[Review]

Organic Monolayers on Silicon: Microprinting, Micromachines, and Microarrays

Zhu Xiao-Yang

(Department of Chemistry, University of Minnesota Minneapolis, MN 55455, USA)

Abstract This account summarizes recent research in my laboratory on the integration of organic functionalities to silicon surfaces. We have discovered and developed novel, two-step strategies for the assembly of organic monolayers on silicon, silica, and related materials. These methods are simple and reproducible and lead to close packed monolayers with excellent physical/chemical properties. Exciting applications of these monolayers include (a) resists in soft-lithography, particularly micro-contact printing; (b) monolayer lubricant in silicon based micromachines, also called micro electromechanic systems (MEMS); and (c) molecular basis for the immobilization of DNA and protein molecules in microarrays.

Keywords: Silicon surface, Self-assembled monolayer, Micro contact printing, MEMS (Microelectromechanical systems), DNA chip, Protein chip

1 Introduction

The formation of covalently bonded organic monolayers on silicon surfaces, particularly the atomically flat H-Si(111), serves as a model for the exploration of monolayer assembly chemistry. On the technology side, organic monolayers on silicon is important to surface passivation in micro-electromechanical systems (MEMS)^[1] and microfluidics^[2], to silicon based biochips^[3], and to soft-lithography^[4]. These organic monolayers allow one to tailor the surface chemical and physical properties at the molecular level. The modification of silicon surfaces, with native oxide termination, has been traditionally accomplished *via* the use of siloxane chemistry, shown schematically in scheme 1^[5]. This approach involves the use of alkylchloro-silanes or alkylalkoxysilanes to form the organic monolayer. The reaction is believed to proceed by the initial conversion of Si-X (X=Cl, -OR) groups on the

silane molecule to silanol (Si-OH) groups. Under ideal conditions, a Langmuir like monolayer is formed on the hydrophilic surface with the presence of a thin water film. A cross-linked surface assembly is then formed by condensation reactions between the -OH groups on the silane molecules with those on the oxide surface or on neighboring silanes. Despite its popularity, the monolayer formation process is very sensitive to a number of experimental factors, such as water concentration, temperature, and substrate -OH density. The reactivity of the silanol groups often results in the formation of polymers, agglomerates, and other microstructures in the solution phase. In addition, the competition between cross linking and surface attachment more often than not leads to the formation of multilayer, polymeric structures, rather than monolayers on the surface, particularly when the organic group to be assembled deviates from

Scheme 1 Formation of siloxane self-assembled monolayer on oxide-terminated silicon

Scheme 2 A two-step strategy for the formation of alkoxy monolayer on silicon surfaces with or without native oxide termination

long chain alkyls.

In order to circumvent the problem of competition between cross linking and surface attachment in siloxane chemistry, we have developed a two-step method in which a silicon surface is first chlorinated to give reactive Si-Cl bonds. It is subsequently exposed to alcohol molecules in organic solution for monolayer formation *via* Si-O linkages, with HCl as a by-product. This approach can be applied to silicon surfaces with or without native oxide termination^[6]. For an oxide terminated surface, reactive Si-Cl groups are generated from an exposure of the surface to $\text{SiCl}_4(\text{g})$ at room temperature, with organic base as a catalyst. Alternatively, a H-terminated silicon surface, particularly H-Si(111), can be obtained from the well-known HF aqueous etching reaction of native oxide terminated silicon^[7]. The H-terminated surface is converted to a Cl-terminated one by reaction with Cl_2 either in the gas phase or in an organic solvent. The advantage of this approach is that the attachment of organic molecules to the solid surface is a selective reaction; there is no competition between surface attachment and intermolecular interaction. We have also applied this

two-step process to amine molecules for monolayer formation on silicon *via* Si-N linkages^[8].

