Structural Phases of Alkanethiolate Self-Assembled Monolayers (C_{1-12}) on Cu[100] by Density Functional Theory

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Abstract

The structure and as such the properties of alkanethiolate self-assembled monolayers (SAMs) on metal surfaces depend on the surface structure, thiolate coverage and chain length. The chain length dependence of alkanethiolate phases on Au surfaces is extensively documented. Much less insight exists for alkanethiolate SAMs on Cu surfaces, despite the relevance for area-selective deposition (ASD) applications. This work therefore studies the phase behavior of alkanethiolates on Cu through density functional theory (DFT) modelling. Short chain thiols ($C_{1,2}$) display no phase behavior and their saturation coverage is determined by steric hindrance. Longer thiols ($C_{6,12}$) show distinct lying-down and standing-up phases. The substrate-adsorbate interactions become weaker with increasing thiolate content, but still dominate in the standing-up phase at the saturation content of $5.1 \cdot 10^{14}$ thiols cm^{-2} . This is in contrast to Au[100] surfaces, where intermolecular interactions dominate at the saturation content, which is slightly higher than that on Cu[100]. The saturation coverage seems to be determined primarily by steric hindrance, which in turn will depend on the lattice parameter of the surface. We conclude that insights for alkanethiolate SAMs on Au cannot necessarily be transferred to Cu.

Introduction

Self-assembled monolayers (SAMs) are supramolecular assemblies, which form spontaneously into well-ordered structural phases. SAMs are of interest for many chemical and nanotechnological applications.^{1,2} In addition, the use of SAMs as passivation layer in area-selective deposition (ASD) has recently been proposed.^{3,4} ASD is an upcoming approach aimed at overcoming challenges related to the fabrication of nano-electronic devices, such as edge placement errors and resolution limits.⁴⁻⁶ For example, deposition of dielectrics on dielectrics selective to Cu is under investigation in the context of advanced interconnect structures.⁷ ASD has also been demonstrated successfully for tone inversion patterning.^{5,6}

Alkanethiols bind selectively to metal versus dielectric surfaces.¹ The SAM forms only on Cu and prevents interaction between the metal and the gas phase precursors in atomic layer deposition (ALD) and chemical vapor deposition (CVD).^{4,8} In order to be suitable as passivation layer, the SAM should be stable and unreactive towards the precursors at the temperature of deposition. A number of ALD and CVD precursors are indeed unreactive toward alkyl termination.⁴ In addition, the SAM should be a continuous and dense layer, effectively blocking access of the precursors to the Cu surface.^{9,10} However, the formation of a continuous and dense monolayer on the Cu surface is not straightforward.^{11,12} Selectivity loss may occur at too low surface coverage due to ineffective blocking. At too high surface coverage, multilayer formation may contribute in vacuum deposition,¹³ and reaction between unreacted thiol groups and the precursors may contribute to selectivity loss. Structural information about thiolate SAMs on Cu surfaces, e.g. saturation coverage, density and thickness, can contribute to the optimization of selectivity of ASD processes.

While countless studies on Au/thiolate SAMs exist, the number of fundamental studies on the structure of Cu/thiolate SAMs is limited due to the higher reactivity of Cu and the difficulty in obtaining clean and atomically flat Cu surfaces.¹ According to the general model for thiolate SAM formation on Au, a number of distinct structural phases are formed as the thiolate surface content increases.¹⁴ At low thiolate content, when the intermolecular distance is much larger than the molecular diffusion length, individual thiolate molecules lie flat on the surface, and stabilization arises from thiolate-surface

interactions. Short thioliates therefore do not form ordered phases at low surface content. At increasing thiolate content, the thioliates form aggregates to maximize dispersive intermolecular interactions. Lying-down and standing-up phases can coexist, and the structure depends on the chain length and the deposition conditions. The saturation coverage at which a fully ordered monolayer forms depends on the chain length. For instance, methanethiolate on Au[111] saturates in the (3x4) phase, while longer thioliates saturate at the $(\sqrt{3}\times\sqrt{3})R30^\circ$ or c(4x2) phase.¹⁵

However, the insight from Au can not necessarily be transferred to Cu, as the SAM structure, its phase behavior and the chain length dependence depend on the surface structure as well as the nature of the interaction between surface and head group. Au and Cu have different lattice parameters (2.87 Å for Au versus 2.55 Å for Cu) and stable Au and Cu surfaces have different symmetries (Au[111] versus Cu[100]). In addition, the Cu-S bond is more ionic than the Au-S bond.^{16, 17} Some observations of Cu/thiolate SAMs indeed point towards differences with Au/thiolate SAMs.¹⁸⁻²¹ The saturation coverage and phases are different for thiolate formation on the Au[100] and Cu[100] surfaces, partly due to differences in surface reconstruction. The (2x7) and $(\frac{1}{7} \times \frac{1}{6})$ phases as observed on Au were not found on Cu[100].^{19, 22, 23} On Au, a stable c(2x2) phase has been observed even for long thioliates, which we will show to be impossible on Cu in this paper.²⁴

This reveals the need to increase fundamental understanding of the alkanethiolate SAM structure and phase behavior on the industrially relevant Cu surface. Computational studies are an ideal tool to obtain atomistic insight. However, computational studies on Cu/thiolate SAM structure have so far considered only methane- and ethanethiolate, while longer thioliates (e.g. undecanethiolate) are relevant for ASD. These longer thioliates are known to behave different than their shorter counterparts.^{25,26} In addition, density functional theory (DFT) does not implicitly incorporate long range dispersion interactions. Nonetheless, these interactions are known to be crucial in self-assembly. A dispersion correction seems indispensable to adequately model these systems, yet, to the best of our knowledge, no such studies on Cu/thiolate SAM systems exist in the literature, while their successful application has been demonstrated on similar systems.²⁷⁻²⁹ Finally, many studies use cluster models to mimic interactions between surfaces and adsorbates.

