

Excellence in Chemistry Research

Announcing our new flagship journal

- Gold Open Access
- Publishing charges waived
- Preprints welcome
- Edited by active scientists



Meet the Editors of *ChemistryEurope*



Luisa De Cola

Università degli Studi
di Milano Statale, Italy



Ive Hermans

University of
Wisconsin-Madison, USA



Ken Tanaka

Tokyo Institute of
Technology, Japan

■ Electro, Physical & Theoretical Chemistry

Combined *ab initio* and XPS Investigations of the Electronic Interactions of L-Cysteine Adsorbed on GaAs(1 0 0)

María F. Juárez,^[a] Ana M. Toader,^[b] Catalin Negri, ^[c] Elizabeth Santos,^{*,[d, e]} and Valentina Lazarescu^{*,[f]}

The adsorption of L-cysteine from ethanol solutions on GaAs(1 0 0) surfaces has been studied by XPS and density-functional theory (DFT). XPS data reveal that the formation of the adsorbate involves preferentially the As-sites for p-GaAs(1 0 0) and the Ga-sites for n-GaAs(1 0 0). The adsorbed species show different orientations of the functional groups to the surface for the different substrates. DFT calculations performed for both Ga-dimers and As-dimers terminated surfaces show that the

adsorption is energetically favourable on both substrates. However, the adsorption energy is more negative on top of Ga-atoms. Here an important contribution for the stabilization of the adsorbate is the interaction of the functional groups with the surface. The parallel orientation found for the Ga-bound species by DFT calculations is in good agreement with the shift in the binding energy of the NH₂/NH₃⁺ species observed by XPS analysis.

Introduction

The characterization of interfaces formed by the adsorption of amino acids on a variety of substrates^[1] is relevant in nanoscience for the fabrication of hybrid biosolid state devices. In particular L-cysteine is interesting since it can interact with surfaces and biological environments through three different functional groups.

The formation of self-assembled monolayers from L-cysteine has been widely studied on metallic substrates, such as Au.^[2–4] In previous works, we have systematically investigated both experimentally and theoretically the electronic interactions of L-cysteine with metallic Ag substrates.^[5–8] Experiments of other groups also confirmed our predictions concerning the electronic structure of these interfaces.^[9] Besides, L-cysteine has also a dipole moment, which varies between 1.8

and 4.7 D for the different conformations.^[10] The electronic redistribution between adsorbate and substrate is expected to be different for p- and n-semiconductors. Therefore, it is an attractive candidate to investigate self-assembled layers on semiconducting substrates.

Consequently, we have extended our studies to semiconducting substrates, where the self-assembling phenomenon also takes place. L-cysteine monolayers spontaneously formed on p- and n-GaAs(1 0 0) electrodes in aqueous solutions have been investigated combining experimental and theoretical approaches.^[11] The XPS data evidenced the preferential of the L-cysteine with As-sites at the p-doped and with Ga-sites at the n-doped substrates, and pointed out different configurations of the adsorbed species at the two types of semiconducting substrate. L-cysteine binds basically to GaAs(100) surface via the thiol group meaning that carboxyl and amino functional groups may act as bio-linker for conjugating other bio-molecules.

A recent publication^[12] has provided direct evidence of an electronically coupled junction fabricated by covalently binding genetically engineered cysteine mutant of protein-chlorophyll complex photosystem I (PS I) to a chemisorbed small connecting molecules on p- and n-GaAs surfaces. This hybrid bio-solid-state electro-optical device can be used as a photo-sensor. According to our previous results,^[11] the PS I could be directly attached to the GaAs surfaces through the thiol group of the cysteine instead of using N-ε-maleimidocaproic acid or N-β-maleimidopropionic acid as linkers. The configuration of the adsorbed species is thus important, and any information in this respect very useful.

Both the solvent and the substrate may play key roles in the adsorption process. In order to investigate the effect of the solvent we have extended the XPS investigations to the L-cys-

[a] Dr. M. F. Juárez

Institute of Theoretical Chemistry, Ulm University,
89081 Ulm, Germany

[b] Dr. A. M. Toader

Institute of Physical Chemistry Ilie Murgulescu, Splaiul Independentei,
Bucharest, Romania

[c] Dr. C. Negri

National Institute of Material Physics, Bucharest, Romania

[d] Dr. E. Santos

Institute of Theoretical Chemistry, Ulm University,
89081 Ulm, Germany
E-mail: esantos@uni-ulm.de

[e] Dr. E. Santos

Instituto de Física Enrique Gaviola (IFEG-CONICET-FaMAF) Universidad de
Córdoba, Argentina

[f] Dr. V. Lazarescu

Institute of Physical Chemistry Ilie Murgulescu, Splaiul Independentei,
Bucharest, Romania
E-mail: vlazarescu@icf.ro



Supporting information for this article is available on the WWW under
<http://dx.doi.org/10.1002/slct.201600589>

teine monolayers formed from ethanol solutions instead from aqueous solutions.

In our previous study, we have performed DFT calculations with the Gaussian 03 package^[13–15] using clusters to model the semiconducting substrates. This approach was combined with the Polarizable Continuum Model (PCM)^[16] and the Self-Consistent Reactions Field (SCRf) method.^[17]

Furthermore, in the present work we have implemented DFT calculations using periodic boundary conditions in the slab configuration instead of clusters to describe better these systems.

It is the aims of this paper to understand the mechanisms that determine the stability of adsorbates with different configurations, and to better characterize their electronic properties. According to previous work^[1] cysteine adsorbs on diverse substrates completely covering the surface. Molecular conformations and overlayer geometries strongly depend on the coverage. The interplay of interaction forces between neighbouring adsorbates and the different functional groups with the surface determine the self-organisation or surface-induced organisation. In order to unravel these contributions, we shall focus on the substrate - adsorbate bonds between the different functional groups of the cysteine and both Ga and As atoms of GaAs(1 0 0) surfaces. Therefore, we investigate the adsorption process at low coverage to avoid intermolecular interactions, which drive self-organization and facilitate the formation of zwitterions species by proton transfer between adjacent adsorbates.

Results and Discussion

1. Theoretical Model

GaAs(1 0 0) surfaces were used as substrate for the L-cysteine adsorption. The tetrahedral coordination of the zinc-blend type of the bulk crystal structure results in a polar surface that could be terminated either with Ga or As atoms. Due to the two dangling orbitals of each surface atom, the pristine GaAs(1 0 0) surface is energetically unstable and exhibits various surface reconstructions depending on the preparation conditions. The mechanism responsible for reconstruction of GaAs(1 0 0) surfaces in an inert atmosphere consists in the formation of surface dimers, which produces a decrease of the number of dangling bonds by a factor of two by only a small change of bond angles of surface atoms.^[18, 19]

The most stable surfaces for the (1 0 0) orientation are the β_2 -(2x4)^[20–22] and the ζ -(4x2)^[23, 24] in the case of As- and Ga-dimers sites, respectively. However, the situation is totally different in an electrochemical environment. These reconstructed surface structures could not be observed at the GaAs(1 0 0) / solution interface. In-situ AFM^[25, 26] and STM^[27] investigations clearly revealed that GaAs(1 0 0) in HCl and H₂SO₄ solutions exhibits only the (1x1) structure. Koinuma and Uosaki^[25] considered that the presence of the stable (1x1) structure is unique in the electrochemical system due to the fact that the dangling bonds of the surface atoms, responsible for the surface reconstruction

under UHV conditions, are terminated with ions in the electrolyte solution.

Therefore, taking into account that the GaAs substrate was previously etched in acid solutions, it is highly probable that the self-assembled organic layers are formed on this (1x1) structure.

Since we are interested in the behaviour at low coverage, we have investigated the adsorption of one cysteine radical on a (2x2) unit cell. We have considered that the initial surface arrangement of the GaAs(1 0 0) slabs consists of Ga–Ga or As–As dimers, for the preferential adsorption on Ga or As atoms, respectively. This reconstruction induces a small change in the (1x1) surface but it highly stabilizes the surface without changing the number of Ga or As atoms per layer. We have also performed some calculations with the reconstructed β_2 , and ζ surfaces in order to introduce defects on the surface and for sake of comparison, which are shown in the Supporting Information.

2. XPS data

XPS investigations carried out on L-cysteine-thiolate monolayers formed at p- and n-GaAs(1 0 0) surfaces in ethanol solutions brought evidence that the binding of this organic molecule is different at the two substrates.

