

EFFECTS OF MOLECULAR CHAIN COVERAGE AND MOLECULAR CHAIN LENGTH ON STRENGTH AND PACKING OF SURFACE COATING MATERIALS: DFT CALCULATIONS

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Abstract

Self-assembled monolayers (SAMs) on an SiO₂ surface were investigated using periodic DFT calculations. The stability of SAMs on SiO₂ surfaces was influenced by modifications in head groups, coverage, and space group length. Three molecules were considered as trial molecular chains: methyltrichlorosilane (CH₃SiCl₃), acetyl chloride (CH₃COCl), and methylphosphonic acid (CH₃PO(OH)₂), with CH₃SiCl₃ being chosen because of the stable chemisorption complex of its -SiCl₃ functional group to the surface and the nonpolar hydrophobic nature of CH₃. The stability of each SAM was evaluated using the molecular chain length in terms of CH₃(CH₂)_nSiCl₃, where n = 0-9, and three distinct coverages (1/4, 1/2, and 1 ML). Our findings revealed that coverage and molecular chain length had a major influence on SAM stability, with van der Waals interactions outweighing steric interactions during molecular chain lengthening.

Keywords: DFT; SAMs; Self-assembled monolayers; SiO₂

Introduction

Silicon dioxide (SiO₂) coatings are a common feature in the electronic industry, typically produced by atmospheric thermal oxidation (ATOX) and plasma-enhanced chemical vapor deposition (PECVD) techniques (Pai *et al.*, 1986). SiO₂ coatings play a crucial role as dielectric or passivation layers when applied to different wafers, including silicon, glass, and other semiconductor

materials. These coatings have been applied in electronics, energy storage devices, microelectromechanical systems (MEMS) and in bio-MEMS (Bhushan *et al.*, 2009). SiO₂ coatings offer a remarkable blend of abrasion resistance, excellent electrical insulation, low thermal expansion, and high thermal stability, making them ideal for various device fabrication purposes.

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Self-assembled monolayers (SAMs) are ordered molecular assemblies formed on a surface through a spontaneous process. They are created by the adsorption of amphiphilic molecules onto a surface, followed by their subsequent reorganization into a well-ordered, densely packed monolayer. Early studies on SAMs focused on prominent adsorbate/substrate pairings, including alkylsilanes on SiO_2 surfaces (Sagiv, 1980; Onclin *et al.*, 2005) and sulfur-containing molecules on gold (Ulman, 1996; Schreiber, 2000; Gooding *et al.*, 2003). SAMs possess unique properties, including ordered structure, chemical and thermal stability, and customizable surface characteristics, making them versatile and reliable for various uses (Pujari *et al.*, 2014; Li *et al.*, 2024). This has attracted considerable attention in materials science and surface engineering due to their potential for innovation.

Figure 1 shows the model of the formation of SAMs on a substrate surface.

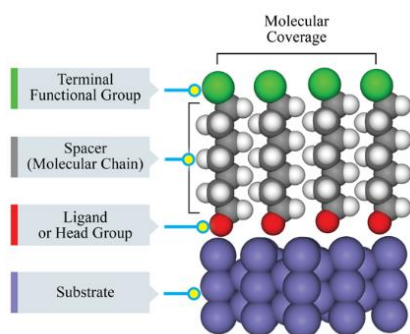


Figure 1. Model of formation of self-assembled monolayers on a surface

From the models, the main components of SAMs can be divided into four parts. The substrate is the surface of the material that needs to be coated, typically a metal or metal oxide surface. The ligand or head group is a crucial component that determines the strength of the interaction between the molecular chain and the surface and can be chosen from a variety of functional groups such as silane, acetal and phosphonate groups. The spacer is a component of the molecular chain connected to the ligand or head group, and its characteristics, including molecular components, bond characteristics, length, and density, directly affect the interactions between neighboring molecular chains. Finally, the terminal functional group is the outermost part of the coating molecular chain and plays a crucial role in designing the properties of the coating, such as preventing rust and corrosion by having superhydrophobic properties, which can prevent water from entering the substrate surface when combined with the appropriate spacer.