However, cluster models that contain few Cu atoms cannot accurately predict the electronic structure of metal surfaces and cannot describe the surface reconstruction and relaxation of Cu surfaces.^{30, 31}

Therefore, this paper investigates the structure, energetics and coverage-dependent phase behavior of thiolates with different chain lengths (C_{1-12}), using dispersion corrected periodic DFT calculations. First, we propose structural models for different surface coverages and chain lengths. Second, we assess the impact of coverage and chain length on the stability of the structural phases and analyze the impact of intermolecular and substrate-adsorbate interactions. Finally, we discuss the thermodynamics of and transition between SAM phases.

Computational Details

We studied alkanethiolate SAMs on Cu[100] using periodic plane wave DFT as implemented in the Quantum Espresso (6.3) package.^{32, 33} These calculations were performed with periodic boundary conditions in three dimensions. The Perdew-Burke-Ernzerhof functional (PBE) was used to describe exchange and correlation.^{34, 35} PBE-specific relativistic projector augmented wave method (PAW) pseudopotentials were used for all elements. Long range dispersion interactions were included through the robust Grimme-D3 method, which has been shown to deliver quantitative structural and energetic results for commensurate meso-tetraalkylporphyrin SAMs.³⁶⁻³⁹

The kinetic energy cutoff was 50 Ry; the charge density cutoff 225 Ry. K points were distributed along Monkhorst-Pack grids. The cells were deemed large enough for the relaxations to be carried out at the Γ point level for the tetragonal cells ((4x4), c(4x4), (2x2), c(2x2)), while 3x1x1 k points were used for the orthorhombic cell (c(2x6)). The force convergence threshold was 10^{-3} Ry/ a_0 or better. Energies were obtained by SCF calculations at higher k point levels. SCF calculations of the tetragonal cell used 4x4x1 k points, the orthorhombic cell 7x2x1. SCF calculations had a convergence threshold of 10^{-7} Ry. Calculations of the bulk Cu atomic energy were facilitated by using Quantum Espresso's face centered cubic symmetry considerations and used 8x8x8 k points.

Marzari-Vanderbilt smearing at 0.02 Ry facilitated convergence for all systems.⁴⁰ For spin polarized systems, the local spin density approximation was assumed and spin symmetry was broken. All parameters were converged with respect to the change in total electronic energy.

The (4x4), c(4x4), (2x2) and c(2x2) phases used a tetragonal 10.2×10.2×35.7 Å³ cell. The c(2x6) unit cell symmetry required the use of an orthorhombic 5.1×15.3×36 Å³ cell. The cells contained four layers of a [100] oriented Cu slab, of which the bottom layer was fixed to simulate bulk behavior with the bulk in-plane lattice parameter 2.55 Å.⁴¹ All cells contained approximately 30 Å of vacuum between Cu slabs to avoid spurious interactions. For the longest molecules, dodecanethiolate in the c(2x2) phase, this results in 12 Å of vacuum between the molecules and the next Cu slab.

The chemical potential of the gaseous molecules was calculated based on their translational and rotational partition functions. For the rotational part, the necessary rotational constants were determined from structures optimized in Gaussian 16 at the B3LYP/6-31G(d) level.

Results and Discussion

Atomic Models

First, we introduce the model systems studied in this work. We model methane-, ethane-, hexane-, and dodecanethiolate on the Cu[100] surface at different coverages. The thiolate coverage is expressed in fractional monolayers (ML) as $\frac{\# \text{ thiolates}}{\# \text{ surface metal atoms}}$ (1). Thus, the coverage can be linked to thiolate surface content by using the Cu[100] surface density of $\sim 1.54 \cdot 10^{15} \text{ at} \cdot \text{cm}^{-2}$.

The choice of the [100] surface is motivated by its known stability compared to other crystallographic planes. Unlike the often-studied [111] surface, the [100] oriented surface is stable with regard to major reconstructions.^{42, 43}

To model low surface coverages, we introduce two hypothetical phases: a 0.0625 ML (4x4) phase and a 0.125 ML c(4x4) phase. At such low coverages, long range ordered phases are unlikely to form for short chain thioliates. The large intermolecular distances (> 1 nm) allow us to approximate isolated molecules on the surface. At an intermediate

coverage of 0.25 ML, experimental studies reveal an organized (2x2) phase.⁴⁴ At a slightly higher coverage of 0.33 ML, a c(2x6) phase dominates.^{42, 45} Below 200 K, an even higher thiolate content of 0.5 ML can be obtained with an undistorted c(2x2) phase for methanethiolate.⁴⁶ These phases are shown in Figure 1. Some structural parameters are collected in Table 1. A validation of the computational approach for these structures, as well as a discussion on the change in density of states upon chemisorption can be found in the supporting information (*Method validation* and *Density of states*).