The intensity of the main GaAs substrate core-level lines, As-3d_{5/2} (BE = 41.08 ± 0.03 eV)^[28] and Ga-3d_{5/2} (BE = 19.20 ± 0.05 eV)^[29] is a reliable measure of the number of As atoms bound to Ga, and Ga atoms bound to As, respectively. At the bare p- and n-GaAs(1 0 0) surfaces, the $I_{As-3d_{5/2}} / I_{Ga-3d_{5/2}}$ ratio has quite similar values, 1.41 ± 0.01 and 1.46 ± 0.01, respectively, as shown in Figure S1 in the Supporting Information. The involvement of the As or Ga atoms in other type of bonding, such as As–S / Ga–S, brings a decrease in weight of the As-to-Ga and Ga-to-As bound species, respectively. Since the usual chemical shift, ΔBE is 1.4 ± 0.3 eV^[28] at As–S species and around 0.6 eV^[30] at Ga–S species, the first one can be easily discerned in the XPS spectra whereas the latter one manifests itself as a slight broadening of the Ga (3d) peak.^[31] As seen in Figure 1, the value of the $I_{As-3d_{5/2}} / I_{Ga-3d_{5/2}}$ ratio is lower at the p-doped substrate (1.30 ± 0.01) than at the n-doped one (1.45 ± 0.01), suggesting that the adsorption of the cysteine in ethanol solution involves rather As-sites at p-doped and Ga-sites at n-doped GaAs(1 0 0), respectively, as previously found for the films formed in aqueous solutions.^[11] This conclusion is further supported by the higher weight of the As–S species observed at the p-doped sample (7.3%) than that found at the n-doped one (4.7%) as well as the higher value of the full width at half maximum (FWHM) parameter of the Ga-3d_{5/2} and Ga-3d_{3/2} components at the n-doped sample (1.16 eV) than at the p-doped one (1.05 eV). The summary of the self-consistent fitting procedure applied to the As-3d and Ga-3d spectral region is shown in Tab. S2 and Tab. S3 in the Supporting Information.

One may also notice that As–O and Ga–O species cannot be discerned in As-3d and Ga-3d core-level regions at the L-cysteine-thiolate covered n-GaAs(1 0 0) sample, suggesting a better protection against the further oxidation in air than at the p-doped substrate.

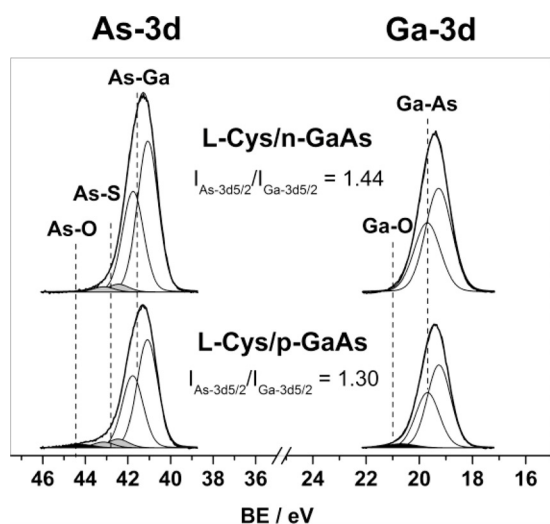


Figure 1. As-3d and Ga-3d core level regions at L-Cysteine adsorbed on p-doped (bottom) and n-doped GaAs(1 0 0) substrates.

Similarly as in the monolayers formed in aqueous solution, in ethanol solution the cysteine seems to exhibit different configurations at the n- and p-doped GaAs(1 0 0) surfaces. Both the binding energy of the species found in the N-1 s core level region (NH_2 and NH_3^+) and particularly their relative weight point to different orientations of the amino group with respect to the semiconductor surface. As seen in Figure 2a, the amount

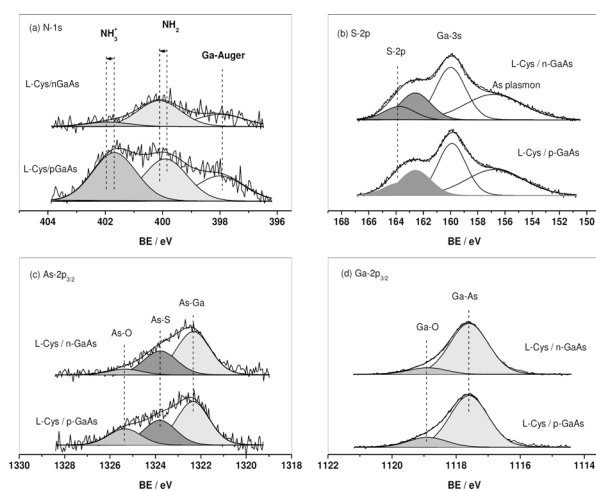


Figure 2. N-1 s (a), S-2p (b), As-2p_{3/2} (c) and Ga-2p_{3/2} (d) core level lines at L-Cysteine adsorbed on p- and n-doped GaAs(1 0 0) substrates.

of NH_3^+ is almost insignificant at the n-doped sample, whereas at the p-doped one it is higher than that of NH_2 . An important advantage to use ethanol as solvent instead water, is that for the cysteine monolayers formed in ethanol solutions the N-1 s core-level region is slightly shifted to higher binding energies than that observed in similar films formed in aqueous solution.^[11] Therefore, it is easier to discern one of the three con-

tributions of the Ga-Auger ($\text{L}_2\text{M}_{45}\text{M}_{45}$) process,^[32] which has the same binding energy ($\text{BE} = 398.0 \pm 0.1 \text{ eV}$) at the both substrates. It is easy to observe that both the amino and the protonated amino groups have, however, different binding energies at p- and n-doped samples (Figure 2a).

The BE values of 399.6 ± 0.1 and $401.6 \pm 0.1 \text{ eV}$ found in our experiments at the p-doped samples are similar to those usually reported for the L-cysteine adsorbed on gold,^[32–34] Pd^[35] or Cu.^[36] At the n-doped samples, the binding energies of the NH_2 and NH_3^+ species are shifted to 400.2 ± 0.1 and $402.2 \pm 0.1 \text{ eV}$, respectively. A similar shift to higher binding energies was observed at the L-cysteine films formed in aqueous solutions at n-doped in comparison to p-doped substrates.^[11] This effect, along with the significant difference in weight of the $\text{NH}_2/\text{NH}_3^+$ at the two types of substrate, clearly implies a different configuration of the amino head within the adsorbed layer.

The adsorption of the L-cysteine in ethanol solution on GaAs substrates involves the thiol group, as in the case of the aqueous solution. The doublet S-2p core-level region (Figure 2b), with binding energies of $162.20/163.38 \pm 0.2 \text{ eV}$, is characteristic for thiolate species.^[33,37,38] No evidence was found for the presence of cysteine and / or a second layer having its amino and carboxyl groups electrostatically bound with the first layer and hence a free thiol group at the top.

The As–S signal ($\text{BE} = 1324.9 \pm 0.2 \text{ eV}$) in the As-2p_{3/2} core-level region (Figure 2c) shows that As is certainly also involved in the adsorption of the L-cysteine. The other two contributions to the As-2p_{3/2} spectra were assigned to As–O species ($\text{BE} = 1326.2 \pm 0.2 \text{ eV}$) and substrate As atoms ($\text{BE} = 1323.2 \pm 0.2 \text{ eV}$), according to the literature data.^[39–42]

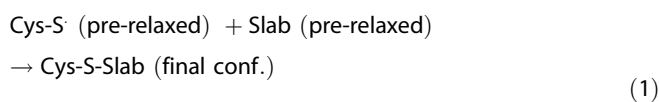
The Ga-2p_{3/2} spectrum (Figure 2d) has only contributions from the substrate Ga atoms ($\text{BE} = 1117.6 \pm 0.2 \text{ eV}$) and Ga–O species ($\text{BE} = 1118.9 \pm 0.2 \text{ eV}$).^[41–43] Unfortunately, the Ga atoms bound to the thiolate species cannot be discerned with our instrumentation as mentioned before.^[43] However the low content of oxidized Ga species is an indirect proof that Ga atoms compete as well with As atoms for the adsorption of cysteine. This behaviour has been observed in the case of other thiolates formed on GaAs substrates.^[43–45]

The low percentage of As–O and Ga–O signals from the total As-2p_{3/2} (Figure 2c) and Ga-2p_{3/2} (Figure 2d) core-level regions shows that only minor amounts of surface oxides are formed on the n- and p-doped samples covered by the cysteine. We may infer from the close contributions of the S-2p and As–S core-level line in their corresponding spectral regions that the surface coverage is similar at both types of substrate. However, the lower weight of As–O and Ga–O species at the n-doped sample attests that the protection against the further oxidation in air of the semiconductor substrate is more efficient than at the p-doped sample. This should be the outcome of a different configuration of the adsorbed cysteine depending on the semiconductor dopant nature. This result may be related to the preferential bonding of the cysteine with the As-sites at p-doped and with Ga-sites at n-doped surfaces suggested by the comparison of the $I_{\text{As-3d}}/I_{\text{Ga-3d}}$ ratio values found at both substrates.

3. Geometrical configurations and energetics

We have studied the geometrical configurations and the energetics of the L-cysteine adsorbed on different GaAs(1 0 0) surfaces. The L-cysteine molecule shows a large variety of conformations. More than 300 structures have been identified in the gas phase, and about 40 of them are stable or metastable.^[10,46] The scatter on the energy between the conformers is lower than 0.2 eV. Therefore, there are several possible orientations of the different functional groups when the cysteine approaches the surface. The adsorbate can also take different conformations depending on which groups are interacting with the substrate. We have obtained diverse stable or metastable systems corresponding to local minima of energy by DFT calculations. We have not investigated the transition processes between these states.