To the best of our knowledge, there have been few theoretical investigations of SAMs on surfaces (for example, Wen *et al.*, 2016). However, the study of SAMs on the SiO_2 surface are scarce. Therefore the goal of the current work was to determine the crucial factors that influence SAM stability on SiO_2 surfaces such as differences in head groups, coverage, and space group length. The findings should offer valuable guidance for designing functional and resilient coatings, thereby enhancing surface engineering in diverse fields.

Computational details

All calculations were carried out within the framework of periodic DFT using the Vienna ab initio simulation package (VASP) (Kresse and Hafner, 1994; Kresse and Furthmüller, 1996a, 1996b). For all systems, spin-polarized computations were presented. The valence electrons and core interactions of the systems were described based on the projector augmented wave (PAW) method (Kresse, 1999; Blöchl, 1994) and the Perdew-Burke-Ernzerhof (PBE) (Perdew *et al.*, 1997) exchange correlation functional with the DFT-D3 method of Grimme with zero-damping function correction (Grimme *et al.*, 2010). Every instance utilized a Gaussian smearing factor with $\sigma = 0.1$ eV and an energy cut-off of 408 eV (~ 30 Ry). Using the Monkhorst-Pack algorithm (Monkhorst and Pack, 1976), the k-points sampling for the Brillouin zone was carried out using $1 \times 1 \times 1$, $11 \times 11 \times 11$, and $1 \times 1 \times 1$ meshes of k-points for isolated molecules, β -cristobalite bulk, and the $\text{SiO}_2(111)$ surface, respectively. All structures were optimized until the forces on all unconstrained atoms were less than 0.01 eV/Å.

Substrate

The substrate was the $\text{SiO}_2(111)$ surface obtained from the cubic Fd-3m space group cubic unit cell of β -cristobalite bulk structure. The optimized lattice parameter for the bulk structure of β -cristobalite was 7.46 Å which was in close agreement with those obtained based on the PBE (Arasa *et al.*, 2005) and PW91 (Demuth *et al.*, 1999) functionals.

The surface supercell was produced in the manner described below to examine the surface interactions. From the calculated bulk structure, a 1×1 crystallographic supercell of the O-terminated $\text{SiO}_2(111)$ surface was cleaved and comprised seventeen atomic layers (see Figure 2(a)). To create the silanol groups (Si-O-H) on both surfaces, the terminating O atoms were saturated with H, leading to four locations on each side, the corresponding

silanol groups were assumed to constitute the active sites on the surface (see Figure 2(b)). In the supercell, the bottom nine atomic layers were fixed at their original positions, while all atoms in the remaining atomic layers were allowed to relax in all directions. A vacuum gap was generated with 20 Å separation in the z direction, which was sufficient to avoid interactions beyond the periodic boundary condition.

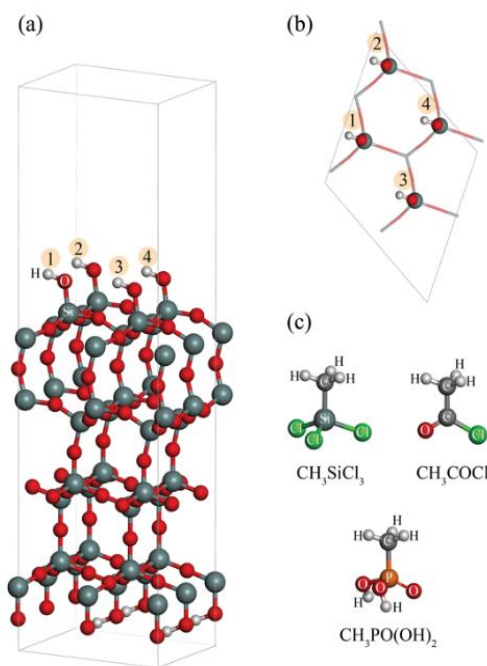


Figure 2. (a) Clean SiO₂(111) surface supercell; (b) Top view of surface showing four silanol adsorption sites (see text); and (c) Three distinct molecules chosen as trial molecular head groups