Table 1. Structural parameters of thiolate SAMs in the (2x2) and c(2x6) phases, averaged over the unit cell. $d_{\text{Cu-S}}$ is the Cu-S bond length. The tilt angle is the angle between surface normal and alkyl backbone. If two significantly inequivalent tilt angles are found, both are shown.

Thiolate	$d_{\text{Cu-S}}$ (Å)		Tilt angle (°)	
	(2x2)	c(2x6)	(2x2)	c(2x6)
Methane	2.30	2.32	--	--
Ethane	2.30	2.38	39.4	14.5/52.8
Hexane	2.31	2.37	23.5	22.2
Dodecane	2.30	2.38	27.2	22.3

Figure 1. Phases of methanethiolate on the Cu[100] surface (top view). The Cu[100] surface has 1.54×10^{15} at/cm² in the top layer. The coverages of the phases are: 0.0625 ML (4x4), 0.125 ML c(4x4), 0.25 ML (2x2), 0.33 ML c(2x6), 0.5 ML c(2x2).

Currently, the exact structure of the c(2x6) phase remains under scrutiny.^{9, 18, 21, 31, 47} The c(2x6) phase has a rectangular unit cell, while the other phases have a square unit cell. Proposed descriptions include a buckled c(2x2) phase, a faulted-row c(2x2) phase and an adatom-rich dimer phase.^{18, 46, 47} The buckled c(2x2) description of the c(2x6) phase has been shown to be unstable.³¹ The remaining two structures are included in Figure 2.

Figure 2. Methanethiolate c(2x6) structures. Left: faulted-row. Right: adatom-rich, with 2 adatoms per unit cell.

To understand the stability of the different phases, we calculated the energies required to form the adatom-rich structure from the faulted-row structure by moving Cu atoms from the bulk to the surface, as in the following reaction:

In addition, we looked at forming the adatom-rich c(2x6) phase from an adatom-free (2x2) phase, in which again Cu atoms were moved from the bulk to the surface:

Formation of an adatom rich c(2x6) structure from the faulted-row structure is endothermic for methanethiolate by 202.3 kJ/mol per unit cell. This result indicates that the adatom-containing phase is destabilized when compared to the adatom-free case. The same picture is obtained when looking at the transition from the adatom-free (2x2) structure to the adatom-rich c(2x6) structure, which is endothermic by an average of 70.7 kJ/mol per added thiolate. This is in stark contrast to the energy associated with the transition from the adatom-free (2x2) phase to the adatom-free faulted-row c(2x6) phase, which is exothermic by -69.9 kJ/mol per added thiolate (see Table 2). Therefore, the existence of the adatom-rich c(2x6) phase as proposed by Yang et al. for short chain thioliates is not supported by our calculations.¹⁸ As a result, we will only discuss the faulted-row c(2x6) phase in the remainder of this paper.

In summary, we will study the low content (4x4) and c(4x4) phases, the (2x2) phase, the faulted-row c(2x6) phase and the c(2x2) phase. The phases are illustrated in Figure 1 for methanethiolate.

Chemisorption and driving forces

Next, we assess the impact of coverage and chain length on the stability of the structural phases and analyze the impact of intermolecular and substrate-adsorbate interactions. In the following paragraph we will therefore first discuss the formation reaction of Cu/thiolate SAMs for the model systems discussed above. The surface free energy will be used as a guide to investigate the thermodynamic stability of the different phases as function of

coverage and chain length. The chemisorption of alkanethiolates is modeled according to the following reaction:

The chemisorption energy is defined as:

$$\Delta E_{chem} = \frac{1}{m} E_{\text{Cu}(-\text{SR})_m} + \frac{1}{2} E_{\text{H}_2} - E_{\text{HSR}} - \frac{1}{m} E_{\text{Cu}_{[100]}} \quad (5)$$

with $E_{\text{Cu}(-\text{SR})_m}$ the energy of the adsorbed thiolate, E_{H_2} the energy of the hydrogen molecule, E_{HSR} the energy of the thiol molecule in vacuum and $E_{\text{Cu}_{[100]}}$ the energy of the Cu slab. ΔE_{chem} is the chemisorption energy of a single thiol and is averaged over all thiols in the unit cell.

To compare phases with different coverages, the most insightful approach is to compare the corresponding surface free energies γ , instead of the chemisorption energies.²⁹ This approach automatically accounts for the fact that different phases correspond to unit cells of different size. Hence, we have computed relative values of $\Delta\gamma$ for the different coverages relative to the clean surface, with reference to the formation reaction (eq. 4):

$$\Delta\gamma(T,p) \cong \frac{m}{A} (\Delta E_{chem} + \mu_{\text{HSR}}(T,p) - \frac{1}{2} \mu_{\text{H}_2}(T,p))$$

where m is the number of thiols, A is the area of the unit cell, μ_{HSR} is the chemical potential of the gas-phase thiols and μ_{H_2} is the chemical potential of gas-phase H_2 .

