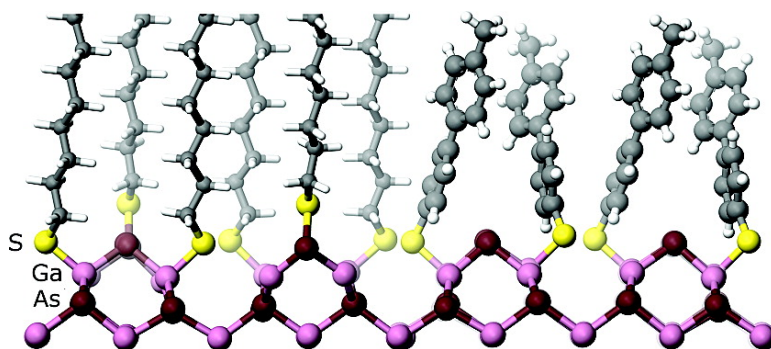


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# Structure of Thiol Self-Assembled Monolayers Commensurate with the GaAs (001) Surface

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Observed properties of thiol self-assembled monolayers (SAMs) on GaAs (001) surfaces can be explained by the presence of surface reconstructions, but their exact form is generally unknown. We propose a new approach to modeling the SAM–surface interface based on using alkanethiol dense packing structures as a starting point and adjusting the surface reconstruction to accommodate them. Obtained in such a way, model SAMs adsorb along the trenches in the [110] direction and exhibit a 19° tilt and  $\pm 45^\circ$  twist angles, in agreement with available experimental data. The molecules of the SAM bind to both Ga and As, and cover only 50% of the available surface sites. The requirements for the SAM formation process to achieve the proposed structures are discussed.

## 1. Introduction

Self-assembled monolayers (SAMs) of organic molecules on solid substrates are of high technological and fundamental interests.<sup>1,2</sup> Particularly on semiconductor surfaces, their potential applications are in bio-<sup>3,4</sup> and chemical sensing,<sup>2</sup> molecular electronics,<sup>5,6</sup> passivation,<sup>7,8</sup> nanolithography,<sup>9</sup> and precursors for growth of other compounds.<sup>10</sup>

Recently, the procedure for the growth of highly ordered and dense alkanethiol SAMs on GaAs (001) was reported.<sup>11</sup> Molecules in such SAMs are tilted  $\sim 14^\circ$  from the surface normal,<sup>11–15</sup> compared to previously reported tilts of  $\sim 57^\circ$ ,<sup>16–18</sup> but the factors affecting the quality of the monolayers are not yet well understood. The structure with  $14^\circ$  tilt suggests denser SAMs than those on Au (111) with the tilt of  $\sim 30^\circ$ .<sup>11,13,19</sup> However, the spacing between thiols in crystalline phase is incommensurate with the underlying square GaAs lattice, and the exact structure of the thiol–substrate interface remains unknown. In previous works it was suggested that maximum density molecular packing may

be important in the film assembly process, and some disruption of the ideal GaAs lattice should arise upon SAM formation, at the same time leaving a significant fraction of surface atoms unbound.<sup>13,14</sup> It should be noted, however, that the morphology of semiconductor surfaces is not represented by the areas of significantly large atomically flat planes, such as on metal or nanocrystalline oxide surfaces, despite the fact that the bulk substrate is monocrystalline. Even ideal GaAs surfaces prepared using molecular beam epitaxy exhibit reconstructions with the roughness of 1–2 atomic layers and the surface unit cell size of 1–2 nm.<sup>20</sup> The wet etching procedure used for thiol deposition is expected to disrupt the surface even more. Formation of the amorphous As overlayer and microroughness are the examples of the possible drastic changes after etching.<sup>12,21</sup> Thus, the complexity of the thiol–GaAs interface is expected. However, it remains unclear whether thiol–thiol interactions play a significant role in the formation of the final surface morphology, or SAMs simply adapt to the available surface reconstruction at any given point.

The bonding chemistry of thiolates to GaAs surface has been of great debate in literature (for a comprehensive review of the problem see, e.g., ref 14). X-ray photoelectron spectroscopy (XPS) of the samples prepared using thiol deposition from liquid can resolve the presence of a component in As 3d spectra, presumably related to As–S binding.<sup>11–16,22</sup> However, this component cannot be unambiguously assigned to As–S, since it strongly overlaps with As<sup>0</sup> component and with As–H, which is usually disregarded, although temperature programmed desorption (TPD) and theoretical studies on Ga-rich surfaces suggest that hydrogen may stay on the surface.<sup>23–25</sup> The spectra of Ga 3d region exhibit no significant differences between freshly etched and thiolated samples, which is usually interpreted as the absence of Ga–S bonding. High-resolution XPS studies<sup>14,22</sup> show the presence of the Ga component shifted less than 0.5 eV from the bulk GaAs peak and assigned to Ga<sub>2</sub>O<sub>3</sub> or surface Ga. However, experiments

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on adsorption of thiols and hydrogen sulfide on Ga-containing surfaces<sup>23,24</sup> and our previous simulations<sup>25</sup> suggest that thiols preferentially bind to Ga, even if both Ga and As sites are available on the surface. Analysis of charges on atoms in our *ab initio* calculations<sup>25,26</sup> suggests that Ga–S related peaks should be between the above-mentioned surface Ga and bulk Ga components and thus be practically undetectable with XPS. The clear presence of a Ga–S signal in recent time-of-flight secondary ion mass spectrometry (ToF-SIMS) results<sup>14</sup> supports our conclusion that the nature of thiol–GaAs bonding cannot be unambiguously determined based solely on XPS.