There have been a number of other reported processes for monolayer formation on silicon surfaces. Particularly noteworthy is the pioneering work of Chidsey and coworkers on the hydrosilylation reaction between alkene and H-Si(111) to form close-packed monolayers with Si-C linkages^[9]. Other reported methods include the reaction of metal organic reagents with Cl- or H-terminated Si surfaces^[10-11] the electrochemical grafting of hydrocarbon radicals with H-terminated silicon^[12], photochemical reaction of alkenes and aldehydes^[13] or carboxylic acid^[14] with H-terminated Si, cycloaddition reactions on clean Si(100)^[15]. Alcohols may also react with H-terminated Si to form organic monolayers *via* Si-O linkages, similar to the surface from Fig. 2, with H_2 as a by-product^[16]. However, we found that the two-step process in Fig. 2 is faster than the direct reaction between alcohol and H-Si. A two-step strategy similar to Fig. 2, but using a different surface activation molecule, $\text{Si}(\text{NEt}_2)_4$, was demonstrated by Yam^[17]. In their approach, surface -OH groups on silicon oxide was converted to Si-NEt₂ groups in one or

Fig. 1 C–H stretching region of FTIR spectra of monolayers of $n\text{-C}_{18}\text{H}_{37}\text{O}-$ and $n\text{-C}_{12}\text{H}_{25}\text{O}-$ on Si(111) (left) and Si(100) (right)

two steps. This surface reacted with alcohol molecules for monolayer formation, with diethylamine (NEt_2H) as a by-product. A recent review by Wayner and Wolkow provides a comprehensive account of organic monolayer formation on H-terminated silicon surfaces^[18].

Like most other reactions reported in recent years for monolayer formation on “flat” silicon and silicon oxide surfaces, similar schemes are well known in the field of small particle surface functionalization, particularly on silica^[19]. In addition, there are extensive studies on the functionalization of porous silicon surfaces^[20].

In the following, I will demonstrate the two-step approach in scheme 2 for the formation of alkoxy monolayers on silicon and silica surfaces. The resulting surfaces are characterized by a host of experimental techniques, including X-ray photoelectron spectroscopy (XPS), multiple internal reflection Fourier transform infrared spectroscopy (MIR-FTIR), atomic force microscopy (AFM), ellipsometry, water contact angle measurements, and X-ray reflectivity. I will discuss briefly the application of these monolayer coatings to microcontact printing directly on the silicon surface, to surface passivation in micromachines, and to microarrays.

2 Alkoxy monolayers on silicon

The two-step monolayer assembly strategy in

scheme 1 for bare silicon starts with a hydrogen terminated surface, obtained from wet NH_4F etching of native oxide terminated silicon. The H-terminated silicon surface reacts with Cl_2 either in an iso-octane solution or in the gas phase to give a Cl-terminated silicon surface. The Cl–Si surface subsequently reacts with alcohol molecules in iso-octane solution at 80 °C with pyridine as a catalyst for monolayer assembly. Characterization by a number of techniques reveal covalently bonded, uniform monolayers with film thickness approaching molecular length at the highest coverage.

Fig. 1 shows MIR-FTIR spectra of dodecanol and octadecanol assemblies on Si(111) and Si(100) surfaces. These spectra are typical for self-assembled monolayers of long chain alkyls, as reported previously for thiolate SAMs on Au, siloxane SAMs on oxidized silicon, and alkyl monolayers on silicon^[5, 9, 21]. On Si(111), the C12 film displays an asymmetric CH_2 stretching frequency of $\nu_a = (2922 \pm 1.0) \text{ cm}^{-1}$ and a symmetric CH_2 stretch of $\nu_s = (2852 \pm 1.0) \text{ cm}^{-1}$. For the C18 film, the frequencies are $\nu_a = (2921 \pm 1.0)$ and $\nu_s = (2851 \pm 1.0) \text{ cm}^{-1}$. The peaks at $\sim 2955 \text{ cm}^{-1}$ and the unresolved shoulder at $\sim 2900 \text{ cm}^{-1}$ are the asymmetric and symmetric C–H stretch in the terminal $-\text{CH}_3$ group. It is well established that the asymmetric C–H stretching frequency (ν_a) for $-\text{CH}_2-$ units is a reliable indicator of film quality for alkyl