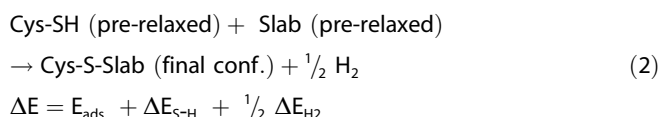
The adsorption energy of L-cysteine on the GaAs surface was calculated by subtracting the energy of the pre-relaxed substrate slab (E_{slab}) and the energy of the pre-relaxed isolated cysteine radical ($E_{\text{Cys-S}}$) from the total energy of the system (E_{system}) with the final configuration:



$$E_{\text{ads}} = E_{\text{system}} - (E_{\text{slab pre-relax.}} + E_{\text{Cys-S}^{\cdot} \text{ pre-relax.}})$$

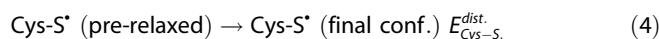
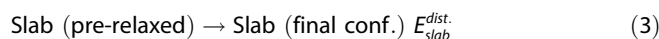
The energy of the isolated cysteine was calculated by relaxing its radical form in the vacuum. According to this definition, a negative value of the adsorption energy indicates an attractive interaction between the cysteine radical and the surface.

The adsorption energy defined in equation (1) is a good measure of the strength of the bond between the surface and the adsorbate. However, it is not enough to determine if the adsorption reaction will be a spontaneous thermodynamical process. A more realistic definition of the reaction energy requires including the energy corresponding to the stable forms of the reactants and a proper mass balance. It is not usual to find the cysteine in an aqueous solution as a radical. Therefore, a better definition of the reaction energy ΔE must consider the energy of the cysteine molecule ($E_{\text{Cys-SH}}$), the energy for the cleavage of the S–H bond ($\Delta E_{\text{S-H}} = 3.885$ eV), and the energy for the formation of molecular hydrogen from the resulting H atoms ($\Delta E_{\text{H}_2} = -4.52$ eV).^[6]

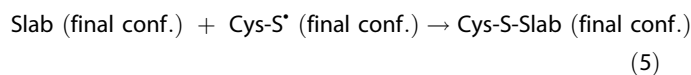


It is also interesting to compare the different contributions to the adsorption energy defined by equation (1). After adsorption, the final configurations of both the adsorbed radical and the slab appear distorted in comparison with the pre-relaxed isolated structures. We can estimate these contributions calcu-

lating the required energy for these particular processes taking place:



Another noteworthy concept is the binding energy (BE) between the adsorbate and the surface defined by:



Therefore, the adsorption energy in the equation (1) can be expressed as:

$$E_{\text{ads}} = BE + E_{\text{slab}}^{\text{dist.}} + E_{\text{Cys-S}}^{\text{dist.}}$$

In this part, we shall first consider the adsorption of L-cysteine on the dimerized Ga and then on the dimerized As surfaces. The reconstructed $\beta 2$ -(2x4) and ζ -(4x2) faces are briefly discussed in the Supporting Information.

Similarly to the adsorption on metals, the number of blocked places of the surface per adsorbed species can be different depending on the orientation of the functional groups. However, the definition of the coverage on these substrates is more difficult than for metallic flat surfaces. The adsorption process can take place on both Ga and As atoms. In addition, the presence of dimers produces a corrugation of the surface. In all the cases, we consider the adsorption of one cysteine radical per unit cell. In the case of the (2x2) structures the area of the unit cell is 74 Å², while the areas corresponding to the $\beta 2$ (2x4) and ζ (4x2) structures are twice larger (148 Å²). Instead of giving numbers for the coverage, we prefer to show the resulting structures and the distances between neighbouring adsorbates, which are included in the Supporting Information.

We started with the adsorption of one cysteine radical on several possible sites on the Ga-dimer of a (2x2) surface unit cell. The adsorption energy was calculated by equation (1) taking the energy of the dimerized surface as reference for E_{slab} . The value obtained was -2.13 eV, indicating that there is a strong bond between the radical and the surface. This value is close to the adsorption energy obtained for cysteine at a similar coverage on the bridge site of Ag(1 1 1)^[6-8] and more negative than that obtained for the adsorption on Au(1 1 1).^[2,3]

Figure 3a shows the clean surface ended with Ga–Ga dimers (bond length: 3.18 Å). The cysteine molecule is first positioned with the thiol group oriented direct to the surface while the other both amino and carboxyl groups are oriented upward, away from the substrate. The optimized structure after adsorption results in a cysteine attached by the S head on top (slightly displaced) of a Ga atom despite the initial approach position of the adsorbate (Figure 3b). The bond length between the S and the Ga atom is 2.47 Å. This value is very close to those observed by the cysteine adsorption on Au and on Ag,^[2-8] indicating that the strength of the bond is similar to

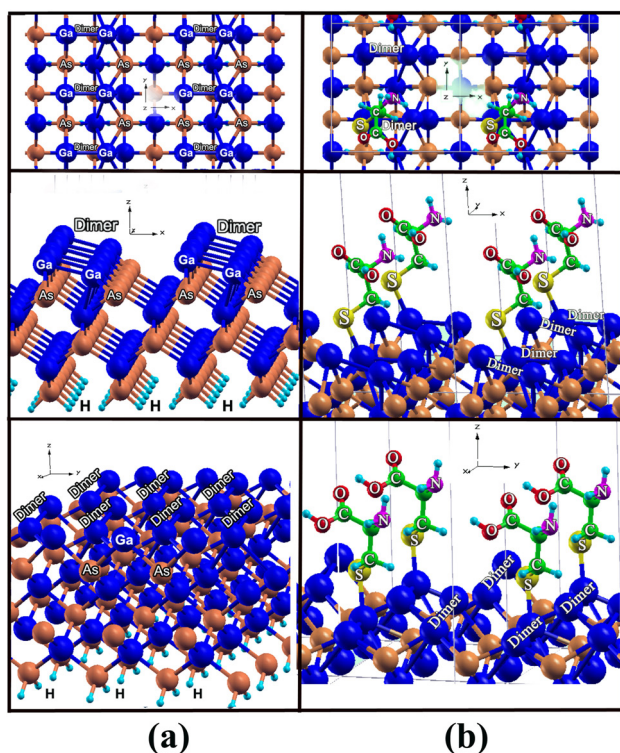


Figure 3. Top and side views of the optimized geometries of the clean surface of GaAs(1 0 0) ended in Ga-dimers (a) and GaAs(1 0 0) covered by cysteine (b) when it vertically approaches the surface by the thiol group while the carboxyl and amino group are oriented upward.

those with metals. The C–S–Ga angle is 98.2° . The latter is less than the tetrahedral angle of a sp^3 hybridization of the S atom. However, it is similar to that of thiol molecules and to that of monoclinic crystallized cysteine. This decrease on the angle can be explained by a predominant p-character of the bond and the greater repulsion of non-bonding electrons, which pushes the two bonding orbitals (S–C and S–Ga) closer together. The analysis of electronic charge difference discussed in the next section shall also support this suggestion.

Because of the interactions between the functional groups and the surface, we have considered different possible initial alignments of the molecule when it approaches the surface. Similar to the case of cysteine adsorption on Au and Ag,^[2–8] the strongest bond is through the thiol group, but the other functional groups can also contribute to the bond with the substrate depending on their orientations. The formation of additional bonds between the surface and the functional groups (carboxyl and amino) is shown in Figure 4. In all the cases the systems are more favourable than that resulting from the vertical approach. The carboxyl group can interact with the surface through the two oxygen atoms. The decrease in the energy is of 0.14 eV if the molecule approaches by the OH (Figure 4a) and 0.19 eV for the other case (Figure 4b). The decrease is about 0.15 eV if both oxygen atoms are almost parallel to the surface (Figure 4c). The strongest effect on the energy is when the amino group is near the substrate (case (d) in Figure 4). In

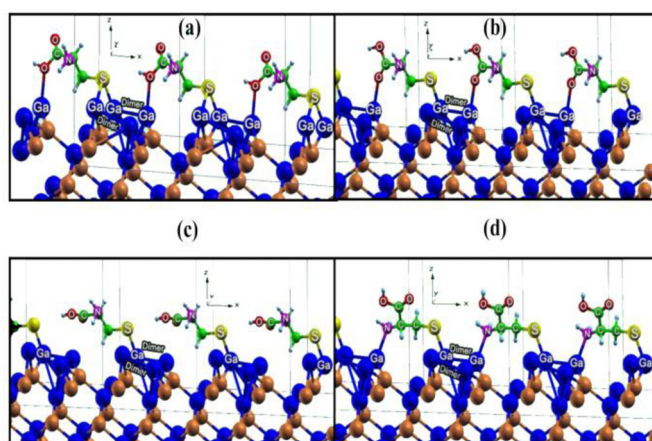


Figure 4. The optimized geometries of L-cysteine radical adsorption on GaAs(1 0 0)-(2x2) surface terminated in Ga-dimers. The orientations promote the approach of the COOH with the HO- (a), C=O (b) or with C=O and HO- parallel to the surface (c) and the approach of the NH₂ group (d).

this case the adsorption energy decreases by about 0.4 eV. A similar result has been observed when cysteine adsorbs on Au (111).^[2,3] In the latter case, the adsorption energy drops about 0.5 eV if besides the thiol head the amino group also participates in the bond with the gold substrate. The S head and the terminal functional group are bonded to Ga atoms of two different dimers, which are placed forming a line. In the case (a) the S atom also interacts with the Ga atom of the neighbour dimer and its position is slightly displaced from top toward bridge.