Another important question is whether thiol SAMs can be used for the passivation of GaAs surface, i.e., improvement and stabilization of electronic properties of GaAs by unpinning the Fermi level (removal of the band bending) and reduction of the surface recombination velocity. Passivation is achieved by suppression of surface states in the bandgap (arising mainly due to surface oxides) and by protecting the surface from further oxidation. Experimental reports, however, do not provide an unambiguous picture concerning the role of thiols in passivation of the GaAs surface. Significant improvement of photoluminescence intensity was reported for intrinsic and n-type samples.<sup>7,8</sup> Also, XPS data indicate reasonable protection from oxidation,<sup>13,14,22</sup> and Raman spectroscopy shows the reduction of band bending and improvement of long-term stability.<sup>27</sup> However, more recent Raman spectroscopy data on samples covered with presumably higher-quality SAMs suggest that the removal of band bending is not achieved on n-type samples but is noticeable on p-type samples.<sup>14</sup>

In view of the recently revived interest in thiol SAMs growth on GaAs and the limited amount of experimental techniques suitable for analysis of this material system, theoretical modeling can provide information crucial for understanding the nature of the thiol SAM interface with GaAs and other semiconductors. In this work, we propose a new approach for searching the exact SAM–surface interface for cases when surface reconstruction is unknown. The approach is based on using thiol dense packing as a starting point and fitting of the surface reconstruction to achieve commensurability with the SAM. Obtained in such a way, thiol SAM structures on GaAs(001) are in agreement with available experimental data<sup>13</sup> and provide new insight into the bonding chemistry and passivation properties of these SAMs. The requirements for the SAM formation process to achieve the proposed structures are discussed.

## 2. Model

Experimental infrared reflection spectroscopy (IRS) data show a high degree of crystallinity of alkanethiol SAMs on GaAs (001), comparable to that of bulk alkanethiols.<sup>11,13,15,17</sup> Fitting of simulated IR peak intensities to experimental data also provides the tilt (deviation from surface normal) and twist (rotation about the chain axis) angles of the molecules in the SAM.<sup>11,13,17</sup> Since the surface structure of the wet-etched GaAs substrate is unknown, the crystalline structure of thiols remains the only known starting point to proceed with modeling of the SAM. This is in contrast to conventional modeling approaches, where surface structure is assumed to be known and a SAM is adjusted on it, e.g., as used for alkanethiols on Au (111).<sup>28,29</sup> The importance of thiol–thiol interactions was realized previously and the assumption of SAM crystallinity was used in the search for thiol

SAMs structure on GaAs (001).<sup>13,14</sup> However, it had not resulted in a successful model, since GaAs surface was still assumed to be atomically flat, and no accurate quantitative characterization of SAMs (distances and angles between thiols) was used.

On the basis of the weak dependence of CH<sub>3</sub> IRS peak intensities on the change from an odd to an even amount of carbons in thiol chains, it was suggested that the SAM should contain two differently oriented chains per unit cell, resulting in a herringbone packing with a 90° setting angle between the C–C–C planes.<sup>13</sup> This type of structure was resolved for  $c(4 \times 2)$  SAMs of thiols on gold,<sup>30,31</sup> Langmuir monolayers,<sup>32</sup> and bulk alkanes,<sup>33,34</sup> on the basis of the presence of splitting in CH<sub>2</sub> scissor deformation mode or grazing incidence X-ray diffraction (GIXRD) data. However, such a splitting can be resolved only with low temperature measurements that were not performed for thiols on GaAs.

To verify the experimental suggestion about chain orientations, we investigated both monoclinic and orthorhombic structures, with one and two chain orientations per unit cell, respectively. To describe the thiol–thiol interactions, we used the DREIDING force field<sup>35</sup> as implemented in the Accelrys Discovery Studio package. Empirical molecular mechanics (MM) is an accurate and reliable theoretical tool for the description of interactions between small organic molecules, as opposed to density functional theory (DFT) calculations, which generally fail to account for van der Waals attractions. Figure 1 shows the two densest possible packing structures of alkanethiols obtained in our simulations. Our observations of thiol packing coincide with previously suggested ideas of interlocking, reduction of empty volume, and steric limits.<sup>29</sup> Our structural parameters (shown in Figure 1) are within 1% error from the most recent experiments.<sup>33,34</sup>

Unlike previous similar studies of thiols on gold that failed to resolve the exact SAM structure,<sup>28,29</sup> we used MM to describe only the interactions between thiols and not those with the surface. As has been previously found in our *ab initio* calculations, thiols bind to GaAs surface sites via the formation of the single highly directed covalent bonds.<sup>25,26</sup> This is simpler than binding to a Au surface, where single, double, and triple coordination of sulfur is possible. Such a strictly defined bonding geometry on GaAs makes the matching of the SAM to the surface more straightforward and allows one to replace the combination of DFT and MM simulations, needed to describe correctly both thiol–surface and thiol–thiol interactions, with a simple geometrical fitting of two crystalline structures. Both DFT and MM simulations were still used in our work to gain deeper understanding of the adsorption process and to facilitate the search of new possible geometries.