Fig. 2 AFM images ($5.5 \text{ nm} \times 5.5 \text{ nm}$) taken in the lateral force mode for an $n\text{-C}_{18}\text{H}_{37}\text{OH}$ assembled Si(100) surface. A line scan is also shown

SAMs. The frequency varies from 2917 cm^{-1} for close-packed solid-like films to 2925 cm^{-1} for disordered, liquid-like films^[5-9]. The ν_a frequencies of $2921 \sim 2922 \text{ cm}^{-1}$ from the dodecanol and octadecanol assembled surfaces are indicative of partial disorder, *i. e.*, the alkyl chains do not possess a high degree of all-trans conformational order.

Despite the fact that the starting H-Si(111) surface is atomically flat while the H-Si(100) surface has a root-mean-square (RMS) roughness of $\sim 2.0 \text{ nm}$, FTIR spectra in the right panel shows higher coverage and better ordering of alkoxy monolayers on Si(100) than corresponding monolayers on Si(111). The ν_a frequency of 2918 cm^{-1} from the octadecanol assembled Si(111) is very close to that from close-packed alkyl monolayers in other SAMs systems. This correlation of substrate roughness to monolayer packing density may be attributed to the large mismatch between the molecular lattice and the substrate silicon lattice. On the Si(111) surface, such mismatch leads to the buildup of significant stress and film disorder. On the other hand, the roughness and small domain size of the alkoxy monolayer on Si(100) assist the release of film stress, resulting in higher molecular coverage and closer packing than the film on Si(111).

The close packing of alkoxy monolayers on the Si(100) surface allows AFM imaging with molecular lattice resolution. Fig. 2 shows AFM lateral force images ($5.5 \text{ nm} \times 5.5 \text{ nm}$) for the C18 assembled Si(100) surface. Lattice resolution is evident in the image, suggesting the presence of molecular order within the monolayer. This is

particularly obvious when we examine line scans. In each line scan, the lateral force shows regular “stick-slip” features, which are characteristic of an ordered surface. The regular interval in the saw-tooth pattern is $\sim 0.46 \text{ nm}$. This kind of “stick-slip” feature is not possible in the absence of order within the monolayer. From Fourier analysis of several images, an average lattice parameter, or inter-molecular distance, of $0.48 \pm 0.03 \text{ nm}$ was obtained. This number is very close to the inter-molecular distance in well-known alkanethiol SAMs.

3 Alkoxy monolayers on oxide terminated silicon

For an oxide-terminated surface, the two-step strategy starts with activating the surface by SiCl_4 (g) at room temperature, with pyridine as a catalyst. This reaction leads to a complete conversion of surface -OH groups to surface $-\text{SiCl}_x$, which

Fig. 3 C-H stretching region of FTIR spectra of monolayers of $n\text{-C}_{18}\text{H}_{37}\text{O}$ - and $n\text{-C}_{12}\text{H}_{25}\text{O}$ - on native oxide terminated Si(111)

Fig. 4 Relative coverage of the $C_{18}H_{37}O-$ film on native oxide terminated Si(111) as a function of reaction time

1 ML(monolayer) is defined as the saturation coverage with film thickness of 2.4 nm. The inset shows AFM images for (A) 0.5 ML and (B) 1 ML. The RMS roughness for either surface is ≤ 0.16 nm

is predominantly $-SiCl_3$. The activated surface reacts with alcohol molecules in an iso-octane solution for monolayer formation *via* Si–O linkages. The addition of CaH_2 as a drying reagent to remove trace amounts of water was shown to increase surface alkoxy coverage and packing density. Characterization of the resulting monolayer by a combination of techniques reveals a densely packed film with partial disorder. Fig. 3 shows MIR-FTIR spectra for dodecanol and octadecanol assemblies(saturation coverage) on native oxide terminated Si(111). These spectra are similar to those in Fig. 1. Ellipsometry and XPS measurement reveal that the thickness of the $C_{18}H_{37}O-$ film is 2.4 nm, which is close to the length of the alkyl group.

