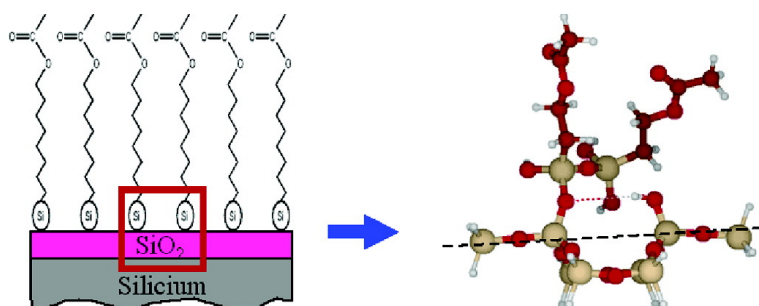**Article**

Self-Assembled Monolayers and Preorganization of Organosilanes Prior to Surface Grafting onto Silica: A Quantum Mechanical Study

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Self-Assembled Monolayers and Preorganization of Organosilanes Prior to Surface Grafting onto Silica: A Quantum Mechanical Study

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Abstract: Quantum chemical calculations have been carried out on the grafting of chain organosilane compounds on SiO_2-hydroxylated solid surfaces. It is shown that a single molecule interacting with the surface lies flat to it, inhibiting further homogeneous film growth. This adsorption exhibits two molecule/surface interactions: a covalent bond on one side of the molecule and a hydrogen bond on the other side. We then investigate the possible preorganization of the molecules before grafting due to the presence of water molecules either in the gas/liquid phase or near the surface. This gives rise to the formation of dimerized chains. We then demonstrate that this preorganization process prevents subsequent lying flat of the molecules to the substrate after grafting. Energetics and associated configurations of the overall deposition process are discussed in detail and provide new insights on the understanding of the formation of self-assembled homogeneous organic films on microelectronics-type substrates.

I. Introduction

The grafting of long chain organosilane compounds on silica surfaces to form self-assembled monolayers (SAMs) is now widely investigated experimentally.[1–14] Currently, they attract considerable attention because of potential applications in biology, chemical sensing, and microelectronics.[15–17]

Intensive ongoing research effort is devoted to the development of various experimental functionalizing procedures. The goal is to form homogeneous organic films onto microelectronics substrates, that is, silica surfaces, to further address bionanotechnology applications. To reach this major goal, it will be necessary to develop advanced nanofabrication techniques, capable of precise and reliable handling of nanometric and subnanometric components of interest. This implies that future nanofabrication methods will have to largely rely on a "bottom-up" chemical approach.[18–20] Recently, Sagiv et al.[21–23] discovered a nanoelectrochemical patterning process that utilizes electrical pulses delivered by a conductive AFM tip for the nondestructive nanometer-scale inscription of chemical information on the top surfaces of certain highly ordered long tail organosilane monolayers self-assembled on silicon. In this framework, the organosilane chains have been grafted on the silica with the intention of maximizing the adsorption.[24–26] Moreover, to better understand the parameters governing the self-assembly mechanisms of multifunctional organosilane compounds on the surface, Fichou et al.[27] synthesized several organic layers differing by their chemical structures. They have

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studied their respective self-assembly properties by means of STM. It is well-known that the use of long chains provides dense and robust SAMs.[24] The presence of the aggregates is often observed[24,25] and may act as a significant perturbation in the case of DNA-based applications.[28] From experimental observations, these aggregates can be correlated to water exposure during the deposition procedure. However, the water is needed to induce the silane condensation with the hydroxylized silica.[29,30] Therefore, the role of water and its presence at every stage of the deposition procedure is of major interest. It has been shown that the proper substrate hydration is the fundamental basis of strategies for the deposition of dense-packed, highly organized, long chain alkylsiloxane monolayers on solid substrates of widely different chemical characters. In the absence of such hydration, the film cannot be decoupled from the substrate chemistry, and in most cases, increased film defect content can be expected.[31,32] Beyond this, it has been demonstrated that in order to better control and enhance the homogeneity of the layers, the effect of two experimental parameters has to be considered: the solvent composition and the reaction time.[24]

To the best of our knowledge, despite several experimental investigations dedicated to the grafting of chain organosilane compounds to the silica, there are only few theoretical descriptions of such grafting and even fewer attempts to understand the self-organization mechanisms.[33] However, there are several theoretical calculations on the SAMs: simulations of hydrated multilamellar bilayers,[34,35] protein−membrane system attached to an organic self-assembled monolayers,[36] molecular dynamics simulations of supported phospholipid/alkanethiol bilayers on a gold (111) surface.[37]