## 3. Results

**3.1. Discrete Tilts.** Both structures in Figure 1 have an area per molecule of  $18.4 \text{ \AA}^2$ ,<sup>33,34</sup> the projection of which on the substrate increases as  $1/\cos \theta$  with tilt. In the case of an atomically flat surface, which is an assumption made for IRS fitting, the area per GaAs surface atom is  $16 \text{ \AA}^2$ . For the reported 14° tilt<sup>11–13,15</sup> this suggests a 100% coverage and a lattice mismatch of at least 9%. For 50% coverage of surface sites, the available

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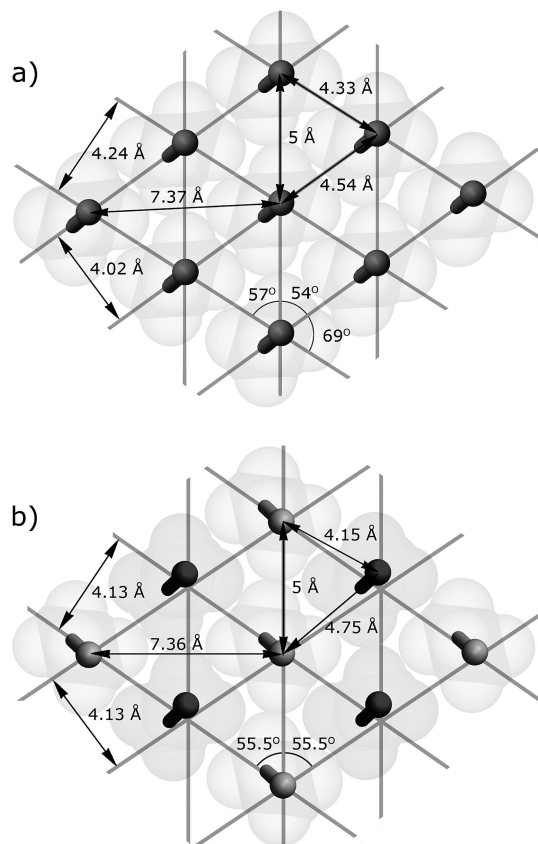
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**Figure 1.** Monoclinic (a) and orthorhombic (b) packing structures of bulk alkanes with interplane and NN distances indicated. Carbon chains are shown as sticks with the topmost carbon as spheres, and hydrogen atoms are omitted for clarity. van der Waals volumes of the molecules are shown in background. Planes potentially responsible for GIXRD peaks are shown as thick gray lines.

area per thiol increases to  $32 \text{ \AA}^2$ . Preserving the densest packing of thiols and taking into account the  $\cos \theta$  dependence, this can be accommodated by a  $55^\circ$  tilt, close to previously reported experimental values.<sup>16–18</sup>

For the dense packing structures shown in Figure 1, the flat surface condition *and* the same orientation of S–surface bonds can be achieved only at discrete values of tilts, the minimal of which is  $32^\circ$  (see Supporting Information). This discreteness of tilt values is responsible for the known phase transitions in Langmuir films.<sup>32,33</sup> For other tilt angles, the sulfur–substrate bond (and, as a result, the  $\text{CH}_3$  endgroup) orientation alternates from molecule to molecule and can significantly diminish the odd–even dependence of  $\text{CH}_3$  IR intensities, as observed experimentally,<sup>13</sup> even for monoclinic (singly twisted) structure.

Tilting a densely packed slab of thiols to reproduce experimental  $43^\circ$  twist and  $14^\circ$  tilt values<sup>11,13</sup> results in a relatively rough interface and randomly oriented headgroups (see Supporting Information). Such conditions could be matched, e.g., to an amorphous As layer covering the GaAs surface. The presence of elemental As is always observed after wet etching of GaAs and even after SAM formation.<sup>12,14,15,22</sup> Stable thiol monolayers with the molecules standing almost upright were also reported on explicitly created thick As overlayers.<sup>12</sup> The choice by the SAM to tilt by  $14^\circ$ , which increases the mismatch of area per thiol and area per surface site even more, compared to that already present at  $0^\circ$  tilt, can be thought of as the way to enhance the disorder in the headgroup orientation to better match the disordered surface.