Head Group and Terminal Functional Group

Three molecules were considered as primitive adsorbent molecules: acetyl chloride (CH₃COCl), methyltrichlorosilane (CH₃SiCl₃), and methylphosphonic acid (CH₃PO(OH)₂). The functional groups –SiCl₃, –C(=O)Cl, and –P(=O)(OH)₂ were taken into account, as they were expected to interact with the active sites on the substrate surface, acting as the head group. The methyl group (CH₃) functioned as the terminal of the molecule, due to its nonpolar and hydrophobic nature (see Figure 2(c)). Both physisorption and chemisorption interactions between the selected head groups and the surface were examined for comparative purposes. The most stable chemisorption complex was selected as the prime candidate for further exploration in the SAM processes.

Molecular chain investigation

The impacts were examined of the length of the selected molecular chain by altering the (CH₂)_n group as the chain's spacer (n = 0-9). The density of molecular chains, or coverage, was also proven in terms of the number of chains per surface active site. As a result, three distinct coverages (1/4, 1/2, and 1 ML) were investigated, which will be discussed further in the Results and Discussion sections.

Stability of the systems

The adsorption energy of the molecular chain on SiO₂(111) was used to investigate the stability of each system. It was computed as using Equation (1):

$$E_{\text{ads}} = E_{\text{molecules/slab}} - E_{\text{slab}} - E_{\text{molecules}} \quad (1)$$

where $E_{\text{molecules/slab}}$ represents the total energy of the SiO₂(111) surface with the molecular chains, E_{slab} is the total energy of the clean SiO₂(111) surface, and $E_{\text{molecules}}$ denotes the total energy of the free molecules. Based on this, preferable system configurations are presented by negative values of adsorption energy, with more negative values suggesting preferable interactions.

Results and Discussion

Adsorptions of molecular chain on SiO₂(111)

The stability for each molecular chain head group on the surface was initially investigated in physisorption modes. To obtain the optimal physisorption structures, as depicted in Figure 3, the head group molecules were first randomly arranged on the surface, allowing the molecule to rotate without restriction. The molecules were stabilized on the surface by intermolecular forces such dipole-dipole interactions and hydrogen bonds. Some selected interatomic distances are represented by values in angstroms (Å) (see Figure 3).

Since the strength of the interaction between the molecular chain and the surface is the crucial factor, the chemisorption complexes, adapted from the corresponding physisorption complexes, were also investigated. The difference in the adsorption energy between these adsorption modes was expressed in terms of the reaction energy, ΔE_{rxn} .

Table 1 shows the adsorption energies for the physisorption and chemisorption complexes of the CH₃SiCl₃/SiO₂(111), CH₃COCl/SiO₂(111), and CH₃PO(OH)₂/SiO₂(111) systems. In all cases, the chemisorption structures demonstrated preferable stability compared to the physisorption complexes. The corresponding adsorption energies for the chemisorption complexes were -20.28, -16.00, and -35.60 kcal/mol for CH₃SiCl₃, CH₃COCl, and

$\text{CH}_3\text{PO}(\text{OH})_2$ on the $\text{SiO}_2(111)$ surface systems, respectively. Based on these results, the transition from physisorption to chemisorption complexes was an exothermic process.

The ΔE_{rxn} values in Table 1 clearly show that the $\text{CH}_3\text{SiCl}_3/\text{SiO}_2(111)$ and $\text{CH}_3\text{PO}(\text{OH})_2/\text{SiO}_2(111)$ systems have a substantial energy difference between the chemisorption and physisorption configurations, indicating a clear preference for the chemisorption state. The ΔE_{rxn} values for these systems were 12.21 and 12.00 kcal/mol, respectively. However, the $\text{CH}_3\text{COCl}/\text{SiO}_2(111)$ system had a smaller ΔE_{rxn} , suggesting a less pronounced energy difference between the chemisorption and physisorption states and indicating that the molecular chain head group in this system may not be as stable in the chemisorption form and could potentially revert to the physisorption structure.