Our preliminary aim is to investigate the basic atomistic mechanisms that govern the grafting procedure via quantum chemical calculations in view to give key parameters to better control the deposition technology. In this context, cluster models are widely used to study theoretically the interaction between molecules and surfaces. In this context, the silica nanostructure[38−41] has received considerable attention in recent years. Molecular dynamics and ab initio calculations have been reported on the structure and properties of silica nanoclusters.[42,43] From a chemical point of view, the cluster approach is justified

by considering chemisorption as a local phenomenon. The advantages of finite surface models are 2-fold; on one hand, the adsorbate geometry is usually reliably calculated,[44,45] on the other hand, the limited extent of the system allows one to apply quantum chemical studies at a sophisticated level to determine accurately the nature of the molecule/surface interaction. In the following, the silica substrate is modeled by a $Si_8O_{10}H_{16}$ tridymite-based molecule that authorizes various OH spatial distributions at the silica surface. For the chain organosilanes to be grafted on the surface, we considered the trihydroxysilanes with only a few alkyl chains, that is, $(OH)_3-Si-CH_2-CH_2-O-CO-CH_3$, where the hydroxyl groups $(OH)_3$ are generated from a previous hydrolysis of Cl_3-terminated chains under water exposure. The resulting organic layer, while being the suitable one for DNA chip applications,[46] has been suggested and synthesized by Bennetau's group.[47]

The present work focuses first on the grafting of one organic molecule on the substrate. The nature of the interaction and the charge transfer from the molecule to the surface is discussed. Second, gas phase reaction, that is, the dimerization of the molecule, is introduced. This part of the work is motivated by the experimental observations which indicate that the preorganization of chain organosilanes just before the grafting depends largely on the nature of the solvent.[25]

Finally, we discuss the interaction of a dimer unit (two attached precursor molecules) with the substrate. The present work brings new advances in our understanding of some key points of the self-assembly of one organic layer on top of a typical microelectronic substrate, from the gas-phase preorganization to the final grafting on the surface.

II. Computational Methods

The structural properties of all the systems (different monomers, their associated dimers, and grafting complexes) considered in this paper have been calculated within the Density Functional Theory (DFT) using the combined Becke's three parameters exchange functional and the gradient-corrected functional of Lee, Yang, and Parr.[48,49]

All calculations have been performed with the DFT/B3LYP method combined with a standard 6-31+G** basis set by means of the Gaussian 98 package.[50] This basis set has been demonstrated to reproduce accurately the energetical and structural properties of molecule/surface interactions.[51−53] Frequency calculations have also been driven to confirm the global minima of each structure. The interaction energies

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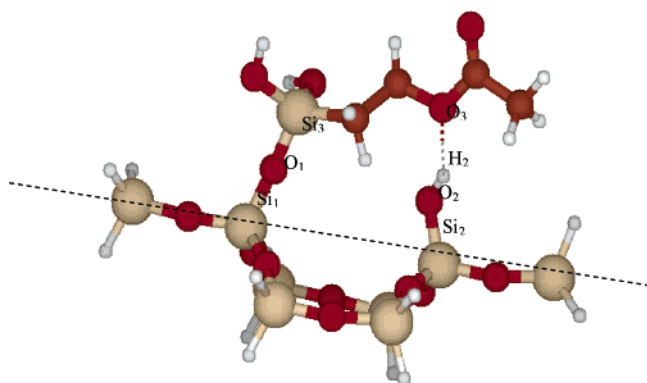
Figure 1. Grafting of one chain organosilane on silica surface; see also Table 1, column 1.

Table 1. Total Energy and Selected Structural Data for Grafting Complexes[a]

grafting complexes	complex (1), Figure 1	complex (2), Figure 4
total energy	−3826.561477	−4574.373298
Covalent Bond: Si−O−Si		
$r(Si_1-O_1)$	1.621	1.634
$R(Si_1-Si_3)$	3.248	3.114
$<(Si_1-O_1-Si_3)$	172.6	142.9
Intermolecular Hydrogen Bond		
$r(O_2-H_2)$	0.970	
$R(Si_2-O_3)$	2.878	
$<(O_2-H_2-O_3)$	151.1	
Intramolecular Hydrogen Bond		
$r(O_2-H_2)$		0.965
$R(O_1-O_2)$		4.00
$<(O_2-H_2-O_1)$		155.3

[a] Energies are in Hartree, distances in angstroms, and angles in degrees.

are derived from the total energy of the final products compared with the total energies of the subunits taken separately.