In all the cases, the distance between the S head and the surface is the same within DFT error (Ga–S: 2.5 Å). Therefore it can be assumed that the bond Ga–S strength is similar in the four systems. The additional bond (O–Ga or N–Ga) becomes an important factor that increases the stability of the new configurations. Effectively, the most stable system is the one with the shortest bond distance to the surface of the functional group (Ga–N: 2.43 Å).

In our case (2x2 unit cell), there is a row of dimers that is not covered by cysteine. However, the change in the orientation of the cysteine (tilted) increases the covered surface while the number of Ga–S bonds remains the same (see details in the Figures shown in Supporting Information).

A final inspection of adsorption energies and structures makes us to conclude that the bond between the surface and the functional groups (carboxyl / amino) plays a fundamental role in the final configuration of the cysteine on the surface. However, the S–Ga bond mainly determines the overall energy.

Figure 5a shows the structure of the clean (2x2) surface terminated in As-dimers, and Figure 5b the most stable optimized structures of the adsorbed cysteine. In contrast to the adsorption on Ga-dimers, we have found several stable structures on different sites of the surface. Similarly to the process on Ga-dimers, the cysteine adsorbed on top of an As atom is the most stable configuration ($E_{\text{ads}} = -2.12$ eV). Similarly, the binding energy for this configuration is very close to that obtained for the adsorption of alkanethiolate.^[47,48] The positions of the atoms of

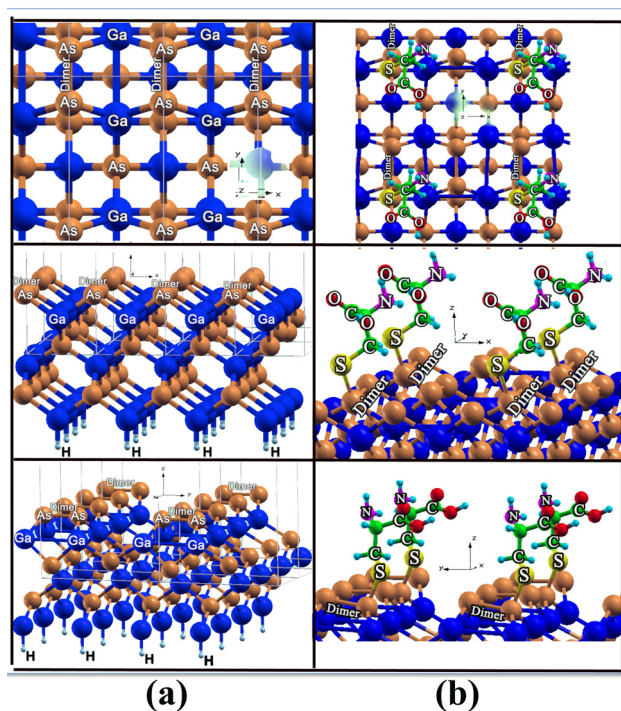


Figure 5. Top and side views of the optimized geometries of the clean surface of GaAs(100) terminated in As-dimers (a) and of the cysteine adsorbed on As-top (b).

the substrate are less perturbed than for the surface containing Ga-dimers. The vertical positions of the As atoms remain almost the same as the clean surface. However, the dimer where the adsorption takes place is disrupted: the distance As–As increases from 2.53 Å to 4.30 Å.

The adsorption state corresponding to a bridge position between two As atoms is still thermodynamically favourable ($E_{\text{ads}} = -1.70$ eV). Adsorption on the Ga atoms that are more coordinated in this surface results in higher energy ($E_{\text{ads}} = -1.27$ eV).

We have also investigated different conformers using as starting configuration the most stable optimized system (the adsorbate on top site in Figure 5). The organic chain has been rotated such that the functional groups (carboxyl / amino) point to the surface. In all the cases, in contrast to the surfaces containing Ga-dimers, the functional groups remain away from the surface after optimizations. This is an important disparity between these both systems.

The additional reconstructed surfaces considered for the adsorption of cysteine are the $\beta 2(2 \times 4)$ (As-dimer), and $\zeta(4 \times 2)$ (Ga-dimer) structures, which are shown in the Supporting Information. Table S1, which contains more details about the geometry, is given in the Supporting Information, where the definition of the angles is also explained.

Table 1 summarizes the results discussed in this section. In order to analyse the thermodynamical stability of the different systems, the more realistic energy values obtained by equation (2) with cysteine molecule as reference instead of the radical

Table 1. Energetics of the most stable structures of the adsorbed cysteine radical on GaAs(1 0 0) surfaces.

	I	II	III	IV
Systems	topGa/ GaAs(100)- (2x2)-Ga dimer	topAs/ GaAs(100)- (2x2)-As dimer	topGa/ GaAs(100)- $\beta 2(2 \times 4)$ -As dimer	topAs/ GaAs(100)- $\zeta(4 \times 2)$ -Ga dimer
Adsorption Energy (eV) E_{ads} from eq. (1)	-2.51	-2.12	-2.09	-1.57
Reaction Energy (eV) ΔE_{rac} from eq. (2)	-0.89	-0.49	-0.46	0.06
Binding Energy (eV) BE from eq. (5)	-2.92	-2.39	-2.18	-1.96
Distortion Energy (eV) $E_{\text{slab}}^{\text{dist}}$ from eq. (3)	0.34	0.29	0.06	0.37
Distortion Energy (eV) from eq. (4)	0.07	-0.02	0.03	0.02

The energy bar chart shows the contributions of different processes to the adsorption energy for systems I, II, III, and IV. The y-axis is energy / eV, ranging from -3.0 to 0.0. The x-axis is labeled with I, II, III, and IV. For each system, there are four bars: a blue bar (top), a green bar (middle), a red bar (bottom), and a pink bar (right). The total energy for each system is the sum of the blue, green, and red bars. The pink bar represents the distortion energy. The total energy values are: I: -2.51 eV, II: -2.12 eV, III: -2.09 eV, IV: -1.57 eV.

are also shown for the most stable systems. This is still negative with the exception for the adsorption on the $\zeta(4 \times 2)$ (Ga-dimer) surface, where it is almost zero. It is interesting to analyse the contributions of the different processes involved in the adsorption. The energy lost in the distortion of the surface is important (about 0.3 - 0.4 eV) with the exception for the adsorption on the $\beta 2(2 \times 4)$ (As-dimer), where there is almost no distortion neither of the surface nor of the adsorbate. In all cases, the energy involved in the relaxation of the adsorbate practically does not play any role.

According to these results, the adsorption is more favourable at the (2x2) surfaces terminated with dimers and it is stronger on the Ga atoms than on As atoms. The same trend had been found for the adsorption of methylthiolate on GaAs

(1 0 0).^[47] The adsorption energy decreases about 1 eV for the Ga-dimer (2x2) surface site compared to the adsorption on the Ga-dimer site of $\zeta(2x4)$ reconstructed surface. Both As-dimer sites of surfaces ((2x2) and $\beta 2(2x4)$) show similar adsorption energies. However, on the (2x2) dimerized surface the amount of active sites is larger and the gained energy per area is then larger too (see Supporting Information).

The functional groups (COOH and NH₂) seem to interact more strongly with the gallium than with arsenic atoms. Therefore, when different orientations of the approaching cysteine molecule are considered, the adsorption becomes stronger only on the (2x2) surface terminated in Ga-dimers, with a reduction in the energy between 0.15 and 0.4 eV.

The situation analysed here is valid for low coverage, where the intermolecular interactions are negligible. Indeed, in the (2x2) unit cells the distance between the S atom heads is 8.6 Å in both *x* and *y* directions. In the case of (2x4) and (4x2) unit cells, this distance is 8.6 Å in the *x* (*y*) direction and 17.2 Å in the *y* (*x*) direction, respectively. We have focused on the driving forces involved in the formation of the adsorbate - surface bonds. At higher coverage, further reorientations of the adsorbed species are expected due to the self-organization of the adlayer. In metallic substrates it is well known that at low coverage the adsorbed thiols show a larger tilt that facilitate the interaction of other functional groups^[1,44] with the surface, while at larger coverage the adsorbate stand up.

