



Self-assembled monolayers of perfluoroalkylsilane on plasma-hydroxylated silicon substrates

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ABSTRACT

In this study, a novel kind of fluoroalkylsilane monomers with different fluoroalkyl chain lengths was synthesized via three steps method and characterized by Fourier transform infrared (FT-IR) spectroscopy, ¹H and ¹⁹F nuclear magnetic resonance (¹H NMR and ¹⁹F NMR), and mass spectra (MS). Fluoroalkyl-terminated self-assembled monolayers (SAMs) on silanol-terminated silicon substrates (O₂ plasma treatment) were chemically fabricated via –Si–O– covalent bonds using the liquid phase deposition method (LPD). The wettabilities of the SAMs were characterized by water contact angles (CA), surface free energies and adhesive force (AF) measurements. 3-(1H,1H,2H,2H-perfluorooctyldecyl)propionamidepropyl-triethoxysilane (PFOPT) assembled monolayer was chosen for in-depth investigation as its CA was higher than the others. Attenuated total reflection infrared spectroscopy (ATR-IR) and X-ray photoelectron spectroscopy (XPS) were used to validate the attachment of PFOPT on the silicon substrate, together with the chemical composition and structure of the SAMs. The surface morphologies and roughness of the monolayers were obtained and calculated through atomic force microscopy (AFM). The migration of fluoroalkyl groups to the outermost surface of the SAMs was confirmed by AFM, XPS, CA, and AF measurements. It was found that the silicon substrate assembled with fluoroalkylsilane after heat treatment has higher contact angle, lower surface energy and adhesive force compared to that without heat treatment, and the outermost surface was rich in fluorine due to the surface microphase separation.

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1. Introduction

Self-assembled monolayers (SAMs) have attracted a great deal of attention in recent years due to a tremendous amount of excellent performances such as the superhydrophobic property [1–3], the physical or chemical adsorption of membranes or proteins [4,5], etc. Generally speaking, monolayers can be prepared through a number of chemistry methods using different attachment chemistries, among which surface attachment with alkylsilanes is one of the most commonly used methods to form SAMs [6]. Reactions of organosilane (R_{4-x}SiX_x, where x is from 1 to 3, R is an alkyl group and X is a leaving group, including alkoxy, chloride, etc.) with hydroxyl-terminated substrates (such as silicon dioxide, diamond, glass or metal oxides, etc.) results in the formation of self-assembled monolayers. The new surfaces with

particular chemical and physical properties can be used in the fields of electrochemistry, protective layers, lubricant films, biological applications and other functional surfaces [7–11]. Among the silanes coupling agents, alkoxy silanes are frequently used as moderately reactive agents to joint the organic molecules and hydroxylated substrates, then stable monolayers were prepared via the stronger multiple covalent and hydrogen bonds [6,12]. 3-aminopropylalkoxy silanes are of great interest due to their bifunctional nature, it provides an anchor to the surface which allows for further attachment of other functional molecules to the surface through the terminal amines [13,14]. Besides, various functional groups, such as alkyl, carboxyl, epoxy and fluoroalkyl groups can be introduced to the substrate surfaces for further modification [15–18].

Two approaches, including chemical liquid phase and vapor phase deposition can be adopted to prepare SAMs. The liquid phase method has been widely studied in the last decades, though some conditions (such as temperature, solvent polarity, viscosity and moisture content, etc.) are still needed to be optimized [9,19–21], most of the self-assembly processes with organosilanes

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are performed at solution/solid interface. The vapor-phase method is another way used for the formation of SAMs, there are only a few studies about the deposition of organosilane at vapor/solid interface, but it is considered to be of great convenience to prepare the organosilane monolayers through chemical vapor deposition (CVD) on a silicon substrate surface [13,17,22,23]. Among which, the liquid phase method is adopted by many researchers, and great efforts have been put into study and optimize the factors affecting the monolayer formation [2,13,14]. Generally, the formation mechanism of the silane-based SAMs on the substrates (e.g. silicon wafer) using liquid phase method is believed to occur through the following procedures: Firstly, organosilanes are hydrolyzed by water molecules that are already adsorbed on the clean, polar substrate surface with alcohol or HCl as the leaving groups, and the corresponding hydroxysilane are obtained. Then, the hydroxysilanes react with the surface silanol groups or the neighboring silanol groups of the silane react with each other to form Si-O-Si bonds. Finally, the silanes are aggregated driven by attractive forces such as van der Waals forces, dipole-dipole interactions or hydrogen-bonding between the hydrocarbon chains to obtain stable, ordered and densely packed SAMs [6,7,14].

The formation of the monolayers depends on the interaction between many experimental variables [24], such as the size, shape and chemical composition of the organic moieties [25,26], the moisture content of the organic solvent or the substrate surface [27], the solubility and concentration of organosilane precursor in solution [25], reaction temperature [27], and adsorption time [28], etc. These factors help to form various structures of the monolayers, as well as different surface properties. Among which, the reaction parameters such as solvent quality, organosilanes concentration, reaction time or temperature play an important role in the final surface quality of the monolayers [6,11,14,18,21]. Previous works reported that the solvents quality affected the density and the formation of silane monolayers [29], thus anhydrous solvent is typically required to produce a more uniform monolayer for alkoxy silane [6]. The thickness and average density of the monolayers always increase with the growth of reaction time as previous investigation has proved [30]. Thus the reaction time is usually kept less than one hour, while longer time may cause the organosilane molecules polymerization, which finally resulted in the formation of multiple layers or nonuniform coverage [31]. The silane concentration in solution is another factor that must be taken into account, for higher concentration may lead to the formation of multiple layers [32]. As a result, the assembly conditions are required to study in depth in order to obtain the optimal parameters.