Kinetic measurement of film growth provides insight into the mechanism of surface reaction and monolayer assembly. Fig. 4 shows the dependence of surface $C_{18}H_{37}O-$ coverage on reaction time (between octadecanol and $SiCl_x$ activated surface) at a reaction temperature of 80 °C. The uptake of $C_{18}H_{36}O-$ groups shows a rapid initial region within the first 10 minutes to give a surface coverage of ~ 0.5 monolayer (ML). Beyond 0.5

ML, the uptake continues, albeit at an increasingly slower rate, to reach a maximum surface coverage of 1 ML. The rate constant decreases by 2–3 orders of magnitude with increasing coverage. The attachment of $C_{18}H_{36}O-$ species to the chlorinated surface is kinetically controlled. At the initial stage, surface sites are easily accessible; this corresponds to the fast reaction rate. When coverage reaches ~ 0.5 ML, surface active sites ($Si-Cl_x$) are effectively blocked by attached alkyl groups. The reaction slows down dramatically. Further attachment requires the re-arrangement of surface $C_{18}H_{36}O-$ groups and the diffusion of precursor $C_{18}H_{36}OH$ molecules through the partially formed molecular layer, an increasing slower process at higher coverages.

AFM topographical images of $C_{18}H_{36}O-$ at 0.5 ML and 1 ML coverages both show ultraflatness, with RMS roughness ≤ 0.16 nm. This roughness is similar to that of the clean oxide terminated Si(111) surface. There is no evidence of inhomogeneity or pin-holes in both films, suggesting that, at low coverages, each attached $C_{18}H_{36}O-$ group is in a low surface density, homogeneous environment. At the highest surface density, the alkyl chains stand up and form a nearly close-packed monolayer.

4 Application 1: microcontact printing

The importance of patterning silicon surfaces is obvious; prominent applications include microelectronics, microfluidics, and MEMS. Since the successful demonstration of softlithography^[22] particularly micro-contact printing (μ CP) using thiol SAMs on gold, a number of groups have extended the technique to silicon and related surfaces^[23]. Past attempts in patterning silicon surfaces *via* μ CP have relied on siloxane SAMs (scheme 1), but a number of complications associated with this chemistry have resulted in difficulties with μ CP.

Scheme 3 Microcontact printing of alkoxy monolayer directly on the silicon surface

Fig. 5 The dependence of film thickness on stamping time for monolayer patterns from the μ CP of dodecanol on Cl-Si(111)

The insets are AFM topographical images for stamping times (min) of (a) 1; (b) 10; (c) 30. Inset (d) shows an AFM image of the surface from stamping on H-Si(111) for 10 min

For example, edge diffusion or island formation often led to low resolution^[23]. The high reproducibility and film quality associated with the two step approach in scheme 2 can provide marked improvement in μ CP directly on the silicon surface.

Scheme 3 illustrates the procedure for μ CP on silicon using the two-step approach^[24]. A chlorinated Si(111) surface is used as the substrate. Alcohol/iso-octane solution ("ink") is applied to a poly(dimethyl siloxane) (PDMS) stamp (5 μ m lines with 5 μ m spacing) with a Q-tip. The inked stamp is brought into contact with the Cl-Si(111) surface in a dry N_2 environment. After certain contact time, the surface is rinsed with organic solvents to remove excess, weakly adsorbed molecules.

Alkoxy films grow in the contact region while remaining Si-Cl species in the non-contact area react with moisture in the air to form surface hydroxyl groups.