Considering the chemisorption structures, the initial physisorption interactions on the surface stimulated chemical reactions, resulting in the formation of the molecular chain's chemisorption to the surface through covalent bonds. Additionally, there were byproduct molecules that remained

adsorbed on the surface. In the $\text{CH}_3\text{SiCl}_3/\text{SiO}_2(111)$ and $\text{CH}_3\text{COCl}/\text{SiO}_2(111)$ systems, HCl served as the adsorbed byproduct molecule, whereas, in the $\text{CH}_3\text{PO}(\text{OH})_2/\text{SiO}_2(111)$ system, the byproduct was the H_2O molecule. For enabling straightforward comparisons of the stability of the chemisorption complexes across the three systems while excluding the contribution of the adsorbed byproduct molecule, we calculated the adsorption energy for the chemisorption complexes using Equation (2):

$$E_{\text{ads}}^* = E_{\text{molecules/slab}}^* - E_{\text{slab}} - E_{\text{molecules}} \quad (2)$$

where $E_{\text{molecules/slab}}^*$ is the total energy of the chemisorption structure of the $\text{SiO}_2(111)$ surface with the molecular chains and the byproduct molecule. The corresponding adsorption energies (E_p^*) and reaction energies ($\Delta E_{\text{rxn}} = E_p^* - E_r$) indicate that of these three systems, CH_3SiCl_3 is the only one in chemisorption form on the $\text{SiO}_2(111)$ surface with the highest stability, as indicated by $\Delta E_{\text{rxn}} = -3.16$ kcal/mol, while the other two had positive ΔE_{rxn} values. Consequently, we decided to focus our research on CH_3SiCl_3 as a molecular chain.

Table 1. Adsorption energies (E_{ads}) for physisorption and chemisorption complexes and reaction energies (ΔE_{rxn}) for three different systems

System	E_{ads} (kcal/mol)		ΔE_{rxn} (kcal/mol)
	Phys ^a , E_r	Chem ^b , E_p (E_p^*)	$E_p - E_r$ ($E_p^* - E_r$)
$\text{CH}_3\text{SiCl}_3/\text{SiO}_2(111)$	-9.05	-20.28 (-12.06)	-12.21 (-3.16)
$\text{CH}_3\text{COCl}/\text{SiO}_2(111)$	-15.58	-16.00 (-5.30)	-0.42 (10.28)
$\text{CH}_3\text{PO}(\text{OH})_2/\text{SiO}_2(111)$	-23.60	-35.60 (-18.65)	-12.00 (4.95)

Phys^a and Chem^b represent physisorption and chemisorption complexes, respectively. E_p^* is the adsorption energy for each chemisorption complex excluding the adsorbed byproduct molecule.