However, for a  $45^\circ$  twist, which is close to the experimentally estimated  $43^\circ$ , the monolayer shows a long-range order in headgroup orientations, contradicting the amorphous surface hypothesis. Adsorption of a SAM on the amorphous overlayer would also make possible tilting in any direction, thus, producing multiple peaks in GIXRD maps for any azimuth, e.g., as observed for Langmuir monolayers on liquids.<sup>32</sup> However, experimental GIXRD results of thiols on GaAs<sup>13</sup> reveal peaks only along distinct azimuthal directions, which suggests an ordered substrate and, likely, a different interface than in the case of an explicitly created As overlayer.<sup>12</sup>

### 3.2. Structure of Alkanethiol SAM on GaAs (001) Surface.

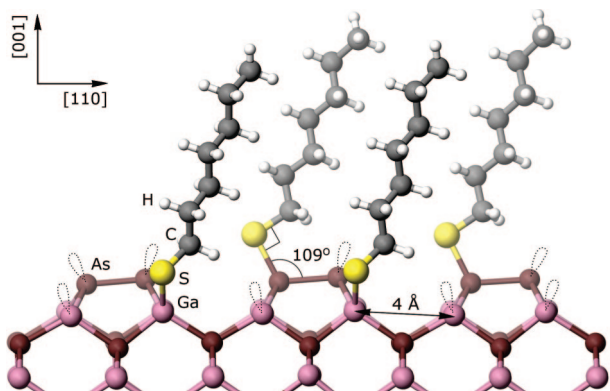
Two equivalent interplane distances in GIXRD data suggest that thiols tilt in either nearest-neighbor (NN) or next-nearest-neighbor (NNN) thiol direction<sup>32</sup> and pack, likely, in the orthorhombic structure (see Figure 1). The azimuthal orientation of the equivalent peaks and GIXRD-derived NN thiol distances<sup>13</sup> indicate that the  $5 \text{ \AA}$  NN distance lies along the  $0^\circ$  azimuth, i.e., along GaAs [110] (or  $[-110]$ ) direction. The angle of  $115^\circ$  between equivalent GIXRD peaks, that is greater than  $111^\circ$  in ideally packed structures, suggests a tilt along the NNN thiol direction, i.e., along the  $7.37 \text{ \AA}$  diagonal.

Our efforts to fit either of the two structures shown in Figure 1 on a square GaAs lattice (i.e., flat surface) were unsuccessful for any combination of SAM parameters (tilt value and direction, SAM orientation relative to the substrate) due to significant differences in NN distances and in the symmetries of the SAM and the substrate. Moreover, MM simulations attempting to put thiols one after another on all available sites of a flat surface resulted in the formation of gauche defects and the impossibility of 100% coverage due to steric repulsion between the molecules.

Since GIXRD data shows preferential alignment of thiols along the [110] (or  $[-110]$ ) direction, it was suggested that adsorption of thiols starts at step edges or etch-pit edges,<sup>13</sup> which are known to appear following the wet etching procedure.<sup>21</sup> Those step edges expose the less reactive (111) Ga plane and run along [110]. Trenches exposing Ga or As atoms from a second (and even third) surface atomic layer naturally exist on all GaAs (001) reconstructions and run along [110] for As-rich reconstructions and along  $[-110]$  for Ga-rich ones.<sup>20</sup> Our previous work suggested that thiols preferentially bind to Ga sites that have empty dangling bonds.<sup>25</sup> Those dangling bonds form weak bonds with the thiols' sulfur lone pairs, increasing the physisorbed thiol dwell time and its chances to chemisorb. In the case when ammonia is added to the thiol solution,<sup>11,13,14</sup> thiols may dissociate into  $\text{SR}^-$  ions,<sup>36</sup> which are also expected to preferentially adsorb on Ga empty dangling bonds rather than on As filled ones.

Introduction of the step edges indeed allowed achieving geometrical commensurability of the SAM with the surface, but only along the step edge and not with the rest of the surface. Thus, further fitting was performed by adding thiols on the surface one after another and performing MM geometry optimization, mimicking the real adsorption process of thiols. Figure 2 shows that a thiol adsorbed on a Ga site in a trench slightly tilts in the direction of the hollow between As dimers. This allows one to accommodate the  $\text{sp}^3$  hybridization of Ga and the  $\text{p}^3$  hybridization of S and, at the same time, to reduce the steric repulsion of the first  $\text{CH}_2$  unit from the surface, as was described previously.<sup>26</sup> The resulting  $\sim 45^\circ$  twist coincides with suggestions from IRS data fitting.<sup>11</sup> Having one thiol adsorbed, the steric repulsion forbids the adsorption of new molecules on the closest Ga sites at  $4 \text{ \AA}$  distance. The closest next adsorption site would be a Ga