Fig. 5 shows the dependence of film thickness as a function of stamping time for dodecanol on Cl-Si(111). The thickness values are obtained from topographical AFM images, shown in insets. Patterns with sharp contrast are obvious for stamping time from 1 to 30 min (insets a-c). There is no evidence of edge diffusion or island formation. The resolution of the patterns seems to be only limited by that of the stamp. At saturation coverage achieved for stamping time ≥ 30 min, the film thickness is 1.6 ~ 1.8 nm, which is close to the molecular length in all-trans configuration. For comparison, image (d) shows stamping for 10 min directly on the H-Si(111) surface without the chlorination step. Although, the covalent attachment of alcohol molecules to the H-Si(111) surface has been reported^[16], we see no deposition of molecule from μ CP under the experimental conditions used. The Cl-terminated Si surface is more reactive towards alcohol molecules than the H-terminated surface does, thus, making μ CP possible within a reasonable time window.

5 Application 2: micromachines

Microelectromechanical systems (MEMS) are bringing the second silicon revolution. However, the difficulty in controlling surface forces is a

Fig. 6 IFM force profiles between a W tip and the surface for native oxide covered (solid) and octadecanol assembled (dashed) Si(100) surface

critical impediment to the success of many MEMS devices^[1, 25]. This is a consequence of the scaling law: the surface-to-volume ratio scales with the inverse of device dimension and surface forces dominate at length scales < 1 mm. A well-known problem in the fabrication of MEMS devices from surface micromachining is stiction, which occurs when surface adhesion forces are higher than the mechanical restoring force of the micro-structure. When a device is removed from the aqueous solution after wet etching of an underlying sacrificial layer, the liquid meniscus formed on hydrophilic surfaces pulls the microstructure towards the substrate and stiction occurs. While this release-stiction problem may be alleviated by dry HF etching or supercritical CO₂ drying, a more difficult problem is in-use stiction which occurs during operation when microstructures come into contact

Fig. 7 Upper: schematic illustrate of a cantilever; lower: Interference microscope image of cantilever beam arrays with beam length of 2 mm

The image (composite of three frames) is obtained after the beams are released in an all-liquid etching-coating process

(intentionally or accidentally)^[1, 25].

One attractive approach to tackle the stiction problem is to provide a low-energy surface coating in the form of an organic passivation layer on the inorganic surface. Such a coating can not only eliminate or reduce capillary forces and direct chemical bonding, but also reduce electro-static forces if the thin organic layer is directly applied to the semiconducting substrate, without the intervening oxide layer. The two-step process in scheme 2 for forming alkoxy monolayers on silicon surfaces has been successfully demonstrated in eliminating sticking in Si MEMS devices. The alkoxy monolayers show excellent mechanical properties, as characterized by Interfacial Force Microscopy (IFM)^[26]. This instrument is unique in that it consists of a noncompliant sensor which makes it possible to obtain accurate measurements of the complete tip/sample interaction force profile, from attraction to repulsion. In addition to measuring the normal force, a simultaneous measure of lateral friction may be obtained by modulating the tip in the lateral direction.

Fig. 6 shows force profiles of a native oxide terminated (solid curve) and an octadecanol assembled (dashed curve) Si(100) surfaces, respectively^[26]. In this experiment, the force between a W tip (~ 500 nm radius) and the silicon surface is measured when tip approaches the surface. The monolayer assembled surface shows negligible attractive force, which is $\sim 2\%$ of that on the native oxide covered surface. In addition to lowering surface energy, the monolayers also function as good lubricant coatings. Measurements of friction as a function of normal force for alkoxy monolayer assembled silicon surfaces give friction coefficients on the order of 10^{-2} for dodecanol and octadecanol assembled surfaces^[26].