The chemical potentials are calculated as follows:

$$\mu_{\text{HSR}}(T,p) = \mu_{\text{HSR}}^{gas}(T,p^0) + k_B T \ln\left(\frac{p}{p^0}\right)$$

where $\mu_{\text{HSR}}^{gas}(T,p^0)$ contains the translational and rotational contribution to the free energy at 1 bar. Vibrations contributions for the gas-phase thiol and hydrogen, the chemisorbed thiolate and the metal substrate are assumed to cancel out, as suggested in previous studies.^{23, 29} The temperature is set to 353.15 K and the thiol partial pressure to $1 \cdot 10^{-3}$ bar, conditions used in our experiments for undecanethiolate deposition. All gaseous H_2 in the gas phase is expected to be generated by the chemisorption reaction, and the thiol is present in large excess. We therefore take the partial pressure of H_2 to be -somewhat

arbitrarily- two orders of magnitude lower than for thiolate, i.e. $1 \cdot 10^{-5}$ bar. Variations in the partial pressure do not change the relative stability of the phases at constant temperature, except for methanethiolate at very low partial pressures, i.e. below $1 \cdot 10^{-7}$ bar, where the c(2x6) phase becomes the saturation phase, instead of the c(2x2) phase at higher pressures. The values for $\Delta\gamma$ and the discussion on partial pressure are collected in the supporting information (*Surface free energy*).

The corresponding surface free energies $\Delta\gamma$ are presented graphically in Figure 3, which makes it possible to compare the relative stabilities of the different phases. In addition, the slope of the curve indicates the average magnitude of stabilization by adsorption of additional thiols (Table 2). A steeper slope corresponds to a more favorable increase in thiolate surface content, while a less steep slope corresponds to a less favorable increase. In the following paragraphs, this data will be related to the SAM structures for all thiols in Figure 4.

Figure 3. $\Delta\gamma$ ($\text{kJ}/(\text{mol} \cdot \text{nm}^2)$) at 353.15 K, $p(\text{H}_2) = 1 \cdot 10^{-5}$ bar and $p(\text{RSH}) = 1 \cdot 10^{-3}$ bar. At 0 ML, the system corresponds to a bare metal surface and gas-phase thiol. At 0.5 ML, the

system corresponds to a SAM in the c(2x2) phase. The intermediate coverages occur between 0 and 0.5 ML.

Table 2. Finite-difference slopes ($\text{kJ.mol}^{-1}.\text{thiolate}^{-1}$) corresponding to the plot (Figure 3) of $\Delta\gamma$ ($\text{kJ.mol}^{-1}.\text{nm}^{-2}$) as a function of coverage (thiolates/nm^2).

Thiolate	[100] $\rightarrow$ (4x4)	(4x4) $\rightarrow$ c(4x4)	c(4x4) $\rightarrow$ (2x2)	(2x2) $\rightarrow$ c(2x6)	(2x2) $\rightarrow$ c(2x2)
Methane	-100.3	-92.7	-86.5	-69.9	-14.1
Ethane	-109.7	-101.3	-101.5	-73.9	47.7
Hexane	-119.6	-122.0	-87.8	-119.5	113.3
Dodecane	-224.3	-41.3	-120.6	-202.3	251.6

Figure 4. Alkanethiolate SAMs as a function of coverage: the (4x4) phase (0.0625 ML), the c(4x4) phase (0.125 ML), the (2x2) phase (0.25 ML), the c(2x6) phase (0.33 ML) and the c(2x2) phase (0.5 ML). Top: ethanethiolate, center: hexanethiolate, bottom: dodecanethiolate.

Intermolecular and substrate-adsorbate interactions

To understand the contributing interactions which lead to the results from the thermodynamic analysis above, the bond dissociation energies (BDE) are calculated. The Cu-SR BDE is defined as:

$$BDE_{tot} = E_{RS\cdot} + \frac{1}{m} E_{Cu[100]} - \frac{1}{m} E_{Cu(-SR)_m} \quad (6),$$

with $E_{RS\cdot}$ the energy of the radical $RS\cdot$. The BDE is averaged over all thiolates in the unit cell. The BDE_{tot} for methane-, ethane-, hexane and dodecanethiolate is collected in

Table 3 and Figure 5.

Figure 5. BDE_{tot} of alkanethiolates on Cu[100] as a function of surface coverage per thiolate.

Table 3 BDE_{tot} of thiolates in different phases (in kJ/mol), per thiolate.

	(4x4) 0.0625 ML	c(4x4) 0.125 ML	(2x2) 0.25 ML	c(2x6) 0.33 ML	c(2x2) 0.5 ML
Methane	312.4	308.5	303.6	298.3	274.3
Ethane	325.0	320.9	319.0	311.6	263.4
Hexane	348.4	349.7	333.2	337.1	263.4
Dodecane	461.1	369.6	363.7	382.6	250.3

The largest BDE_{tot} per thiolate is found for long chain thiolates at low coverage. The BDE_{tot} generally decreases when the surface coverage increases, except for a few exceptions. For example, for hexanethiolate and dodecanethiolate, the BDE_{tot} increases for the phase transition from the (2x2) to the c(2x6) phase. This difference is attributed to larger intermolecular stabilization in the c(2x6) phase, as discussed below. The BDE_{tot} increases as a function of the chain length for surface coverages up to 0.33ML. The increasing stabilization of thiolates as function of chain length is in agreement with experimental observations.⁴⁸ However, at the highest surface coverage of 0.5ML, methanethiolate becomes more stable than the longer chain thiolates.