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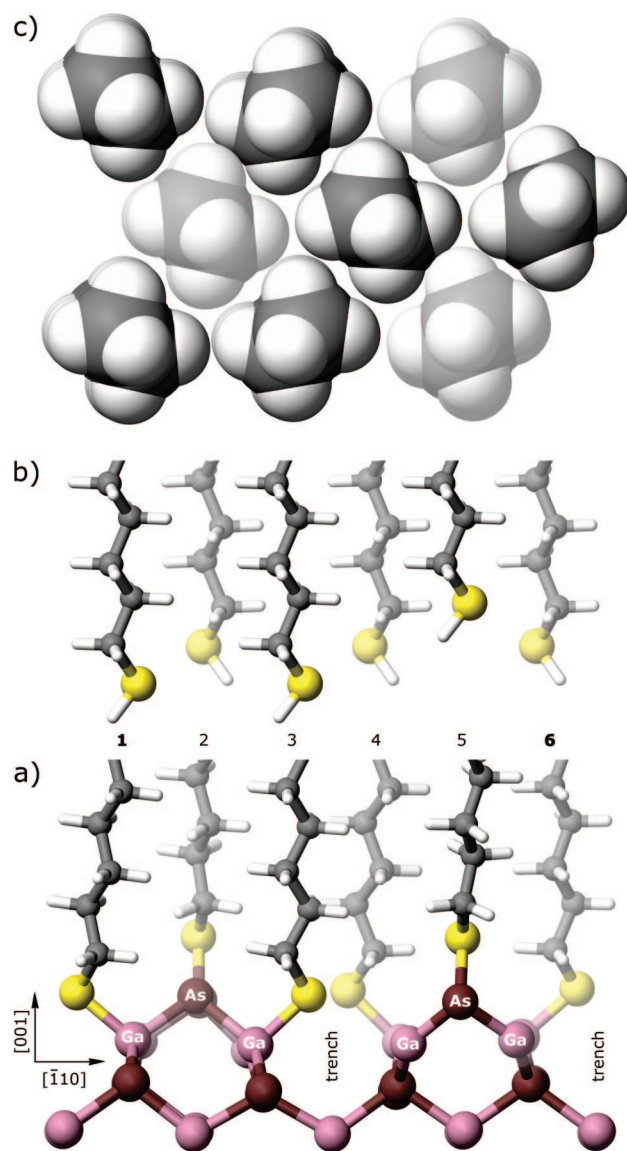
**Figure 2.** Adsorption of thiols on a step edge exposing the Ga-rich (111) plane. Dangling bonds, i.e., sites available for thiol adsorption, are shown with dotted lines.

site on the same side of the trench, which is 8 Å away, or a Ga site on the other side of the trench, along the  $\sim 5.65$  Å diagonal of the GaAs lattice. Thiols adsorbed along both sides of the trench form a zigzag structure, reminiscent of the ideally packed structure tilted in the NNN direction, and in agreement with the above-mentioned expectations from GIXRD data. Further adsorption sites are the As sites in the ridge of As dimers which are located above the forbidden Ga atoms (see Figure 2). Those sites coincide with the pockets in the zigzag structure of thiols and provide the maximal van der Waals interaction with the already adsorbed molecules. It should be noted that to grow such a SAM without defects there should be no adjacent ridges of As dimers, which are observed, for example, in As-rich  $\beta 2(2 \times 4)$  reconstruction.<sup>20</sup> Figure 3 shows the resulting structure, which requires a set of trench-ridge pairs rather than one step-edge. This reconstruction differs from the known stable reconstructions of free GaAs (001) surfaces.<sup>20</sup> We anticipate that the liquid etchant together with adsorbed thiols is responsible for the creation of such a structure.

Our model SAM tilts by  $19^\circ$  along the trench direction and is less densely packed than the ideal crystalline structures shown in Figure 1. The available spacing of 8 Å along the trench between the surface sites participating in bonding with thiols (Figure 2) is 2.5% larger than the corresponding distance of 7.8 Å in the bulk thiol slab tilted in the NNN direction by  $19^\circ$ , a tilt providing the flat-surface condition along the trench direction. In the perpendicular direction, the GaAs lattice is 6% larger than required by the ideally packed structure (Figure 3ab). Such a mismatch reduces the extent of thiols interlocking; however, it does not induce compressive strain neither in the SAM nor in the surface structure. Reduced density SAMs provide less protection against oxygen penetration to the surface and also allow thiols to pivot about their binding sites, which may be responsible for the broadening of diffraction peaks observed experimentally.<sup>13</sup>

In the proposed SAM model, thiols cover only 50% of exposed surface atoms and have an area of  $21.33 \text{ \AA}^2$  per thiol, which is larger than  $16 \text{ \AA}^2$  per thiol available on a flat surface at 100% coverage. For ideally packed thiols,  $21.33 \text{ \AA}^2$  would correspond to a  $30^\circ$  tilt. A structure with a wider trench, exposing an additional As row in the middle of the trench (as observed in As-rich  $\beta 2(2 \times 4)$  reconstruction<sup>20</sup>), can also accommodate a SAM (see Supporting Information), but its density would be even smaller.

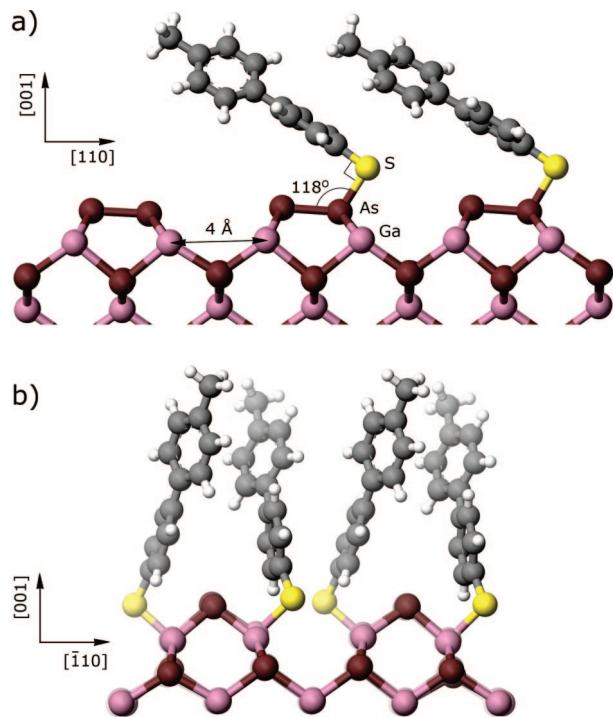
Another interesting feature of our model is that adsorption on Ga sites located on the opposite sides of As ridges requires opposite orientation of thiols (see the first vs third and third vs fourth columns in Figure 3a and Figure 3b), which breaks the periodicity observed for either of the thiol structures shown in