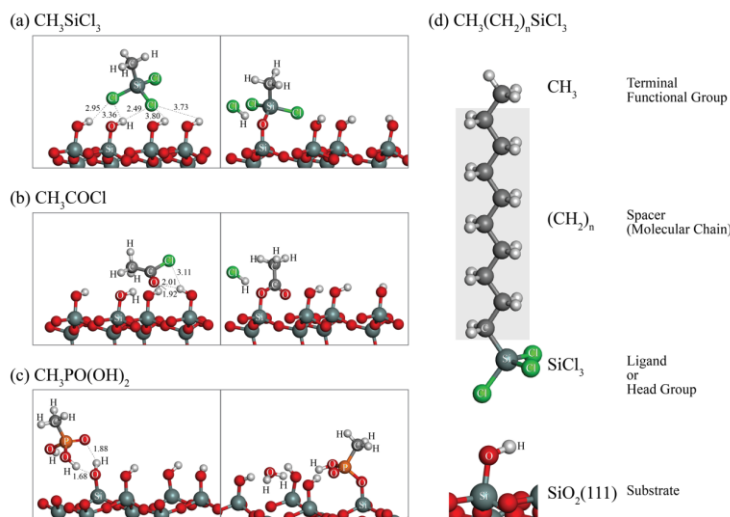


Figure 3. Physisorption (left panel) and chemisorption (right panel) complexes of: (a) $\text{CH}_3\text{SiCl}_3/\text{SiO}_2(111)$, (b) $\text{CH}_3\text{COCl}/\text{SiO}_2(111)$, and (c) $\text{CH}_3\text{PO}(\text{OH})_2/\text{SiO}_2(111)$ systems; (d) Selected molecular chain for self-assembled monolayer on $\text{SiO}_2(111)$. Chosen interatomic distances in physisorption complexes are represented by the numbers in angstroms (Å)

Self-assembled monolayer of CH_3SiCl_3 on $\text{SiO}_2(111)$

The SAM of CH_3SiCl_3 on $\text{SiO}_2(111)$ systems was further investigated by considering two important factors: the length of the molecular chain and the number of active site coverages. The molecular chain was represented by the notation $\text{CH}_3(\text{CH}_2)_n\text{SiCl}_3$, where $n = 0-9$, corresponding to the number of carbon atoms, which ranged from 1 to 10. The effects of molecular chain coverage at active sites were investigated for 1/4, 1/2, and 1 ML, indicated by one, two, and four molecular chains, respectively, in the systems.

Table 2 and Figure 4(a) show the E_{ads} values for all systems. One molecule chain was chemically attached to a silanol active site for the 1/4 ML coverage, meaning that adjacent interactions between the molecular chains among periodic pictures could be disregarded because of their approximate 10 Å distance from one another. The interaction between the molecular chain and the surface, which can serve as a reference system when the effects of coverage are taken into account, was the only source of adsorption energy for the 1/4 ML coverage system. The adsorption energies for all molecular chains were in the range -9.85 to -12.21 kcal/mol, without any clear trend with increasing chain length. This lack of a trend could be attributed to the absence of interactions from neighboring molecular chains that are very crucial in SAMs, causing the free rotation of the molecular chain at the active site to attain the most stable structures.

Table 2. Adsorption energies (E_{ads}) for self-assembled monolayer of $\text{CH}_3(\text{CH}_2)_n\text{SiCl}_3$ ($n = 0-9$) on $\text{SiO}_2(111)$ surface

n	Coverages		
	1/4 ML	1/2 ML	1 ML
0	-12.21	-25.96	-20.82
1	-11.57	-24.20	-24.10
2	-9.95	-25.61	-27.92
3	-10.41	-26.70	-34.22
4	-10.35	-27.30	-39.77
5	-10.64	-27.30	-44.09
6	-10.30	-27.78	-48.23
7	-10.26	-28.58	-54.28
8	-10.06	-29.39	-58.61
9	-9.85	-30.33	-64.87

For the 1/2 ML coverage, two molecular chains were chemically bonded to two silanol active sites, leading to interactions between molecular chains in the periodic cell since the shortest distance between the chains is about 5 Å. The adsorption energies are in the range between -24.20 to -30.33 kcal/mol. For $n = 0$ to 2, show there were only minor differences among the adsorption energies,

suggesting small interactions from the neighboring molecular chains. These results were very similar to those for the 1/4 ML results. However, when the chain lengths were increased from $n = 3$ to 9, the adsorption energies slightly increase from -26.70 to -30.33 kcal/mol, indicating the role of molecular chain length in the interactions between the neighboring molecular chains.

