units would always approach the surface too close. Thus, the observed geometries can be seen as a compromise between the favorable As−S bond direction and As−S−C angle, and bigger distance of the first three CH_2 units from surface. Similar conclusions have been made for the adsorption site of mercapto and methylthiolate on gold.[13]

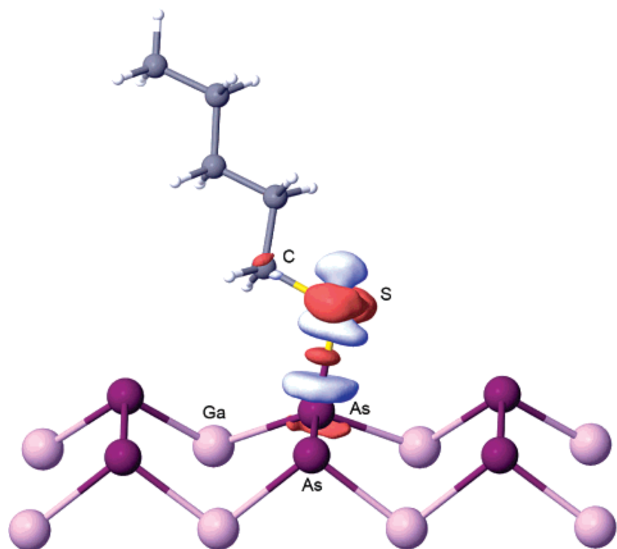

Figure 3. Regions of loss (light blue) and gain (red) of electron density induced by adsorption of thiolate on surface of (001) GaAs. Isodensity surfaces correspond to ± 0.006 a.u.

Simulations with removed adjacent As dimer show that thiol can adopt smaller As−S−C angles and rotate around As−S bond more easily, supporting our conclusions.

Examination of the lower density isosurfaces of the orbitals shown in Figure 2 shows that this is a π-type orbital antibonding with respect to both S−As and S−C bonds, similar to that found for ethanethiol on copper.[30] Lower energy orbitals (not shown here) have σ-character. From Figure 2 one can see that the orbitals of As in the top layer are substantially dehybridized in comparison with that of bulk and have p_z character. For the surface reconstruction with full monolayer of As used here, this leads to lowering of two of four dimers in the unit cell to maximize the overlap of dehybridized p_y As orbitals with Ga atoms in the underlying layer at the expense of elevation of another two dimers. The p_z orbitals of one of the dimers (atoms 7 and 8 in Figure 2) have energy higher than Fermi level, resulting in the formation of undesired surface states. As can be seen from Figure 2, thiol adsorption removes the energy states near the valence band edge from underlying arsenic. Although the overall density of states of the slab have not changed at low coverage regime, since the rest of As dimers remained unaffected by thiol, higher coverage with thiols would partially eliminate the surface states. This could explain, for instance, the observed increase in photoluminescence intensity of thiol-treated GaAs surface.[4,11,32,33]

We have further investigated the charge density redistribution due to adsorption of thiolate on surface. Figure 3 shows the regions of loss and gain of electron density induced by the bond formation for the geometry of Figure 1a. Charge redistribution for the structure of Figure 1b is essentially the same. Only electrons around sulfur and the first CH_2 unit of the thiolate are involved in bonding, which confirms our suggestion that pentanethiol would correctly reproduce the chemisorption of longer chain thiols on GaAs surface. Electron density is depleted in the As dangling bond region and gained between S and As, showing a formation of the covalent bond. Examination of lower density isosurfaces (not shown here) also reveals accumulation of charge below As and on the p_z orbital of the second As atom in the dimer (see also Figure 2). A small depletion of electron density along the S−C bond suggests its weakening upon adsorption. There is also a redistribution of charge around sulfur atoms, showing the accumulation of charge on sulfur p_x orbital, same as in Figure 2 and similar to that reported for methanethiol on copper.[30] This density gain would be smaller when compared to thiol rather than to thiolate, since in free thiolate nonbonded p_x and p_y orbitals mix in a homogeneous ring around sulfur, while in thiol (or thiolate on surface) p_y becomes involved in a bond to H (or As) thus making p_x and p_y orbitals more distinguishable. The charge redistribution on surface atoms other than underlying arsenic is minimal in contrast to that reported for gold[31] and copper sufaces.[30] For qualitative description of the charge transfer, the Mulliken population analysis has also been performed. Since Mulliken charges are known to be strongly dependent on the basis set, we have carried out calculations for a less complete DZP basis as well as for several shorter bases. All these calculations have shown a small electron transfer of about 0.05 electrons from surface to thiolate, which compares with 0.4 and 0.6 electrons for thiolate on gold[15] and copper[30] surfaces, respectively. This indicates low ionicity and high covalency of the bond, consistent with our previous conclusions from energy dependence on the As−S−C angle and suggesting strong binding of thiolate to GaAs surface. It also supports our suggestion that the gain of density on the p_x orbital of sulfur is due to the redistribution of its own density rather than from underlying arsenic.

The calculated binding energy of thiolate to As-rich GaAs (001) surface is 2.11 eV. This compares to 1.64−2.3 eV reported for Au (111)[12−16,29] and 2.19 eV for Cu (111)[12,30] surfaces calculated using a similar theoretical technique. Such a big binding energy is consistent with the successful use of high temperatures (100 °C) for growth of self-assembled monolayers of thiols on GaAs,[5] survival of 200 °C annealing,[34] and ultrasonic bath,[35] confirming that thiols form a robust interface with GaAs. Unfortunately there are no experimental measurements of the binding energy of thiol on As-rich GaAs (001) surface to date, and available temperature programmed desorption (TPD) data for Ga-rich (001)[36] and (110)[37] surfaces shows a very different and complex behavior complicating their comparison with our results. One of the features of the TPD data is the absence of thiolate desorption peaks, showing instead the recombinative desorption of thiol, dithiol, alkane, and molecular hydrogen with energies around 1.45 eV. This suggests that hydrogen obtained by the cleavage of S−H bond stays on the surface and plays an important role in thiol adsorption−desorption process, and that the energy of As−S bond is higher than the energy needed for recombinative desorption.

Our results also qualitatively address some important issues. First, the large energy difference between bridge and on-top positions provides a substantial barrier for diffusion of thiols on the GaAs surface, higher than that on copper, silver, and gold,[12] complicating the growth of self-assembled monolayers.[26] Second, the chemisorbed molecule tends to go upright from the lying flat on surface position, similar to reported theoretical results for gold and copper.[12,30] Such a behavior is explained by steric repulsion of the first CH_2 unit from the surface and a relatively short chemical bond acting as a lever. This implies that chemisorbed short-chain thiols would be connected to surface only via the headgroup, liberating the adsorption sites for other thiols. Longer chain thiols can be still lying on the surface attracted by van der Waals forces, although strongly bended near the headgroup.

In summary, we have investigated the adsorption of pentanethiol on an As-rich GaAs (001) surface in DFT using the PBE functional. The geometry of the thiolate on the surface is dictated by the high directionality of the As dangling bond, sulfur 3p orbital and steric repulsion of the first three CH_2 units

from the surface. Thiolate adsorption is shown to partially eliminate the electronic surface states. Small charge transfer between thiolate and surface, strong dependence of total energy on tilt angle, and short S−As bond length (2.28 Å) indicate a highly covalent nature of the bonding. Calculated binding energy of 2.11 eV is consistent with the available experimental data.

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Supporting Information Available: Pseudopotentials, basis sets, and 3D structures of optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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