Surface distortion by adsorption has a destabilizing effect on the Cu lattice and a stabilizing effect on the Cu-thiolate interaction, as discussed in the supporting information (*Surface reconstruction*). These two opposing effects tend to cancel out for all coverages and thereby cannot explain the overall decrease of the Cu-thiolate interaction with increasing coverage. This is different for to Cu[111], where much larger distortions are induced.³¹

To better understand the changes in the BDE_{tot} of the alkane thiolates as a function of the surface coverage and chain length (Figure 5), we quantify the intermolecular and adsorbate-substrate interactions, which play a role in SAM formation. For this purpose, we use the following definitions. ΔE_{R-R} is the average interaction energy of a thiolate molecule in the SAM with the other thiolate molecules in the SAM:

$$\Delta E_{R-R} = E_{RS, vac} - \frac{1}{m} E_{RS, SAM} \quad (8)$$

where $E_{RS, SAM}$ is the energy of the SAM with the Cu slab removed (i.e., only of the RS• radicals). $E_{RS, vac}$ is the energy of the optimized isolated RS• radical molecule in vacuum. This allows the isolation of the part of the BDE_{tot} arising solely from interactions with the Cu surface:

$$\Delta BDE_{Cu-SR} = BDE_{tot} - \Delta E_{R-R} \quad (9)$$

These results are collected per thiolate in Table 4 and Figure 6.

Table 4. ΔE_{R-R} and BDE_{Cu-SR} for thiolates in kJ/mol. The sum of ΔE_{R-R} and ΔBDE_{Cu-SR} is the BDE_{tot} (

Table 3). A larger positive energy represents a greater stabilization.

Thiolate	ΔE_{R-R}					ΔBDE_{Cu-SR}				
	(4x4)	c(4x4)	(2x2)	c(2x6)	c(2x2)	(4x4)	c(4x4)	(2x2)	c(2x6)	c(2x2)
Methane	-3.4	-4.3	-0.1	20.2	31.5	315.7	312.8	304.4	278.1	242.8
Ethane	-5.3	-16.2	2.6	24.8	7.2	330.3	337.2	316.4	286.8	256.2
Hexane	-11.8	-1.6	19.5	47.5	1.5	360.3	351.3	313.7	289.6	261.8
Dodecane	18.4	25.4	46.8	91.6	-12.7	442.7	344.2	316.9	291.1	263.0

The ΔBDE_{Cu-SR} per thiolate decreases with increasing thiolate coverage, indicating that the Cu-S bond becomes weaker (Figure 6). At surface coverages higher than 0.25 ML, Cu atoms are shared between thiolate molecules (Figure 1), which reduces their bonding interaction.

The thiolate-thiolate interaction becomes stronger when the coverage increases from 0.0625 ML to 0.33 ML. As expected, the increase is most pronounced for the longest thiols (Figure 6). As coverage increases, the alkane chains approach each other more, thereby strengthening the dispersion interactions. Beyond 0.33 ML the thiolate-thiolate interaction becomes stronger for methanethiolate, while it becomes weaker for ethanethiolate and even repulsive for the longer thiols due to steric hindrance. This indicates that the steric hindrance results from the alkyl group and not from the thiolate head group. A more comprehensive discussion on the contributions to the BDE is included in the section on phase behavior as a function of coverage and chain length.

Cu/thiolate SAMs have stronger bonds with the metal substrate than Ag/thiolate SAMs and Au/thiolate SAMs.⁴⁹ The thiolate-substrate interactions dominate for Cu/thiolate SAMs (Table 4), while thiolate-thiolate interactions dominate for Au/thiolate SAMs.^{50, 51} The decrease of Cu-thiolate interaction with coverage (Figure 6) then is the cause of the decrease in BDE_{tot} (Figure 5). As coverage increases, the BDE_{tot} decreases slightly (e.g., by 70.7 kJ/mol for hexanethiolate from 0.0625 ML to 0.33 ML). This decrease is not

compensated by thiolate-thiolate interactions, which increases by only 59.3 kJ/mol. As a result, the BDE_{tot} decreases with coverage.

Figure 6. Energetic contributions to ΔBDE_{tot} : ΔBDE_{Cu-SR} per individual molecule as a function of coverage, ΔE_{R-R} per individual molecule as a function of coverage.

In conclusion, the reaction energy for the formation of alkanethiolate SAMs on Cu[100] is determined primarily by interactions with the Cu surface. The alkanethiolate-Cu interaction decreases when the surface coverage increases. Intermolecular stabilization is of most importance in the c(2x6) phase for the long thiolates. Small distortions of the Cu[100] surface structure have a limited impact on the energetics of SAM formation.