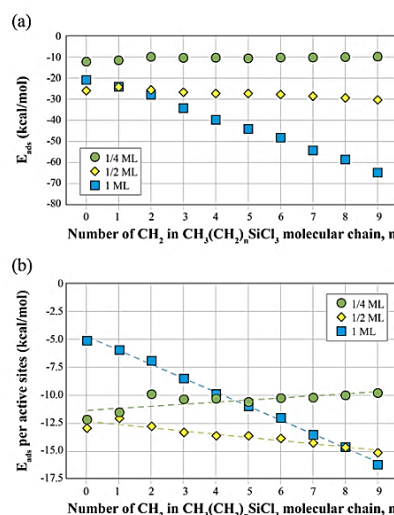


Figure 4. (a) Adsorption energies (E_{ads}) for self-assembled monolayer of $\text{CH}_3(\text{CH}_2)_n\text{SiCl}_3$ ($n = 0-9$) on $\text{SiO}_2(111)$ surface; and (b) Adsorption energy per active sites

For the 1 ML coverage, all the silanol active sites were chemically bonded with four molecular chains. The adsorption energies increase linearly from -20.82 to -64.87 kcal/mol with an increase in the molecular chain length. This indicated that the adjacent molecular chains, as well as the chain lengths, played vital roles in the stabilization of the structures via the van der Waals interactions.

The adsorption energies per silanol active sites are presented in Figure 4(b) based on the number of coverage effects. These adsorption energies for the 1/2 ML and 1 ML systems roughly compared with those of the 1/4 ML system, though in the 1/2 ML system, the adsorption energy per active site tended to slightly increase with increasing the molecular chain length compared to that of the 1/4 ML system. However, for short molecular chain systems in 1 ML ($n = 0-4$), the adsorption energy per active site resulted in weaker interactions between the molecular chains and the surface than for the 1/4 ML cases. This could be explained by the stronger steric effects between all adjacent molecular chains, as well as with the molecular chain on the surface.

Table 3 displays the selected optimized molecular structure parameters for the 1/4 ML and 1 ML systems to highlight the steric effects in the system. The molecular chain structures were affected by steric effects, resulting in certain structural changes in the head group locations. In the 1/4 ML case, with less steric impact in the system, the Cl atoms at the head group of the molecular chain interacted with the H atoms of the nearby silanol active sites on the surface (see Figure 5(b)), causing the Si-Cl bonds to lengthen to 2.08 Å from the 2.06 Å of the free molecule. This indicated a higher strength of adsorption than for the 1 ML case. Increasing the number of coverages to 1 ML caused strong steric effects in the head group of each molecular chain due to the strong repulsion of the

Cl atoms among neighboring molecular chains, as shown by the locations of Cl atoms in Figure 5(c). In addition, the molecular chains were somewhat raised from the surface as a result of the Si(1)–O–Si(2) angle increasing from 141.7° (1/4 ML) to 144.8°.

Even steric effects played a major role in high coverage systems, where longer molecule chains ($n \geq 5$) resulted in higher adsorption energies for the 1 ML molecular chain system than for the 1/4 ML system. This behavior demonstrated that the van der Waals interactions stabilized the molecular chains on the surface by outweighing the steric interactions. The outcome indicated that the stability of SAMs was strongly aided by both coverage and molecular chain length (Wen *et al.*, 2016).

Table 3. Optimized molecular structure parameters of $\text{CH}_3(\text{CH}_2)_9\text{SiCl}_3$ on $\text{SiO}_2(111)$ surface systems for 1/4 ML and 1 ML coverages