**Figure 3.** Proposed structure of an alkanethiol SAM and the GaAs (001) surface reconstruction needed to accommodate it (a) compared to the ideal orthorhombic structure tilted by the same angle (b). Columns 1 and 6 have different thiol twists in the ideal structure and our model. Note also the shift between the 3rd and 4th columns in our model. Top view along the chains (c) shows the packing density and relative orientation of molecular chains. Thiols adsorbed on As sites are indicated with lighter gray.

Figure 1, but can be nevertheless easily accommodated due to the slightly smaller density of the SAM on surface. As a result, thiols adsorbed on As ridges (columns 2 and 5) can be oriented (twisted) perpendicular to either the left or right neighbor (Figure 3c), which may also be responsible for blurring of the GIXRD signal. Thiol chains adsorbed on top of As ridges are forced to orient the C–C plane near the surface along the ridge, to accommodate the ideal As–S direction (Figure 3a). Only at some distance from the surface can the longer chain thiols rotate to accommodate the twist observed in the densest packing structures (Figure 3c).

The SAM structure proposed in Figure 3 is in qualitative agreement with available experimental data. Despite the tilt angle of  $14\text{--}15^\circ$  estimated from IRS fitting and near-edge X-ray absorption fine structure (NEXAFS) data,<sup>11,13</sup> the area per thiol obtained from GIXRD data and corrected for  $\cos \theta$  dependence suggests a tilt of  $\sim 20^\circ$  or a nonmaximum packing density of



**Figure 4.** Adsorption of biphenyl thiols on As sites (a) and on Ga sites exposed at the trench edges (b).

thiols. Similar tilt value is also obtained from comparison of the  $115^\circ$  azimuthal separation between the equivalent peaks in GIXRD data with the  $111^\circ$  angle in the ideal packing structures (Figure 1). The angles estimated from our model at which GIXRD peaks should be observed are  $0^\circ$  and  $\pm 57^\circ$  from the GaAs  $[-110]$  direction (see Supporting Information), well in agreement with the broad experimental peaks at  $1^\circ$ ,  $-51^\circ$ , and  $64^\circ$ . The so-called pattern II, observed on some of the samples,<sup>13</sup> with  $\sim 30^\circ$  separations between diffraction peaks, in contrast to  $\sim 60^\circ$  in a pattern defined as I, can be explained by a  $30^\circ$  rotation of the SAM domains, as was proposed in the original paper. However, rotation by  $90^\circ$  should produce the same results, and can be explained in our model as an adsorption along the trenches in both  $[110]$  and  $[-110]$  directions.

### 3.3. Structure of Biphenyl Thiol SAMs on GaAs Surfaces.

To further test the proposed alkanethiol SAM structure, we have investigated whether the 4'-methyl-biphenyl-4-thiol (MBT) SAM can be fitted on the same GaAs surface with a trench-ridge-trench reconstruction. The obtained SAM structure is then compared to the available GIXRD data for MBT SAMs fabricated using the same GaAs surface preparation procedure as for alkanethiols,<sup>13</sup> and thus presumably producing the same surface reconstruction. Fitting of NEXAFS and IRS data suggests that the tilt of molecules in MBT SAMs is  $25^\circ$ – $30^\circ$ .<sup>13,22</sup> Figure 4a shows that the  $p^3$  and  $sp^3$  orbital configurations of S and As, respectively,<sup>25,26</sup> restrict the direction of the S–As bond so that the molecule tilts by  $\sim 60^\circ$ . At the same time, molecules adsorbed on the edge of the trench naturally tilt by  $\sim 25^\circ$ , and one of the ways to put all the molecules close enough for interaction, but without adsorption on the ridges, is to create the same trench-ridge-trench surface reconstruction as for the alkanethiol SAMs case. Figure 4b shows such a configuration, with thiols on both sides of As ridges, slightly tilting in opposite directions and overlapping the top phenyl rings to increase the van der Waals interactions. Molecules in the obtained structure align along the directions close to those observed in GIXRD experiments.<sup>13</sup> However, interplane distances

are harder to evaluate for comparison with experiment due to the complex structure of phenyl rings producing many atomic planes.