To model the silica surface, we have built a cluster model in a step by step procedure. The cluster is based on a cleaved tridymite silica-based structure containing eight silicon atoms. A study of the cluster size has shown that this cluster is relevant to perform reliable energetics on these systems (data not shown). Minimization is then performed with hydrogen atoms to saturate the dangling bonds. Hydroxylation is considered next by adsorbing two OH species on top of the surface. This cluster model authorizes various OH distributions as it exhibits four surface silicon atoms. In all calculations, the substrate silicon atoms are frozen except the SiO_2-like silicon atoms bonded to OH.

III. Results and Discussion

(A) Grafting of One Organic Chain on the Surface. The grafting of one isolated organic chain on the silicon dioxide surface can be written as the following reaction 1:

$$cluster + organic\ chain \rightarrow grafted\ complex\ (1) + H_2O \quad (1)$$

Before minimization, the organic chain is positioned normal to the surface (starting geometry). The resulting grafted complex (1) is sketched in Figure 1, and its main structural characteristics are reported in Table 1, column 1.

After minimization, the grafted complex (1) lies flat to the surface and is finally stabilized by two different interactions: (i) the organic chain is grafted on one side with a covalent $Si_1-O_1-Si_3$ bond and (ii) in the other side of the chain with an electrostatic force defined by one specific local structure

indicating the presence of an $O_2-H_2\cdots O_3$ hydrogen-type of bond. In particular, the O_2-H_2 bond length is largely modified between the monomer and the grafting complex. In the present work, we will focus our analysis on these two interaction behaviors.

The chain is covalently bonded to the cluster with an angle $<(Si_1O_1Si_3)$ of 172.6°, a nearly perfect linear bond consistent with the wide range of possible Si−O−Si angles expected in silicon dioxide structures. Concerning the electrostatic interaction that takes place at the other side of the chain, the predicted H-bond angle indicates a deformation of the H-bond, that is, the angle $<(O_2H_2O_3)$ is around 151°. One of the most interesting structural qualities is the elongation of the X−Y bond since this elongation is the key to a reliable interpretation (X−Y frequency shifts) in the infrared vibrational spectra. For this purpose, the elongation of the bond lengths, $r(Si_1-O_1)$ and $r(O_2-H_2)$, are about −0.030 and −0.012 Å with respect to the same bond lengths before grafting, for covalent bond and hydrogen bond (proton donor), respectively. The intermolecular distance $R(O_2-O_3)$ in the hydrogen bond is about 2.878 Å. This predicted distance is in good agreement with experimental distances of the moderated hydrogen-bonded complexes.[54]

The axis of the organic layer is nearly parallel to the axis of the surface. The interaction energy of the grafted complex (1) is about 0.92 eV exothermic (BSSE and ZPE corrections are not accounted for in the calculations). This confirms the significant modification in the structural properties.

Another important physical property in the case of grafting on the surface is the charge transfer since the partial charge transfer between molecule and surface is a key parameter for determining the chemical potential, which is close to the opposite of the work function. This appears in the calculation of Mulliken charge distribution, which shows a partial positive charge (0.47 |e|) located on the organic molecule and a partial negative charge on the cluster. This charge transfer and the geometric changes of these two units upon adsorption are clear evidence of the chemical nature of the interaction.

(B) The Preorganization of the Organosilane Chains. The second discussion is devoted to the dimerization of the organosilane chains before the grafting. We point out the fact that the aggregate will form in the condition where the initial $(Cl)_3-Si-CH_2-CH_2-O-CO-CH_3$ synthesized chains are hydrolyzed under water exposure to give rise to the $(OH)_3-Si-CH_2-CH_2-O-CO-CH_3$ molecules considered here; otherwise, no dimer can be formed. It is, therefore, implicit that, in anhydrous solution, dimerization occurs in contact with the thin water layer attached to the substrate. Thus, the chains condense among themselves, giving rise to the dimer (reaction 2) shown in Figure 2.

$$2 \times trihydroxysilanes \rightarrow dimer\ (1) + H_2O \quad (2)$$
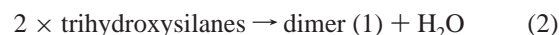
The main structural characteristics of the dimer (1) are reported in Table 2. The interaction energy of the dimer (1) is about 0.31 eV exothermic. The dimer (1) is stabilized by a covalent $Si_1-O_1-Si_2$ bond with an angle of 127.3°. The predicted intermolecular distance $R(Si_1-Si_2)$ is around 2.969 Å. The structure of this organization clearly shows that the alignment of the two chains is disturbed (the distance between the two