Optimized structural parameters*	System						
	Isolated molecule	$\text{CH}_3(\text{CH}_2)_9\text{SiCl}_3 / \text{SiO}_2(111)$ surface					
		1/4 ML	1 ML				Average**
		Site 1	Site 1	Site 2	Site 3	Site 4	
Bond (Å)							
Si(1)–O	-	1.65	1.64	1.63	1.65	1.63	1.64
Si(2)–O	-	1.62	1.63	1.62	1.63	1.62	1.63
Si(2)–Cl(1)	2.06	2.08	2.05	2.05	2.08	2.04	2.06
Si(2)–Cl(2)	2.06	2.08	2.05	2.05	2.05	2.05	2.05
Si(2)–C(1)	1.86	1.87	1.86	1.86	1.87	1.86	1.86
C(1)–H(1)	1.10	1.10	1.10	1.10	1.10	1.10	1.10
C(1)–H(1')	1.10	1.10	1.10	1.10	1.10	1.10	1.10
C(1)–C(2)	1.54	1.54	1.53	1.53	1.54	1.54	1.54
C(2)–H(2)	1.10	1.10	1.10	1.10	1.10	1.10	1.10
C(2)–H(2')	1.10	1.10	1.10	1.10	1.10	1.10	1.10
Angle (°)							
Si(1)–O–Si(2)	-	141.7	139.9	143.0	153.4	142.9	144.8
O–Si(2)–C(1)	-	112.9	115.7	113.0	120.8	116.1	116.4
Si(2)–C(1)–C(2)	114.1	116.1	113.5	114.3	109.2	111.2	112.1

* Labels of optimized structural parameters presented in Figure 5(a).

** Average optimized structural parameters for 1 ML system taken from sites 1-4.

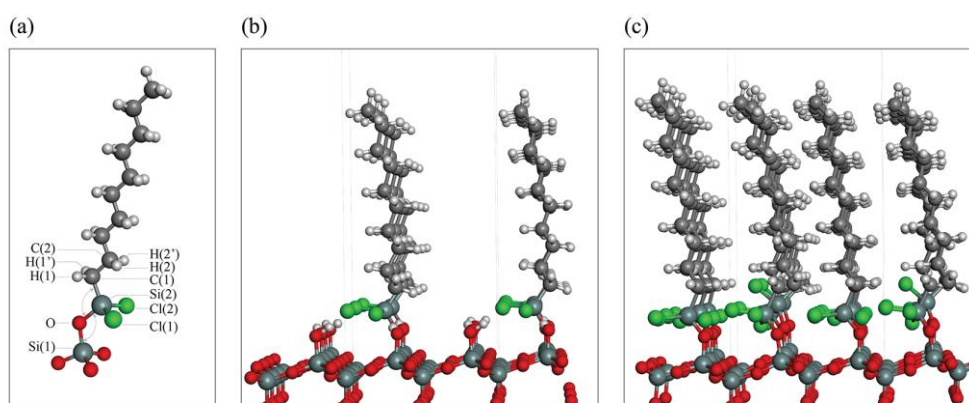


Figure 5. (a) Structural parameters corresponding to data in Table 3, where (b) and (c) present structural arrangements for self-assembled monolayer of $\text{CH}_3(\text{CH}_2)_9\text{SiCl}_3$ on $\text{SiO}_2(111)$ surface for 1/4 ML and 1 ML, respectively

In the 1/2 ML case, when the length of the molecular chain increased, a similar increase occurred in the van der Waals interactions. Nonetheless, compared to the steric effects, the van der Waals interactions were not as great because of the low molecular chain density in the system.

The results from present theoretical calculations supported the conclusion that the molecular chain $\text{CH}_3(\text{CH}_2)_n\text{SiCl}_3$ with $n \geq 5$ for a full coverage could make a good combination for the process of self-assembled monolayers on the surface. This might be a suitable combination for enhancing the properties of the coating and preventing rust and corrosion on the surface.

Conclusion

Based on the study of SAMs on SiO_2 surfaces using DFT simulations, the stability of SAMs on SiO_2 surfaces can be summarized using the following key factors:

1. The functional group exhibiting the maximum stability in covalent contact with the surface during chemisorption must be the head group.
2. The appropriate number of coverages and the molecular chain length have a major impact on the strength and organization of surface coatings.
3. Steric effects are important in high coverage systems, notably for short molecule chains ($n < 5$), as indicated by lower adsorption energies compared to the low coverage situations.
4. When molecular chain extension occurs, the van der Waals interactions outweigh the steric interactions, enhancing the stability of SAMs on SiO_2 surfaces.

Our findings should provide valuable guidance for developing robust and useful coatings and improving surface engineering across various domains.

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