## 4. Discussion

The assumption of the ideal, i.e., lowest energy free surface of the solid substrate for adsorption and self-assembly of thiols is an idealized situation and provides less freedom for the formation of SAMs commensurate with the surface. However, this seems to be the most logical starting point for the study of SAMs, especially when no other information about the surface structure is available. This consideration has normally been neglected when switching from the prototypical Au to less studied GaAs surfaces, which, in contrast to Au (111), are not atomically flat even after vacuum preparation. In fact, even for the Au (111) case previous simulations assuming an atomically flat surface could not explain the observed  $c(4 \times 2)$  structure of thiol SAMs,<sup>28</sup> while more recent experimental results suggest considerable reconstruction of the surface,<sup>37</sup> and DFT calculations<sup>38</sup> support them. The physical reasoning for the reconstruction of the surface remains the same: it aims to lower the surface energy, although now it is affected by thiol–surface and thiol–thiol interactions.

The possibility of having a nonflat interface has its consequences. For instance, the observed weak odd–even chain length dependence of  $\text{CH}_3$  IRS peak intensities, used to justify the need for two differently oriented chains in a thiol SAM unit cell,<sup>13</sup> could be explained by a nonflatness of the surface even within a single-twist SAM model. For thiol SAMs on Ag (111), where even the assumption of doubly twisted structure is not capable of explaining the absence of odd–even effect,<sup>30</sup> the nonflatness of the surface would be a more reasonable explanation than a change of sulfur–surface bonding geometry upon the change of thiol length.

The kinetics of thiol adsorption and SAM formation on GaAs (001) still requires a more detailed investigation. However, several conclusions can be drawn based on our model. The estimated from GIXRD average domain size of  $\sim 74 \text{ \AA}$ <sup>13</sup> corresponds to nine adjacent trench–ridge pairs of the proposed structure. We expect that the presence of a regular pattern on such a large lateral scale is unlikely after wet etching. This suggests that thiolates, or some other agent in solution, can etch away the surface atoms that do not match the needed structure, while keeping untouched those sites that do allow the dense packing of thiols. Diffusion of surface atoms could lead to similar results, but it is unlikely at room temperature. Reconstruction via etching can be accomplished if we assume that the surface sites on which the SAM has already formed become more stable against etching due to increased interaction between thiols. The size of the domains is then expected to increase proportionally to thiol length. However, the SAM domain can grow only until its boundary reaches some obstacle, e.g., a deep etch pit formed on the previous step of wet etching or even during the deposition. Similarly, two adjacent SAM domains, whose trench–ridge patterns do not laterally coincide, cannot merge to form a bigger domain, since this would require rebuilding of the whole surface under one of the domains, which in term would require desorption of that domain.

Since the initial adsorption sites of thiols are random but 50% coverage and a regular pattern of adsorption sites is required by our model, it is necessary that thiols change their positions on surface during SAM formation even on the surface possessing

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the proposed matching structure. Similarly to the etching mechanism described above, thiols adsorbed on the sites matching the dense packing pattern are likely to get stabilized by the attraction to the already adsorbed molecules, while on other sites they are prone to diffusion or desorption. As was found previously, the barrier for diffusion of thiols on the GaAs surface is about 1 eV (thermal energy of  $\sim 370$  K),<sup>26</sup> while the interaction between thiols becomes of comparable strength only for chains longer than 15 carbon atoms.<sup>19</sup> This may be one of the reasons responsible for the absence of GIXRD signal from SAMs with thiols shorter than 15 carbon atoms.<sup>13</sup> Desorption of thiolates is possible via recombination with hydrogen present on the surface (requiring  $\sim 0.85$  eV,<sup>25</sup> equivalent to  $\sim 330$  K) or via disulfide formation. Cleavage of the thiolate-surface bonds is unlikely since it requires  $\sim 2$  eV ( $\sim 700$  K).<sup>26</sup> The high values of the energetic barriers involved in these processes are likely to have an effect on the SAM domain sizes and monolayer formation rates.

Since the surface reconstruction is expected to be driven by the thiol-thiol interactions, the MBT SAMs, which were used as a test case for the proposed trench-ridge-trench reconstruction, are likely to produce a different interface with GaAs than that of alkanethiol SAMs. This may be responsible for the observed discrepancies between our MBT SAM model and experiment. For instance, our model suggests no sulfur bonding to the ridge, while XPS data show the shift in As 3d spectra.<sup>22</sup> Nevertheless, this apparent discrepancy can be explained even within the proposed surface geometry by the presence of As sites in the ridge that are saturated with H (having a shift similar to As-S) or by replacement of Ga atoms in the second atomic layer (i.e., at the exposed trench sides) by As. Such a replacement of Ga by As, resulting in the formation of As-S bonds, is possible, due to equivalent tetrahedral bonding geometries of Ga and As, and is expected, based on XPS data which suggests noticeable amounts of As<sup>0</sup> component, i.e. that the surface is As-enriched. Similarly, As-S bonds could appear in our model by switching from As-rich to Ga-rich reconstruction, i.e., by replacement of all Ga atoms by As and vice versa. This would result in the change of the trench direction from [110] to  $[-110]$ , which is nevertheless not detectable by GIXRD. In general, our approach predicts only the positions of the surface atoms but not their type (As or Ga), providing enough room for flexibility of different surface properties. Our findings regarding the orbital configurations and the resulting molecular tilt, which favor the adsorption of MBT on the trench sides, should remain valid even for different interface structures of MBT SAMs on GaAs.