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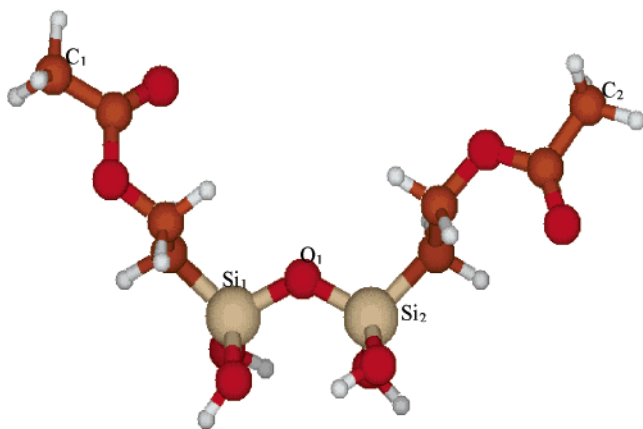
Figure 2. Structure of dimer (1); see also Table 2, column 1.

Table 2. Total Energy and Selected Structural Data for Dimer Molecules[a]

dimer molecules	dimer (1), Figure 2	dimer(2), Figure 3
total energy	−1572.123057	−1194.974908
	Covalent Bond: Si−O−Si	
$R(Si_1-Si_2)$	2.97	3.10
$r(Si_1-O_1)$	1.656	1.657
	$(0.005)^b$	$(0.004)^b$
$R(C_1-C_2)$	11.48	7.42
$<(Si_1-O_1-S_2)$	127.3	138.6

[a] Energies are in Hartree, distances in angstroms, and angles in degrees. [b] Numbers in parentheses correspond to the elongation of the Si−O bonds with respect to the monomers.
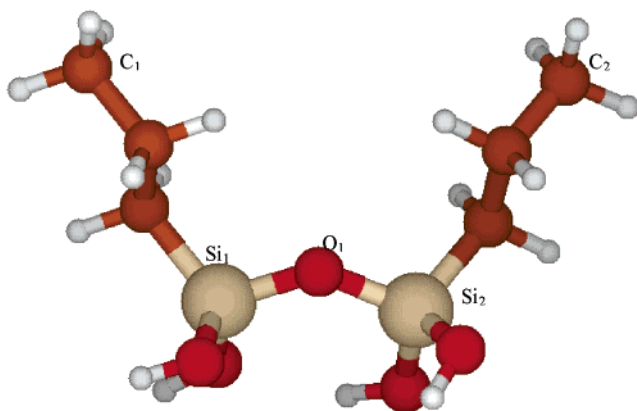

Figure 3. Structure of dimer (2); see also Table 2, column 2.

chain terminations ($R(C_1-C_2)$) is about 11.4 Å. This is due, possibly, to the steric repulsion between the alkyl chains and/ or to the −OCO−CH$_3$ groups exhibiting a Coulombic repulsion. Note that some distortions in the alkyl groups alignment occur.

To better understand the part of responsibility between these two possible repulsive mechanisms for losing the alignment of the two chains, the dimerization reaction of two Si(OH)$_3$−(CH$_2$)$_2$−CH$_3$ molecules is now considered with the chains free of their reactive C=O terminations (see Figure 3 and Table 2).

The interaction energy of dimer (2) is around 0.22 eV. This dimer is also stabilized with covalent Si−O−Si bonds having an angle ($<(Si_1-O_1-S_2)$) of 138.6°. The intermolecular distance $R(Si_1-Si_2)$ is about 3.10 Å. These results confirm that at least the Coulombic part of the repulsive interaction takes place during dimerization. First, the Coulombic repulsion is confirmed by the fact that the presence of the terminated C$_1$ and C$_2$ oxygen
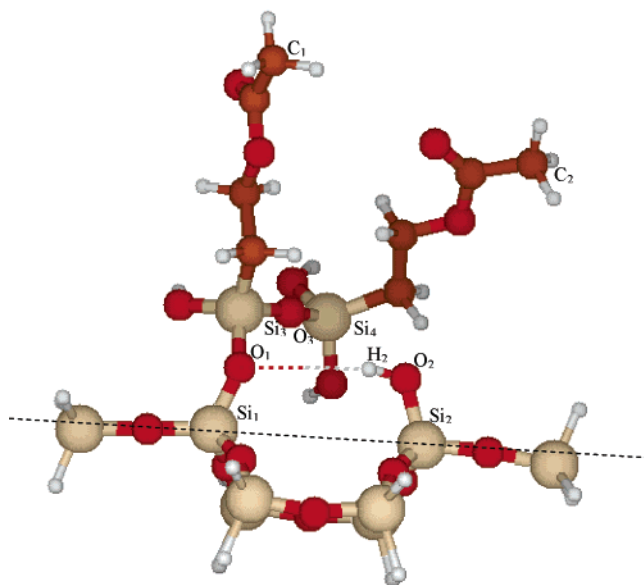

Figure 4. Grafting of two chains of organosilane on the silica surface; see also Table 1, column 2.

groups in Figure 2 increases the opening of the angle between the axis of both chains (see $R(C_1-C_2)$) and the Si$_1$−O$_1$−Si$_2$ angle in Table 2). This opening acts in favor of the formation of two hydrogen bonds between the bulk hydroxyl groups instead of a single one in the truncated case.