4. Correlation with experimental data

These results are in an excellent agreement with the XPS data. Comparing the optimized geometries of the most energetically favourable cysteine radical adsorption on the top of an As atom and on the Ga atom with the cysteine parallel to the surface, it is obvious that the amino group experiences a different environment at As- and Ga-sites. They should exhibit distinct binding energies in the N-1s core-level region as experimentally found.

Another solid proof is the considerably higher weight of the signal corresponding to the protonated species observed for the p-doped sample (Figure 2a). In aqueous solutions (pH 4.25) the zwitterions may not only be formed by lateral interactions but also adsorbed in such form. However, in the L-cysteine layers formed in ethanol solution, the zwitterions result solely by neighbour interactions. The DFT calculations show that on the Ga-sites the relative orientation of the two functional groups is clearly prohibitive to the formation of zwitterions, whereas on the As-sites, the relatively close positions of the -COOH and -NH₂ groups is visibly favourable to the internal proton transfer. As it was previously pointed out, we have used a sufficiently large unit cell in order to avoid the interaction between neighbouring cysteine radicals. A detailed investigation of the formation of hydrogen bonds and proton transfer between the COOH and NH₂ groups will be the objective of a further study.

As mentioned before, the lower value obtained for the I_{As}/I_{Ga} ratio at the p-doped (1.30 ± 0.01) substrate than that found at the n-doped samples (1.44 ± 0.01), points to a preferential bonding of the cysteine with As-sites in the first case and with

Ga-sites in the latter one. The lower weight of the As-O and Ga-O species found at the n-doped substrate brings a further proof in this respect. By comparing the energetically most favourable configurations of the cysteine formed at the Ga-sites and As-sites described above, it is pretty clear that the parallel orientation to the surface found for the Ga-bound species is expected to cover better the substrate surface than the perpendicular position on the As on-top sites. Therefore, the surface is less exposed for oxidation, as experimentally found.

5. Electronic properties

In order to characterize the electronic properties of the systems, we have calculated the electronic density difference resulting for the adsorption process, the charge transferred between adsorbate and substrate, and the changes on the dipole moment of the interfaces according to the usual procedures found in the literature.^[4,49] The electronic density difference was obtained from the electronic densities of the cysteine adsorbed on the surface ($\rho_{\text{System, relax}}$), the free GaAs surface ($\rho_{\text{Slab, fix}}$), and the free cysteine radical layer ($\rho_{\text{Cys-S, fix}}$):

$$\Delta\rho(x,y,z) = \rho_{\text{System, relax}} - \rho_{\text{Slab, fix}} - \rho_{\text{Cys-S, fix}} \quad (6)$$

It is important to notice that in the previous equation, the electronic density of the surface ($\rho_{\text{Slab, fix}}$) and of the cysteine radical ($\rho_{\text{Cys-S, fix}}$) were calculated using the same geometry that they have in the adsorbed system ($\rho_{\text{System, relax}}$). According to the equation (6), a depletion (accumulation) of electrons will correspond to negative (positive) values of density differences $\Delta\rho(x,y,z)$, and positive (negative) charges.

The integration over the *xy*-plane of the spatially density difference given by eq. (6) leads to the planar averaged electron density change induced by the adsorption at a given distance *z* to the surface:

$$\Delta\rho_{xy}(z) = \int_{\text{unit cell}} \Delta\rho(x,y,z) \, dx \, dy \quad (7)$$

The charge transferred up to a given *z* is obtained by a second integration:

$$Q(z) = \int_{z_0}^z \Delta\rho_{xy} \, dz \quad (8)$$

Finally, we have also analysed the surface dipole moment of the cysteine adsorbed on the surface, $\mu_{\text{Cys/surf}}$. This has three contributions:

$$\mu_{\text{Cys/surf}} = \mu_{\text{Cys-layer}} + \mu_{\text{surf}} + \Delta\mu \quad (9)$$

Here $\mu_{\text{Cys-layer}}$, μ_{surf} and $\Delta\mu$ are surface normal components of the dipole moment of the isolated cysteine layer, of the slab, and of the changes induced by the electronic interaction between adsorbate and substrate, respectively. The latter can be calculated from the planar averaged electron density change:

$$\Delta\mu = - \int_{z0}^{\text{vacuum}} \Delta\rho_{xy}(z) z \partial z \quad (10)$$

In equations (8) and (10) the lower integration limit $z0$ must be chosen deep in the bulk such that no changes in the electronic density are observed ($\Delta\rho_{xy}=0$). An important convention is to move the centre of the slab to $z=0$. The changes in the dipole moment are due to two factors: the creation of a surface dipole, and the changes in the molecular dipole. The last one could be the result of changes in the position or internal rotations of the functional groups in the molecule. The position of the molecule as a whole is also important in the final dipole moment change. Only the components of the dipole vector that are perpendicular to the surface will count on the calculation of $\Delta\mu$. A negative value of the change in the dipole means that the surface dipole is pointing to the surface, and a positive value of $\Delta\mu$ means that electronic charge has been transferred from the adsorbate to the substrate.

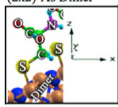




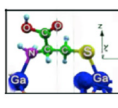




In order to discuss and analyse the bonding at the surfaces we shall use two tools that come from solid-state physics: projected density of states (pDOS), and crystal orbital overlap population (COOP). As it is well known, DOS provides information of how many crystalline orbitals or bands exist at a certain energy level.^[50] In this work, we shall use the projected DOS to disentangle the contribution of each orbital in each atom to the newly formed bonds. However, to determine the bonding/anti-bonding character of the bonds the COOP analysis will be used as described by Hoffmann.^[51] COOP provides the total overlap population, which is not identical to the bond order, but scales like it. Positive regions refer to bonding, while negative regions indicate anti-bonding. The amplitude of the curves depends on the number of states in that specific interval, the magnitude of the coupling overlap, and the size of the coefficients in the molecular orbital under consideration.

We have investigated the electronic properties only for the most stable systems: (2x2) As- and Ga-dimer terminated surfaces. Firstly, we shall show the surface normal component of the dipole moment induced by L-cysteine adsorption and analyze in details their contributions according to equation (9). The dipole values and orientations are given in Table 2 for both systems.

The dipole moment at the interfaces when the cysteine is adsorbed ($\mu_{\text{Cys/surf}}$) is mainly dominated by the dipole of the free surface (μ_{surf}). In both cases, i.e. the adsorption on As and Ga, the resulting dipole is negative implying that it is oriented to the surface. The sign of the dipole corresponding to the isolated layer is opposite to the dipole of the surface, but its magnitude considerably smaller.

Estimations of the total dipole of the free adsorbates are 2.47 and 2.77 D for the configurations corresponding to the adsorption on As and Ga, respectively. Their surface normal components are substantially smaller (0.50 and 0.70 D, respectively), probably due to the tilting of the adsorbate. Calculations using larger super cells do not show appreciable variations, indicating that possible depolarization effects caused by neighbouring adsorbates are absent. Therefore, the dipole of the substrate

Table 2. Dipole moments of the (2x2) As- and Ga-dimers terminated interfaces in the presence of adsorbed cysteine ($\mu_{\text{Cys/surf}}$), of the isolated cysteine layer ($\mu_{\text{Cys-layer}}$), of the substrate (μ_{surf}) in the supercell, and the difference ($\Delta\mu$) calculated from equation (9). The arrows indicate the orientation and their length are proportional to the dipole magnitude.

System:	$\mu_{\text{Cys/surf}}$ (D)	$\mu_{\text{Cys-layer}}$ (D)	μ_{surf} (D)	$\Delta\mu$ (D)
topAs/GaAs(100)-(2x2)-As Dimer 	-1.806 	+0.500 	-2.58 	+0.278 
topGa/GaAs(100)-(2x2)-Ga Dimer 	-3.46 	+0.695 	-3.59 	-0.564 

determines the resulting orientation. In the system containing As-dimers, there is an additionally induced interface dipole ($\Delta\mu$) oriented to the vacuum side, in contrast to the system containing Ga-dimers, where it is oriented to the surface. The dipole corresponding to the isolated layer is slightly larger for the L-cysteine configuration adsorbed on the interface terminated in Ga dimers. One reason for the preferential bonding of L-cysteine to As atoms at the p-GaAs(1 0 0) and to Ga atoms at the n-GaAs(1 0 0) observed in the XPS data may be originated in the interaction of the molecular dipole with the electrostatic field driven by the diffuse distribution of the semiconductor space charge region.