Phase behavior as a function of coverage and chain length

The following paragraphs rationalize energetic trends by looking at the different structural phases that form at increasing surface thiolate content per chain length. To do so, we use our energetic data, discussed above, to assess relative stability of the phases. Then, we link the relative stability to structural evolutions in the SAMs. Finally, we compare alkanethiolate SAMs on Cu[100] and Au[100].

Methane- and ethanethiolate

Methane- and ethanethiolate show no specific phase behavior as a function of surface coverage, due to limited intermolecular interactions. As a result, the process is described

better as a self-limiting surface reaction rather than self-assembly. Since the two short thiolates behave similarly, only ethanethiolate is presented in Figure 4. For methanethiolate, the reaction saturates at 0.5 ML or $7.7 \cdot 10^{14}$ thiolates $\cdot\text{cm}^{-2}$ (Figure 3). This is in agreement with experimental observations, as higher coverages have not been reported.⁴⁶ The saturation coverage is lower for ethanethiolate, i.e. 0.33 ML or $5.1 \cdot 10^{14}$ thiolates $\cdot\text{cm}^{-2}$, as this structure shows the lowest surface free energy. The longer alkyl chain results in steric hindrance at the high coverage of 0.5 ML, as indicated also by the change in tilt angle of the ethanethiolate at this surface coverage.

As discussed above, thiol chemisorption on Cu is dominated by Cu-S interactions. In the c(2x6) phase, ΔE_{R-R} for methanethiolate accounts for 20.2 kJ/mol of the stabilization (Table 4). For ethanethiolate, the number increases slightly to 24.5 kJ/mol. For short chains, the intermolecular interactions are weak and arise mainly from the S headgroups, not the alkyl chains. The thiolate-thiolate interactions in these cases make up only 6.7 % and 7.9 % of the BDE_{tot} (

Table 3). The BDE_{Cu-RS} are thus 277.9 kJ/mol and 286.8 kJ/mol.

The Cu-thiolate interactions (BDE_{Cu-RS}) weaken with increasing surface coverage (Figure 6). While nanoparticles generally become less mobile when their size increases, the thiolate islands on Cu have been found to be more mobile than individual molecules.¹⁸ No islands can be modeled here, however the high coverages correspond to the densities found in thiolate islands, while neglecting island boundaries.¹⁸ Accordingly, we suspect the weakening of the adsorbate-substrate interaction to at least partly explain the increase in mobility of thiolate islands.

Hexanethiolate

In contrast to short thiols, hexanethiolate SAMs exist in different phases as a function of coverage. In the (4x4) and c(4x4) phase the molecules lie down on the surface. In the densest lying-down phase, c(4x4), hexanethiolate-hexanethiolate interaction offers no stabilization to the SAM. Hence, the entirety of the BDE_{tot} is a result of interactions between the Cu surface and the thiols (Table 4). The thiols are not long enough to provide significant overlap with neighboring molecules and are spaced relatively far apart. The closest distance between hexanethiolates in the c(4x4) phase is 5.1 Å.

Kondoh et al. used scanning tunneling microscopy (STM) and X-ray absorption fine structure spectroscopy (XAFS) to study hexanethiolate structure on Cu[100].⁴⁷ They found that hexanethiolates lie down when the surface coverage is below 0.132 ML, which is 40% of the saturation content. Our structural data agree (Figure 4): the SAM transitions from lying-down to standing-up at a surface coverage between 0.125 ML and 0.25 ML.

The transition is also apparent in the calculated energies. The lying-down to standing-up transition from 0.125 ML c(4x4) to 0.25 ML (2x2) is less favorable than the transition between the lying-down phases (Figure 3). In the transition between the two lying-down phases ((4x4) and c(4x4)), the SAM is stabilized by -122.0 kJ/(mol.th). During the lying-down to standing-up transition however, the stabilization drops to just -87.8 kJ/(mol.th). After the standing-up phase has formed, the stabilization becomes more negative again and the transition between the standing-up phases ((2x2) and c(2x6)) reaches -119.5

kJ/(mol.th). The reduction in average stabilization is due to a loss of interaction with the surface, while the density is still too low to enable full strength thiolate-thiolate interactions, as was noted in the Results section (*intermolecular and substrate-adsorbate interactions*).

The saturation phase is the 0.33 ML c(2x6) phase with a content of $5.1 \cdot 10^{14}$ thiolates $\cdot$ cm⁻². Due to steric hindrance, the c(2x2) phase is not energetically favorable. The c(2x6) to c(2x2) transition corresponds to an endothermic reaction of 113.3 kJ/(mol.th) (Table 2). These results agree with the experiments conducted by Kondoh et al.⁴⁷

At saturation coverage, hexanethiolate-hexanethiolate interactions are supported by the average tilt angle of 26°, in close agreement with the 27±5° experimentally obtained by Kondoh et al.⁴⁷ These interactions amount to 47.5 kJ/mol per thiolate, thereby making up 14.1 % of the BDE_{tot} . The thiolate-thiolate interactions are relatively weak for methane-, ethane- and even hexanethiolate. Our results quantify the findings by Driver et al., who found C₁₋₈ SAM structure to be primarily impacted by interactions with the Cu substrate.²⁰

The BDE_{Cu-RS} is 289.6 kJ/mol, similar to the value for ethanethiolate and only slightly larger than that for methanethiolate. These findings suggest that interaction of the thiolates with the Cu substrate in standing-up phases are mainly determined by the S head group and the two first methylene units. Increases in BDE_{tot} and the associated higher stability of long chain thiolates in standing-up phases when compared to their shorter homologues are therefore entirely due to thiolate-thiolate interactions.