It should be noted that the proposed structure of alkanethiol SAMs does not obey the electron counting rule<sup>39</sup> and produces one extra electron per six surface atoms, which results in the presence of partially filled dangling bonds and the formation of undesirable surface states. Since on an ideal surface empty Ga dangling bonds fall in energy above the conduction band minimum and filled dangling bonds of As are located below the valence band maximum,<sup>39</sup> partially filled Ga dangling bonds would act as donors, while those of As would act as acceptors. It is well-known that only acceptor-like surface states affect the band bending in n-type semiconductors, while for p-type, only donor states are important. Doping can also potentially affect the population of the dangling bonds and, as a result, the adsorption probability of hydrogen and thiols on every site. In our model, the electron counting rule can be restored by the adsorption of hydrogen on the remaining As site. Replacement of Ga surface sites with As or vice-versa would also change the electronic balance of the surface. Such a variability of surface properties

within the same geometrical model may account for the differences in passivation effect of thiol SAMs on differently doped samples or prepared using different preparation procedures.<sup>7,8,14,22</sup> A more systematic study of the thiol passivation effect on differently doped samples, prepared using the same procedure, can potentially provide information about Ga versus As involvement in bonds with thiols.

The presence of hydrogen on surface and, thus, roughness and partial coverage of the surface proposed in our model can be tested with TPD experiments, which should distinguish intact thiols from thiolates or disulfides desorbing from the surface. According to our model, hydrogen cannot be adsorbed on Ga sites (see empty sites in Figure 2) since it would be situated too close to the sulfur on the opposite side of the trench. The distance between S atoms on different sides of the trench is  $\sim 4$  Å (see Figure 3a), facilitating desorption of disulfides. If H is present on As atoms in the ridge, intact thiols would be detectable in TPD, while, in the absence of H on As, the desorption of thiolates or disulfides should be observed. It should be noted that the distance between S atoms adsorbed on As ridge and those in the trench is  $\sim 5.5$  Å. It is greater than the above-mentioned 4 Å and, consequently, would require a different temperature for desorption, producing an additional peak in TPD spectra. A greater amount of intact thiols than disulfides in the desorption spectra may be indicative of the structure with a wider trench, exposing an additional As row in the middle of the trench (see Supporting Information). The presence of hydrogen on surface is important, since it may passivate the uncovered surface sites and may also help in the formation of the SAM, as discussed above. At the same time, it may be responsible for the faster degradation of SAMs via recombination of thiolates with hydrogen. Thus, removal of hydrogen from the surface might be one of the ways to improve the SAM stability.

The azimuth-dependent Fourier transform infrared spectroscopy (FTIR) measurements, currently in progress in our group, are expected to provide more information about the SAM structure. While the spectra measured with the electric field of the incident beam perpendicular to the surface (p-polarized reflection spectra) are sensitive to molecular tilt angle,<sup>11,13</sup> the spectra with the electric field parallel to the surface (polarized transmission or s-polarized reflection spectra) are sensitive to the tilt azimuth and can be used to verify whether thiols indeed tilt only along trenches in [110] and/or  $[-110]$  directions, as our model proposes. More accurate GIXRD measurements differentiating the [110] and  $[-110]$  directions based on marking the crystallographic orientation of the sample during preparation (otherwise indistinguishable by pure GIXRD) would also help to clarify the exact direction of the trenches from which the adsorption starts. Since Ga-terminated versus As-terminated surfaces should exhibit trenches in perpendicular directions, this should help to resolve S-Ga versus S-As bonding. The presence of both types of trenches, as observed experimentally in pattern II,<sup>13</sup> may be indicative of the surface covered with several monolayers of As, thus, making the trenches in [110] and  $[-110]$  directions equivalent.

## 5. Conclusions

We have proposed a new method for finding the interface structure between SAMs and solid substrates, based on the modification of surface reconstruction to match the dense packing patterns of thiols. Introduction of the atomic roughness of the surface allows overcoming the incommensurability of the SAM with the surface, owing to the exposure of more binding sites per unit area and thus providing thiols with more freedom to

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achieve higher packing density. For alkanethiols and MBT-thiols on GaAs (001), the application of the proposed method suggests the formation of interfaces comprising the trench–ridge–trench surface reconstruction. Comparison of our model for alkanethiols–GaAs with available experimental data concerning the SAM domain sizes suggests that interactions between thiols are strong enough to enforce the required interface structure rather than leaving thiols to adapt to the surface reconstruction available after etching. At the same time, half of the surface sites remain uncovered by thiols, which may significantly affect the passivation effect of the SAM. The proposed models are in agreement with IRS and GIXRD data and provide important information regarding the bonding chemistry and the structure of the SAM–GaAs

interface. Application of the proposed approach to other SAM–substrate systems is envisioned.

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**Supporting Information Available:** 3D structures of the SAMs, discrete tilt and twist angles leading to the flat-surface condition, and a procedure for determination of the potential GIXRD peak directions for our models. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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