There is a difference of about -0.8 eV in the Fermi level energy of the p- and n-GaAs.^[12] The flat band potential values of the n and the p GaAs(1 0 0) are -1.28 V and 0.33 V (SCE) [see Figure S2 in Supporting Information]. The open circuit potential observed in the same solution was about 0 V (SCE). It can be assumed that the free carrier concentrations^[52] are zero, so that the surface space charge is equal to that of the majority-carrier.^[52]

The local charge balance and the position of the Fermi level at the surface are also tributary^[19] to the high densities of surface states usually present at GaAs surfaces. Beside the dopants, which introduce themselves electronic levels within the semiconductor band-gap,^[20,53] there are the antisite lattice defects, As_{Ga} and Ga_{As} ^[54] which are also involved in the band bending, i.e. the formation of the space charge layer. Therefore the experimental systems investigated are expected to be under depletion conditions.^[52] The semiconductor bands near the surface are hence bent up-wards at the n-GaAs junctions (dipole pointed out from the surface) and down-wards at the p-GaAs junctions (dipole pointed into the surface).

However, according to the calculations discussed above, the adsorption of cysteine favoured on Ga-sites at n-GaAs(1 0 0) and on As- at p-GaAs(1 0 0) cannot be attributed to the alignment of the dipoles. The upward band bending at the n-

GaAs(1 0 0) interface should favour the electron transfer from the adlayer to the substrate, while the magnitude of the barrier for electronic charge injection in the opposite direction should be larger. A similar analysis for the adsorption on As sites at p-GaAs(1 0 0) shows that the downwards band bending at this interface should facilitate the electron transfer from the substrate to the adlayer. According to the calculated induced interface dipole ($\Delta\mu$), the electron transfer, although small, should be facilitated to occur in opposite directions.

In order to obtain a better understanding of the systems and elucidate the contradiction mentioned above, we shall next analyse the electronic charge density changes occurring upon cysteine adsorption on both surfaces. Figures 6a and 7a show the spatial electronic density differences resulting when the cysteine is adsorbed on the As- and Ga-dimer terminated surfaces, respectively.

The electronic density difference $\Delta\rho(x,y,z)$ was calculated according to equation (6) and later integrated over the xy -plane using equation (7) to obtain the averaged $\Delta\rho_{xy}$ along the coordinate z normal to the surface (Figures 6b and 7b). An additional integration of $\Delta\rho_{xy}$ (equation (8)) gives the charge transferred between the substrate and the adsorbate up to a given distance z to the surface (Figures 6c and 7c). Finally, the induced dipole change $\Delta\mu$ along the z coordinate is calculated using equation (10). The profile of the contribution to the dipole change obtained by truncating the integration at different distances z from the surface is shown in Figures 6d and 7d.

Both Figures 6 and 7 show that the redistribution of electronic charge is not simple and it contains different regions of accumulation and depletion of electrons. There are displacements of electronic charge not only between the substrate and the adsorbate, but also within the molecule. It is interesting to compare both the change in the electronic density distribution around the atoms (a) and the net electronic density at different positions perpendicular to the surface obtained by the integration over the xy -plane (b). In the case of As-dimer as well as of Ga-dimer terminated surfaces, electrons are pushed down below the surface. However, the Ga–S bond seems to be different to that of As–S bond.

The As–S bond distance obtained for the adsorption of cysteine on GaAs(1 0 0) – (2x2) As-dimer terminated surface (2.28 Å) is very close to the sum of the covalent radii of As (1.208 Å) and S atoms (1.09 Å), suggesting a covalent bond.

On the As-dimer terminated surface (Figure 6), the As atom accumulates electrons under the surface level while it lost electrons above it. Similar isosurfaces have been obtained for the adsorption of alkanethiolates.^[53] Apparently, the sulphur atom lost electrons from the p_z orbital and gained electrons into the p_y orbital. This is confirmed by comparison of the DOS of the isolated radical and the adsorbed species, which shows an increase on the occupation of the p_y orbital by adsorption. After the integration in the xy -plane, the S atom seems to gain electrons. The analysis of the total electronic charge $Q(z)$ shows that below the upper As layer there is a net accumulation of electrons, but it is compensated just at the surface. Between the surface and the S atom takes place a depletion of the electronic charge, but it is again cancelled at the S atom. At larger

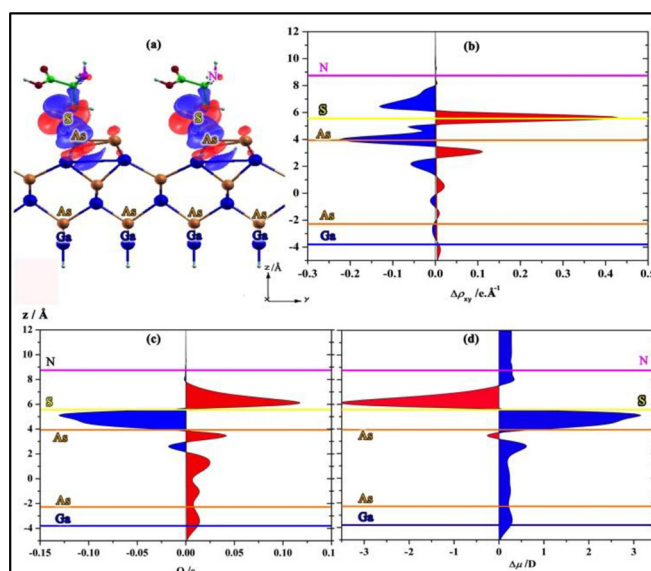


Figure 6. (a) Spatial view of the electronic density difference (eq. (6)) induced by the adsorption of cysteine on GaAs(1 0 0) – (2x2) As-dimer terminated surface. Isocontour value: $0.0017 \text{ e}\text{\AA}^{-3}$. (b) Averaged electronic density changes over the xy -plane (eq. (7)) at given distance z from the surface. (c) Total electronic charge transfer (eq. (8)) from the substrate to the adsorbate below z . (d) induced dipole change along the surface normal obtained by truncating the integration of eq. (10) at the corresponding position z . The colours lines indicate the position of the atoms labelled on (a). Blue (red) correspond to depletion (accumulation) of electronic charge.

distances appears once again an excess of electrons, which finally vanish below the N atom. The C–S bond of the organic chain is only slightly affected. No change in the electronic density is observed around the carboxyl group oriented away from the surface. Thus these electronic charge oscillations indicate that the adsorption takes place through a primarily covalent bond but with a weak ionic character involving a small electronic charge displacement to the substrate. This behaviour is reflected in the dipole moment change: its magnitude is small ($\Delta\mu = +0.278 \text{ D}$), and it points away from the surface. However, it is interesting also to analyse the profile of the dipole change (Figures 6d and 7d). Actually, it is negative in the region above the S atom, showing a sharp peak of about -3.5 D . The depletion of electrons just below the N atom produces a sudden decrease turning it slightly positive at large distances from the surface. We have to notice that the dipole is weighted by the distance z (see equation (7)). Therefore, the depletion of electrons in the outer “tail” region due to the rearrangement of electronic charge density inside the cysteine, when weighted by z , is sufficient to turn the sign of $\Delta\mu$ from negative to positive.

On the Ga-dimer terminated surface the situation is still more complex since both S and N atoms contribute to the bond with the substrate. Figure 7a shows an important accumulation of electronic charge density between the Ga and S atoms, which is typical for a strong covalent bond. This feature is different from the electronic redistribution in the formation of the As–S bond discussed above. Comparing the occupation

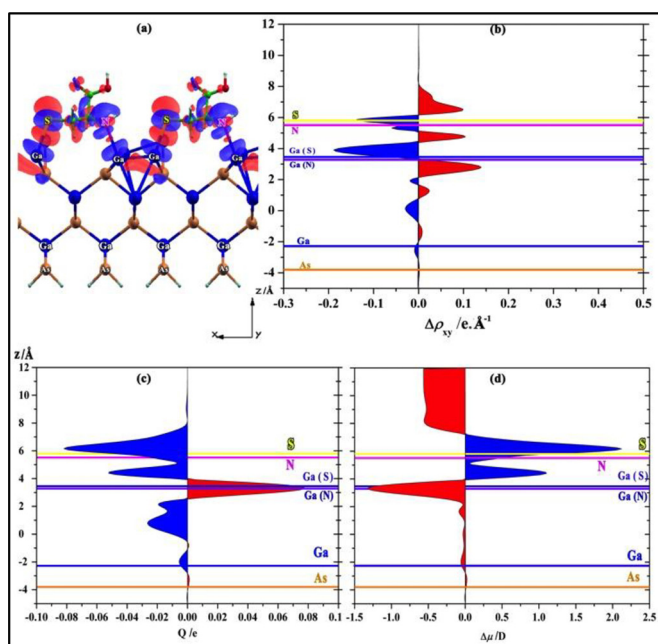


Figure 7. (a) Spatial view of the electronic density difference (eq. (6)) induced by the adsorption of cysteine on GaAs(1 0 0) – (2x2) Ga dimer terminated surface. Isocontour value: $0.0017 \text{ e}\text{\AA}^{-3}$. (b) Averaged electronic density changes over the xy -plane (eq. (7)) at given distance z from the surface. (c) Total electronic charge transfer (eq. (8)) from the substrate to the adsorbate below z . (d) induced dipole change along the surface normal obtained by truncating the integration of eq. (10) at the corresponding position z . The colours lines indicate the position of the atoms labelled on (a). Blue (red) correspond to depletion (accumulation) of electronic charge.

obtained from the difference between the DOS of the free radical and the adsorbed species, it shows an increase on the occupation of the p_z orbital by adsorption in agreement with the picture of electronic charge differences. The Ga–N bond also changes the electronic charge density difference in the plane, however its accumulation between both atoms is less than between Ga and S atoms, indicating a weaker bonding. It is noticeable that the electronic distribution around S and N atoms seems to be opposite (see Figure 7a). Near the N atom there is an accumulation while near the S atom there is a depletion of electrons, which is consistent with the larger electronegativity of nitrogen. The C–S bond shows a small increase of the electronic charge density toward the surface. As a result of this complex redistribution, the dipole moment change is completely different than in the As-dimer surface sites. The dipole now points in the opposite direction (to the surface), and its value is: -0.564 D , indicating a slight electronic charge transfer from the substrate to the adsorbate. Similar to the situation for the adsorption on As-dimer surfaces sites, the changes in the induced dipole (Figure 7d) at different distances from the surface show an interesting pattern. Here, the value of $\Delta\mu$ just over the S atom is about $+2.2 \text{ D}$. However, the redistribution of electronic charge inside the cysteine at large distances (accumulation electron “tail” in Figures 7b) produces the sudden decrease of $\Delta\mu$ and turn its sign from positive to negative.