Dodecanethiolate

Dodecanethiolate SAMs are ordered already at low coverage and the transition to standing-up occurs in two steps. Experiments indicate that dodecanethiolate forms long-range ordered structures on Cu[110], while short thiolates do not form ordered lying-down phases.⁴⁴ The pin stripe model on Cu[110] proposed by Kühnle et al. is similar to the most favorable low coverage model we developed for Cu[100]. In this model, Figure 7 (left), the thiolate pinstripes are parallel to the lattice, while the alkyl chains form a 29° angle with the lattice. The angle allows optimal packing (of flat thiolates) and maximizes contact with the surface. If the angle were 0° or 45°, the alkyl chain would vertically overlap with

the thiolate in the next unit cell and be unable to form a lying-down phase. In comparison to the densest lying-down phase for hexanethiolate, the thiolates approach each other more closely, and the closest C-C distance reduces from 5.1 Å for hexanethiolate to 3.9 Å for dodecanethiolate. Even at such low coverage, the thiolate-thiolate interaction is favorable by 18.4 kJ/mol per thiolate (4 % of the BDE_{tot} , Table 4).

Figure 7. Left: Top view of dodecanethiolate in the (4x4) phase. The flat-lying thiolates form a 29° angle with the lattice. Right: top view of dodecanethiolate in the c(2x2) phase. The structure consists of alternating pinstripes characterized by angles in the plane of the alkyl backbone.

The transition between lying-down and standing-up phases occurs already between the (4x4) and c(4x4) phases, earlier than the c(4x4) and (2x2) phases as in hexanethiolate. This corresponds to a transition between $9.6 \cdot 10^{13}$ thiolates $\cdot\text{cm}^{-2}$ and $1.9 \cdot 10^{14}$ thiolates $\cdot\text{cm}^{-2}$. It should not surprise that the transition for dodecanethiolate occurs at lower coverage than for hexanethiolate: the surface area occupied by the alkyl backbone is two times higher for dodecanethiolate as compared to hexanethiolate.

We can link deviations in the average stabilization to the lying-down to standing-up phase transition, as well as to an intermediate structure. The initial absorption of thiolates on the bare Cu[100] surface in the (4x4) phase corresponds to a stabilization of -224.3 kJ/(mol.th). Upon transition from lying-down to standing-up ((4x4) to c(4x4)), the stabilization becomes remarkably less favorable at -41.3 kJ/(mol.th). This reduced value

can be explained by a loss of interaction with the surface by 98.5 kJ/mol, which is not compensated by increased thiolate-thiolate interactions, due to the low density of the (4x4) phase (Table 4). Adding thiolates destabilizes the lying-down molecules already present on the surface, while the added thiolates in the c(4x4) phase are not stabilized to the same degree as those in the (4x4) phase.

After that, the average stabilization rebounds somewhat to -120.6 kJ/(mol.th) for the c(4x4) to (2x2) transition. However, this value is still significantly lower than the value for initial deposition (-224.8 kJ/(mol.th)) and the value for the transition from the (2x2) to c(6x2) phase (-202.3 kJ/(mol.th)). We propose that the c(4x4) phase is an intermediate structure in which the loss of Cu-thiolate intermolecular interactions is not yet fully compensated by thiolate-thiolate dispersive interactions.

As can be seen in Figure 3, the most stable phase is the c(2x6) phase. This phase benefits from attractive thiolate-thiolate interactions (ΔE_{R-R}) at -91.6 kJ/mol. These interactions make up 23.9 % of the BDE_{tot} . The BDE_{Cu-RS} remains 291.1 kJ/mol, which is close to the values for hexane- and ethanethiolate. This further indicates that stabilization of thiolates longer than ethanethiolate in standing-up phases is solely due to thiolate-thiolate interactions.

Transition to the highest coverage phase, c(2x2), is again not energetically favorable due to steric hindrance. The lowest energy structure has the alkyl backbone oriented perpendicular to the surface. The planes of the alkyl backbones form alternating pinstripes (Figure 7, right). Bent thiolate chain configurations reminiscent of those found by Arefi et al. on Si[111] were also considered in our calculations on Cu[100], but were found to be higher-energy local minima here, 123.7 kJ/mol less stable per thiolate than the all-trans configuration.²⁷