Based on the excellent properties of C-F bonds, perfluorinated chemicals have been widely employed in a variety of fields including liquid (water/oil)-repellency, lubricating ability, adhesion, friction, oxidation resistance, and so on [10,33,34]. C-F bonds are stronger in organic chemistry with a binding energy of 485.7 kJ/mol, which ascribed to the large gap in the electronegativity between fluorine and carbon elements (F: 4.0, C: 2.5). The high electronegativity of F helps to reduce the polarizability of the bond, then weakening the van der Waals interactions, such that the perfluorinated materials possess extremely lower surface energy [10]. Thus, various structures of monolayers consisting of perfluoroalkylsilanes have been developed to obtain lower surface energy layers or coatings. In contrast to the disorder fluorocarbon layers, a number of ordered perfluorinated monolayers with lower surface energy have been reported [35–37]. Two approaches can be adopted in order to reduce the surface energy of fluorinated silane assembled monolayers: One is to optimize the reaction conditions to fabricate ordered and uniform monolayers, which can avoid the side reaction during the assembly process. Another is to treat the monolayers under high temperature since the fluoroalkyl groups can migrate from inner part of the layer to the outermost surface,

which not only helps to adjust the structures and orientation of the layers, but also assists to obtain a surface with vast fluorine. Moreover, the monolayers shows good thermal stability after high temperature treatment for the heat treated organoalkoxysilanes tend to form three covalent bonds with the hydroxylated surface, while it only forms one or two covalent bonds within air-dried organoalkoxysilanes [14].

3-aminopropyltriethoxysilane (APTES) is widely used as the silanating agent to prepare the aminopropyl-terminated substrate surface in most of previous studies, which provides an anchoring point for the attachment of more functional molecules. However, it is difficult to obtain a uniform monolayer with the amine groups orientated away from the substrates, because APTES is very sensitive to a number of reaction conditions [14,38]. So, there is an inevitable problem associated with the self-assembly of APTES on substrates, as the amino groups make the reaction more complicated. To make the assembly procedure controllable and to fabricate uniform, lower surface energy monolayers, fluoroalkylsilanes are chosen as the organosilanes for self-assembly, instead of APTES and fluorochemicals.

In this study, a new kind of fluoroalkylsilanes were synthesized (see Fig. 1), and a series of reproducible fluoroalkylsilanes monolayers on silicon substrates were then prepared through a liquid-phase method (see Fig. 2). During the activation step, oxygen plasma was used to clean the organic contamination and enrich the substrate surface with hydroxy groups. The properties of the SAMs were characterized by Fourier transform infrared spectroscopy, contact angle measurement, X-ray photoelectron spectroscopy, adhesive force measurement, atomic force microscopy, and energy dispersive X-ray spectroscopy (EDS).

2. Experimental

2.1. Materials

N,N'-Carbonyldiimidazole (CDI, 98%) and 3-Aminopropyl triethoxysilane (APTES; anhydrous; 98%) were obtained from Energy chemical and stored in desiccator. Toluene and methanol (anhydrous; analytical purity) were obtained from Shanghai SQS Chemical Co.,Ltd. Succinic anhydride (99%) was purchased from Shanghai Lingfeng Chemical Reagent Co.,Ltd. 1*H*,1*H*,2*H*,2*H*-perfluoro-1-hexanol (PFH, 99%), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol (PFO, 99%), and 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanol (PFD, 99%) were obtained from Hengtong Fluorine Chemical technology Co., Ltd. One-side polished n-type silicon (100) wafers (One hundred oriented, with resistivity of 0.01–0.09 Ω cm and thickness of 400 ± 20 μ m) were purchased from Xinxing Braim Technology Co., Ltd. (Beijing, China), and they were cut into squares ($1\text{--}2$ cm^{-1}). *N*-(3-triethoxysilylpropyl)-carboxypropyl formamide (TSCF) was prepared followed one previous literature [39].

2.2. Synthesis and characterization

2.2.1. Synthesis of 3-(1*H*,1*H*,2*H*,2*H*-perfluorohexyloxy carbonyl)-propionamidepropyl- triethoxysilane (PFHPT)

To a 100-mL three-necked-flask, TSCF (3.21 g, 10 mmol) was dissolved in 20 ml of toluene at room temperature under N_2 atmosphere. The mixture was stirred and *N,N'*-Carbonyldiimidazole (1.62 g, 10 mmol) was added into the mixture. After stirring for 2 h, 1*H*,1*H*,2*H*,2*H*-perfluoro-1-hexanol (2.64 g, 10 mmol) was added into the mixture. The reaction was continued for 6 h at 70 $^\circ\text{C}$ and the insoluble imidazole by-products were then removed by filtration, the solvent was removed under reduced pressure to get a colorless oil product. ^1H NMR (400 MHz, CDCl_3 , δ): 7.15 (s, 1H, NH), 4.05 (t,

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