According to the discussion given above, the analysis of the sign of the total induced dipole change is not enough to predict an effect of the doping on the preferential site for adsorption. The complexity observed on the redistribution of the electronic charge makes it difficult. It is not clear, how far away should extend the interaction between the dipole resulting from the space charge at the interface of the semiconductor surface and the dipole induced by the adsorption. If the range of influence is restricted only to the bond between the S-head and the surface, there is no contradiction with the experimental finding that cysteine preferentially adsorbs on Ga-sites for n-doped and on As-sites for p-doped GaAs(1 0 0).

However, we have to stress that it is not simple to model the doping of a semiconductor. In our case, in order to correlate the favoured adsorption on Ga and As site, it would require a detailed study of the adsorption process in the presence of an electrical field that mimics the space charge region. Such investigations are outside of the scope of the present work and shall be addressed in the future.

6. COOP and pDOS Analysis

Finally, we have calculated the projected density of states (pDOS) and carried out the COOP analysis for the most stable L-cysteine configuration on the (2x2) As- and Ga-dimer terminated surfaces (Figure 8). At the bottom, we show the total

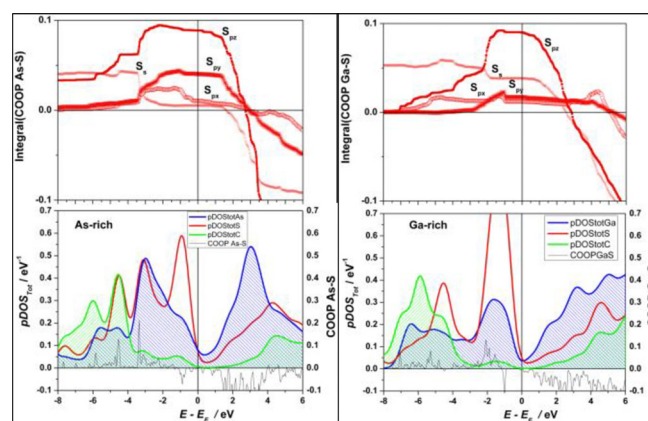


Figure 8. Upper part: Integrated COOPs obtained from the interactions between components of different electronic states of the S atom and the surface atoms (left: As, right: Ga). Bottom: Projected density of states on the S-head (red lines) of L-cysteine adsorbed on As-sites (left) and Ga-sites (right). Also are shown: the electronic states participating in the bond projected onto the surface atoms (As and Ga) (blue lines) and the electronic states of the first C (green lines) participating in the bond with the S atom. The patterns of black lines correspond to the COOP of the systems. The vertical line indicates the position of the Fermi level.

density of states projected onto the atoms most involved in the bonds between the adsorbate and the surface: S and As (Ga) atoms. Also, we show the electronic states corresponding to the C bonded to the S, and the COOP analysis for the S–As (Ga) bonds. The integrated COOPs are shown at the upper part

of the Figure 8. The overlap between S and C states located below -4 eV relative to the Fermi level mainly corresponds to the bond between these two atoms. Above -4 eV, the overlap between electronic states of the surface atoms and those of the S becomes evident. A more detailed analysis of the components s , p_x , p_y and p_z shows the contributions to the bond of these orbitals and their character (bonding / anti-bonding). For the adsorption on both sites (As and Ga) the main contribution to the bond is that of the orbital p_z of the S atom.

Besides, in the case of the As–S bond, the states of the p_y orbital of the S atom also participate in the bond with bonding character. In contrast, the s and p_x states show anti-bonding interactions below the Fermi level, which weakens the bond. This is not the case for the adsorption on Ga sites, where especially the s -states of the S contribute to the bond with the surface. These results are in agreement with the energetics of the systems discussed previously, which have shown that the adsorption energy on Ga sites is more favourable. Nevertheless, the majority of anti-bonding states are mainly located above the Fermi level.

Conclusions

The XPS data pointed to distinct configurations of the functional groups of the adsorbed species depending on the dopant nature and indicated the prevalence of the As-bond species at the p-doped and of the Ga-bond species at the n-doped substrates. The density-functional theory calculations performed for cysteine adsorption on both Ga- dimer terminated and As- dimer terminated surfaces showed that the most stable configurations involved cysteine adsorbed on top of both As atoms or Ga atoms of the dimer. However, the optimized configurations found by the rotation of the L-cysteine molecule showed that an important contribution for the stabilization of the adsorbate comes from the interaction of the other two functional groups with the surface. The adsorption energy is stronger on Ga-dimers surface-sites, where the cysteine has both S–Ga and N–Ga bonds. This is in agreement with the XPS results, which indicate a strong interaction of the amine group with the surface when the adsorption preferentially takes place on Ga-sites. However, the weaker interaction of cysteine with As-sites involving only the thiol head should favour the mutual interaction between the other functional groups. Therefore, it is expected that at higher coverage the interaction between neighbouring should be the driving force for the adsorption process and self-organization. In this case, the formation of zwitterion species by interaction between neighbouring is more probable.

The energetics and the Ga(As)-S bond distances obtained by DFT are very close to previous results for the adsorption of alkanethiols and hydrogen sulphide,^[48,55] indicating the local character of this bond.

The different optimized configurations of the most stable cysteine species formed at Ga-sites and As-sites found in the DFT calculations are in a very good agreement with the XPS results. Although at the first view the sign of the total induced dipoles cannot explain the preferential adsorption on Ga-sites

in the case of n-GaAs(1 0 0) surfaces and on As-sites in the case of p-GaAs(1 0 0) surfaces, a more detailed analysis of the complex redistribution of the electronic charge between the adsorbate and the substrate throw some light on this contradiction. Strong oscillations of electronic charge and the concomitant sharp changes in the dipole direction in the region of the bond between the S and As (Ga) make it difficult to understand the distinct interaction of the induced dipole by the adsorbed species with the electrostatic field driven by the diffuse distribution of the semiconductor space charge region. If we consider only the region localized up to just above the S atom, $\Delta\mu(z)$ is large and negative (positive) for the adsorption on As (Ga) sites, respectively, which could explain the prevalence of the As-bond cysteine species at the p-doped samples and that of the Ga-bond cysteine species at the n-doped samples observed experimentally.

Supporting Information

Experimental details. Computational technicalities of the DFT calculations. Optimized systems with geometrical parameters of the adsorbed cysteine radical on GaAs(1 0 0) surfaces. Summary of the self-consistent fitting procedure applied to the As-3d and Ga-3d XPS spectral region at L-cysteine-thiolate covered p- and n-GaAs(1 0 0). As-3d and Ga-3d, XPS-spectra in core-level regions for bare p- and n-GaAs(1 0 0) surfaces exposed in air. Mott-Schottky plots for p- and n-GaAs(1 0 0) electrodes.

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-ID-PCE-2011-3-0304 and it is part of the research network financed by the Deutsche Forschungsgemeinschaft FOR1376. Financial support by PICT-2012-2324 (Agencia Nacional de Promocion Cientifica y Tecnologica, FONCYT, préstamo BID) and PIP-CONICET 112–201001-00411 (Consejo Nacional de Investigaciones Cientificas y Técnicas, CONICET) and a generous grant of computing time from Baden-Württemberg grid are also gratefully acknowledged.