The energy demand for the transition from c(2x6) to c(2x2) is 251.6 kJ/(mol.th). The destabilization can be attributed to a large increase in steric hindrance, associated with a transition from attractive to repulsive ΔE_{R-R} (Table 4). The nearest C-C approach reduces to 3.6 Å, infringing upon the 2.0 Å Van der Waals radius of each CH₂ group.⁵² The steric hindrance becomes apparent upon quantification of the thiolate-thiolate interactions. At

such high coverage, the thiolate-thiolate interactions become unfavorable by -12.7 kJ/mol per thiolate, in contrast to the c(2x6) phase, where they were still favorable by 91.6 kJ/mol. The above findings demonstrate that for longer chain thiols ($C_{\geq 2}$), c(2x6) is the saturation phase, while methanethiolate has access to the higher coverage c(2x2) phase. These results are in line with experimental findings and theoretical calculations.^{19, 28, 45-47}

Comparison with Au

The findings of this paper show that observations on Au cannot simply be applied to SAMs on Cu. Firstly, we found that interaction between the thiolate and the Cu surface is the dominant driving force in SAM formation. This finding contrasts with recent reports indicating the weak, even physisorbed, nature of the thiolate-Au interaction and the important role of dispersion interactions in these systems.^{50, 51} Secondly, the difference in lattice parameter results in different saturation coverages on comparable surface orientations. On Cu[100], for hexanethiolate, the saturation phase is the c(2x6) phase with $5.1 \cdot 10^{14}$ thiolates $\cdot\text{cm}^{-2}$. On Au[100], the saturation phase for hexanethiolate has not been fully resolved and might be the (2x7) or $\begin{pmatrix} 1 & -1 \\ 7 & 6 \end{pmatrix}$ phase, and corresponds to $5.3 \cdot 10^{14}$ thiolates $\cdot\text{cm}^{-2}$.²²⁻²⁴ These results illustrate that both the driving forces and the saturation phases are different for thiolate SAMs on Cu and Au. Nonetheless, the similar surface contents might suggest that passivation in ASD of monocrystalline Au[100] and Cu[100] by alkanethiolates would be comparable.

Conclusion

The phase behavior of alkanethiolate SAMs depends strongly on the chain length, surface structure as well as the nature of the surface, as our study reveals differences for Cu and Au substrates. Cu/thiolate SAMs have stronger bonds with the metal surface than Au/thiolate SAMs. The adsorbate-substrate interactions dominate for Cu/thiolate SAMs, while intermolecular interactions dominate for Au/thiolate SAMs.

Alkanethiolate SAMs on Cu[100] form coverage-dependent structural phases. Hexane- and dodecanethiolate follow the generic model for SAM formation, forming ordered lying-down phases at low surface coverage and standing-up phases at high surface coverage.

The transition from lying-down to standing-up phase was observed at 0.25 ML. The substrate-adsorbate interactions become weaker with increasing thiolate content, but still dominate in the standing-up phase at the saturation content of 0.33 ML or $5.1 \cdot 10^{14}$ thiolates $\cdot\text{cm}^{-2}$. Methane- and ethanethiolate do not show phase behavior, due to the lack of significant thiolate-thiolate interaction restricting self-assembly.

Our insights may aid the development of area-selective deposition processes, by revealing benefits and drawbacks for thiolates with different chain lengths. Methanethiolate can form a monolayer with a saturation content as high as $7.7 \cdot 10^{14}$ thiolates $\cdot\text{cm}^{-2}$. The saturation coverage is lower for the other thiolates ($5.1 \cdot 10^{14}$ thiolates $\cdot\text{cm}^{-2}$) due to steric hindrance, but effective long chain packing may block access of ASD precursors to the substrate. In addition, the saturation contents as calculated in this study could be used to guide the experimental development of thiolate SAM deposition processes, as they correspond to the highest coverage that can be obtained before forming multilayers. Comparison of the theoretical saturation content with the experimental S content from XPS or other techniques is possible.

Additionally, the insights in structures and impact of chain length could be applied in computational studies on reactivity. Note that our models consider monocrystalline Cu[100] substrates, and the impact of grain boundaries and surface orientation for polycrystalline surfaces remains to be investigated.

Finally, we demonstrate that the use of a dispersion correction in DFT is of paramount importance to accurately describe phase behavior. It is the balance of attractive and repulsive intermolecular interactions with the surface and neighboring thiolates that determines molecular structure and lying-down or standing-up phase.

Associated Content

The following file is available free of charge:

Supporting information: containing the method validation, a discussion on density of states upon chemisorption, additional information on the surface free energies and the energetics of surface distortion.

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Conflict of Interest

The authors declare no conflict of interest.

Abbreviations

SAM Self-Assembled Monolayer

DFT Density Functional Theory

C_x Alkyl chain of x Carbons

ASD Area-Selective Deposition

ALD Atomic-Layer Deposition

CVD Chemical Vapor Deposition

Cu Copper

SiO₂ Silicon Dioxide

Au Gold

PBE Perdew-Burke-Ernzerhof functional

PAW Projector Augmented Wave method

SCF Self-Consistent Field

BDE Bond Dissociation Energy

SEXAFS Surface-Enhanced X-Ray Absorption Fine Structure spectroscopy

STM Scanning Tunneling Microscopy

XAFS X-Ray Absorption Fine Structure spectroscopy

S Sulfur

Units

Ry Rydberg

a_0 Bohr Radius

Å Ångström

at Atoms

ML Fractional monolayers

cm Centimeter

K Kelvin

kJ kilo Joule

mol mol

nm Nanometer

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