Second, the steric repulsion should be clear from the geometry shown in Figure 3, where the chains are truncated so that Coulombic effects are avoided at the termination of the chains. Unfortunately, the cluster is also stabilized by one hydrogen bond arising from the bulk hydroxyl groups terminations acting in the same direction as the steric repulsion.

(C) Grafting of Dimerized Chain Organosilanes on the Surface. The adsorption of the dimer (1) on the silica surface is given by the following reaction:

$$\text{cluster} + \text{dimer (1)} \rightarrow \text{grafted complex (2)} + \text{H}_2\text{O} \quad (3)$$

The grafted complex (2) is sketched in Figure 4, and their calculated structural data are reported in Table 1, column 2.

The initial positioning of the dimer is, as in the previous case of the isolated chain, normal to the surface. In contrary to the grafted complex (1), the grafted complex (2) is stabilized by only one covalent Si−O−Si bond, having an angle $<(Si_1-O_1-Si_3)$ of 142.9° compared to a nearly linear bond in complex (1). The fact that the dimer is not interacting with the cluster by the hydrogen bond is probably due to the presence of the covalent Si$_3$−O$_3$−Si$_4$ bond between the two chain organosilane molecules. This bond does not allow the rotation of the second chain around the Si−O−Si axis. Finally, the two chains remain nearly perpendicular to the surface, which is in good agreement with the experimental picture.

The bond length $r(Si_1-O_1)$ decreases by 0.017 Å with respect to the same bond length before grafting. This means that the frequency $v(Si_1-O_1)$ is less blue-shifted in the case of grafting complex (2) than that in (1). The bond length of OH is nearly unchanged. Within the dimer, the calculated angle $<(Si_3-O_3-Si_4)$ changes from 127.3 to 166.3°, and the intermolecular distance $R(Si_3-Si_4)$ varies from 2.97 to 3.25 Å. The steric hindrance between the two chains is still present, which therefore

slightly keeps the two chains far from each other (the larger intermolecular distance between carbon atoms $R(C_1-C_2)$ is around 7.33 Å). Note that this distance is much shorter than the same distance in the dimer before the grafting. The decrease in bond length is due to some distortion in the alkyl groups' alignment occurring in one of the two chains after their interaction with the surface. This explains that the grafting of the dimer on the silica surface gives a better organization of the chains themselves.

The interaction energy of the grafting system is around 0.63 eV. The difference in the interaction energy between the two grafting complexes is due to the absence of the intermolecular hydrogen bond and the deformation of the covalent $Si_1-O_1-Si_3$ bond in the case of complex (2) (142.9° compared to 172.6°).

The analysis of the charge indicates a partial charge of 0.31 |e| located on the dimer and −0.31 |e| located on the cluster. As noted for complex (1), the charge transfer and the modification of the two systems upon adsorption are clear evidence of the chemical nature of the interaction.

IV. Conclusions

The formation of self-assembled organic monolayers on microelectronics-type substrates is a key issue of emerging nanobiotechnologies. Quantum chemical calculations are performed to better understand the grafting of chain organosilane compounds on the silica surface. We observe that a single molecule chain interacting with the surface tends to lie flat on the SiO_2 through two different types of bonding: covalent and hydrogen bonds. In this view, the initial OH surface distribution, as well as the chain length, is the key parameter of further growth of the layer. Beyond the single molecule picture, we investigate the gas phase possible precursor/precursor interaction. It is shown that stable dimers may form that can subsequently be chemisorbed on the surface. This gives rise to a complex that, contrary to the single molecule picture, stands on the surface, potentially nucleating a well-defined homogeneous monolayer growth. We, therefore, believe that the growth of homogeneous self-assembled monolayers requires the presence of water molecules at some stage of the experimental deposition procedure to preorganize (through dimerization) the chain organosilane compounds before grafting. The role of water thus appears to be dual as its presence may be at the origin of aggregate formation on top of the self-assembled monolayer.

Moreover, we believe that the experimental calibration (process conditions, nature of the solvent..., hydrolysis of the precursor molecule under current investigation) could benefit from this type of calculation in order to form self-assembled monolayers efficiently and reliably.