Keywords: Adsorption · DFT · GaAs(100) · L-cysteine · XPS

- [1] D. Costa, C.–M. Pradier, F. Tielens, L. Savio, *Surface ScienceReports* **2015**, *70*, 449–553.
- [2] R. Di Felice, A. Selloni, *J. Chem. Phys.* **2003**, *120*, 4906 – 4914.
- [3] R. Di Felice, A. Selloni, E. Molinari, *J. Phys. Chem. B* **2003**, *107*, 1151 – 1156.
- [4] B. Höffling, F. Ortmann, K. Hannewald, F. Bechstedt, *Phys. Rev. B* **2010**, *81*, 045407.
- [5] E. Santos, L. B. Avalle, R. Scurtu, H. Jones, *Chem. Phys.* **2007**, *342*, 236 – 244.
- [6] E. Santos, L. B. Avalle, K. Potting, P. Velez, H. Jones, *Electrochim. Acta* **2008**, *53*, 6807 – 6817.
- [7] N. B. Luque, P. Velez, K. Potting, E. Santos, *Langmuir* **2012**, *28*, 8084 – 8099.
- [8] N. B. Luque, E. Santos, *Langmuir* **2012**, *28*, 11472 – 11480.
- [9] K. R. Koswattage, K. Hiroumi, Y. Nakayama, H. Ishii, in *Advances in Future Manufacturing Engineering - Yang (Ed.) CRC Press. Taylor & Francis Group, London* **2015**, pp. 19-23.

- [10] R. Maul, F. Ortmann, M. Preuss, K. Hannewald, F. Bechstedt, *J. Comput. Chem.* **2007**, *28*, 1817–1833.
- [11] V. Lazarescu, A. M. Toader, M. Enache, L. Preda, M. Anastasescu, G. Dobrescu, C. Negrila, M. F. Lazarescu, *Electrochim. Acta* **2015**, *176*, 112–124.
- [12] L. Frolov, Y. Rosenwaks, S. Richter, Ch. Carmeli, I. Carmeli, *J. Phys. Chem. C* **2008**, *112*, 13426–13430.
- [13] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, Ö. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, **2003**, Gaussian, Inc., Pittsburgh.
- [14] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- [15] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213–222.
- [16] C. Amovilli, V. Barone, R. Cammi, E. Cancès, M. Cossi, B. Mennucci, C. S. Pomelli, J. Tomasi, *Adv. Quantum Chem.* **1998**, *32*, 227–261.
- [17] M. W. Wong, M. J. Frisch, K. B. Wiberg, *J. Am. Chem. Soc.* **1991**, *113*, 4776–4782.
- [18] C. B. Duke, *Chem. Rev.* **1996**, *96*, 1237–1259.
- [19] W. Mönch, in *Semiconductor Surfaces and Interfaces*, Springer-Verlag, Berlin, **1995**.
- [20] S.-H. Lee, W. Moritz, M. Scheffler, *Phys. Rev. Lett.* **2000**, *85*, 3890–3893.
- [21] D. W. Pashley, J. H. Neav, B. A. Joyce, *Surf. Sci.* **2005**, *582*, 189–201.
- [22] W. G. Schmidt, S. Mirbt, F. Bechstedt, *Phys. Rev. B* **2000**, *62*, 8087–8091.
- [23] C. Kumpf, L. D. Marks, D. Ellis, D. Smilgies, E. Landemark, M. Nielsen, R. Feidenhans, J. Zegenhagen, O. Bunk, J. H. Zeysing, Y. Su, R. L. Johnson, *Phys. Rev. Lett.* **2001**, *86*, 3586–3589.
- [24] C. Kumpf, D. Smilgies, E. Landemark, M. Nielsen, R. Feidenhans, O. Bunk, J. H. Zeysing, Y. Su, R. L. Johnson, L. Cao, J. Zegenhagen, B. O. Fimland, L. D. Marks, D. Ellis, *Phys. Rev. B* **2001**, *64*, 075307–075317.
- [25] M. Koinuma, K. Uosaki, *J. Electroanal. Chem.* **1996**, *409*, 45–50.
- [26] K. Uosaki, M. Koinuma, N. Sekine, S. Ye, *ACS Symposium Series*, **1997**, *656*, 189.
- [27] H. Yao S.-L. Yau, K. Itaya, *Appl. Phys. Lett.* **1996**, *68*, 1473–1475.
- [28] C. L. McGuinness, A. Shaporenko, M. Zharnikov, A. V. Walker, D. L. Allara, *J. Phys. Chem. C* **2007**, *111*, 4226–4234.
- [29] E. Antonides, E. C. Jose, G. A. Sewatzky, *Phys. Rev. B* **1977**, *15*, 1669–1679.
- [30] E. D. Lu, F. P. Zhang, S. H. Xu, X. J. Yu, P. S. Xu, Z. F. Han, F. Q. Xu, X. Y. Zhang, *Appl. Phys. Lett.* **1996**, *69*, 2282–2284.
- [31] T. Hou, C. M. Greenleaf, S. W. Keller, L. Nelen, J. F. Kauffman, *Chem. Mater.* **1997**, *9*, 3181–3186.
- [32] G. Dodero, L. De Michieli, O. Cavalleri, R. Rolandi, L. Oliveri, A. Dacca, R. Parodi, *Colloids and Surfaces A* **2000**, *175*, 121–128.
- [33] G. Gonella, S. Terreni, D. Cvetko, A. Cossaro, L. Mattera, O. Cavalleri, R. Rolandi, A. Morgante, L. Floreano, M. Canepa, *J. Phys. Chem. B* **2005**, *109*, 18003–18009.
- [34] V. De Renzi, L. Lavagnino, V. Corradini, R. Biagi, M. Canepa, U. Del Pennino, *J. Phys. Chem. C* **2008**, *112*, 14439–14445.
- [35] I. Feliciano-Ramos, M. Caban-Acevedo, M. Aulice Scibioh, C. R. Cabrera, *J. Electroanal. Chem.* **2010**, *650*, 98–104.
- [36] J. Won Kim, H.-N. Hwang, C.-C. Hwang, *J. Phys. Chem. C* **2007**, *111*, 13192–13196.
- [37] Y. Jun, X.-Y. Zhu, J. W.P. Hsu, *Langmuir* **2006**, *22*, 3627–3632.
- [38] C. L. McGuinness, G. A. Diehl, D. Blasini, D.-M. Smilgies, M. Zhu, N. Samarth, T. Weidner, N. Ballav, M. Zharnikov, D. L. Allara, *ACS Nano* **2010**, *4*, 3447–3465.
- [39] T. Aqua, H. Cohen, O. Sinai, V. Frydman, T. Bendikov, D. Krepel, O. Hod, L. Kronik, R. Naaman, *J. Phys. Chem. C* **2011**, *115*, 24888–24892.
- [40] B. A. Cowans, Z. Dardas, W. N. Delgass, M. S. Carpenter, M. R. Melloch, *Appl. Phys. Lett.* **1989**, *54*, 365–367.
- [41] J. S. Ha, S.-J. Park, S.-B. Kim, E.-H. Lee, *J. Vac. Sci. Technol. A* **1995**, *13*, 646–651.
- [42] G. Neshet, A. Vilan, H. Cohen, D. Cahen, F. Amy, C. Chan, J. Hwang, A. Kahn, *J. Phys. Chem. B* **2006**, *110*, 14363–14371.
- [43] L. Preda, C. Negrila, M. F. Lazarescu, M. Enache, M. Anastasescu, A. M. Toader, S. Ionescu, V. Lazarescu, *Electrochimica Acta* **2013**, *104*, 1–11.
- [44] O. Voznyy, J. J. Dubowski, *Langmuir* **2008**, *24*, 13299–13305.
- [45] T. P. Huang, T. H. Lin, T. F. Teng, Y. H. Lai, W. H. Hung, *Surf. Sci.* **2009**, *603*, 1244–1252.
- [46] S. Gronert, R. A. J. O'Hair, *J. Am. Chem. Soc.* **1995**, *117*, 2071–2081.
- [47] W. Gao, S. E. Zhu, M. Zhao, *J. Mater. Sci.* **2011**, *46*, 1021–1026.
- [48] O. Voznyy, J. J. Dubowski, *J. Phys. Chem. B* **2006**, *110*, 23619–23622.
- [49] S. Yanagisawa, K. Lee, Y. Morikawa, *J. Chem. Phys.* **2008**, *128*, 244704.
- [50] A. Gross, in *Theoretical Surface Chemistry. A microscopy perspective*. Springer Verlag: Berlin Heidelberg, **2009**.
- [51] R. Hoffmann, in *Solid & Surface: A Chemist's View of Bonding in Extended Structures*. First ed., Wiley-VCH, New York, **1989**.
- [52] S. M. Sze, K. K. Ng, in *Physics of Semiconductor Devices*. 3rd Ed., Ch. 1.5.8, Wiley Interscience, John Wiley & Sons, Inc., Hoboken, New Jersey, **2007**.
- [53] L. Zhang, W. E. McMahon, S.-H. Wei, *Appl. Phys. Lett.* **2010**, *96*, 121912–121914.
- [54] J. E. Northrup, S. B. Zhang, *Phys. Rev. B* **1993**, *47*, 6791–6793.
- [55] O. Voznyy, J. J. Dubowski, *J. Phys. Chem. C* **2008**, *112*, 3726–3733.

Submitted: May 23, 2016

Accepted: July 26, 2016