To test the application of alkoxy monolayers as anti-stiction coatings for silicon based MEMS, we use cantilever beam arrays (CBAs) fabricated by the SUMMiT process of Sandia National Lab-

oratory. A cross section of the structure is shown schematically in Fig. 7. The structure consists of poly-crystalline silicon (*p*-Si) beams with thickness of 2.25 μm , anchored at one end by *p*-Si support posts. The sacrificial PSG layer under each beam is $\sim 2 \mu\text{m}$ thick. The bending of *p*-Si beams on each CBA sample is characterized by an interference microscope. Out-of-plane bending of the beams is shown as optical fringes; each fringe corresponds to the bending of $\lambda/2$ or 311 nm. The lower part of Fig. 7 shows typical images of beam arrays (2 mm in length) with alkoxy coating. All beams are completely released. The fringes reflect (downward) bending due to residual stress. The maximum bending is $\sim 1.8 \mu\text{m}$. Therefore, the above monolayer coating process eliminates release stiction. Electro-static actuation of these coated beams also revealed little in-use stiction with relative humidity as high as 90%^[27].

6 Application 3: microarrays

Microarray technology is revolutionizing disease diagnostics and drug discovery^[28]. In this technology, thousands of bio-probe molecules, such as oligonucleotide, cDNA, protein, and antibodies, are immobilized on a matrix in a way that preserve their activity and are accessible to their targets. In many ways, microarray is a surface chemistry problem. This is particularly true for protein microarrays. With great advances in genomics, such as the completion of human genome sequencing, the next grand challenge becomes apparent: understanding biological functions of proteins encoded by genes. Using the microarray technology, thousands of proteins or antibodies could be studied in parallel to establish their biochemical properties and biological activities.

Ideally, we would like a surface which possesses the following attributes:

- The surface resists non-specific adsorption of bio-samples, such as proteins and cells.

- The surface is hydrophilic and compatible with aqueous-based fluidic systems.

- The surface presents structurally well defined functional groups in a homogeneous environment.

- The surface allows versatile immobilization chemistry with easily controllable immobilization density.

These conditions may be met with a high density polyethylene glycol, $\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, monolayer grafted onto the silicon surface *via* the two-step strategy in scheme 2. This approach involves the direct interaction of the HO-functional group on polyethylene glycol (PEG) with a chlorine terminated silicon surface^[29]. The resulting monolayers show exceptional flatness, with mean roughness on the 0.1 nm scale. Film thickness is determined by ellipsometry, X-ray photoelectron spectroscopy, and atomic force microscopy, as shown in Fig. 8. At low molecular weight (MW < 1000), the film thickness approaches that of molecular length, indicating that the grafted PEG molecules are in a brush-like configuration. Incubation of the PEG brush grafted surface with protein or serum solutions shows the inertness of the surface towards non-specific adsorption^[29].

A number of chemical approaches can be used to activate the surface $-\text{OH}$ groups on the PEG

Fig. 8 Film thickness of PEG monolayers on Si (111) as a function of molecular weight. The data points are from ellipsometry (circles), AFM (squares), and XPS (triangles). The solid line is the molecular length in helical conformation

Scheme 4 Immobilizing bio-probe molecules onto the PEG brush

brush for bio-probe immobilization. Bi-linker molecules, such as *N*-[*p*-maleimidophenyl]isocyanate (PMPI), may be used to link a bio- molecule with $-SH$ functional groups, scheme 4. Alternatively, surface $-OH$ groups may be converted to $-CHO$ groups *via* partial oxidation. The aldehyde group may react with $-HN_2$ on bio-probe molecules *via* Schiff base linkage. Fig. 9 shows fluorescence microscope images of oligonucleotide and green fluorescence protein (GFP) covalently attached to the PEG brush on Si(111).

7 Concluding remarks

This brief account summarizes recent research in my laboratory on monolayer assemblies on silicon surfaces. The excitement in this field is fueled by a fundamental interest in monolayer assembly chemistry as well as a number of important applications, as illustrated briefly above. One can easily identify the inter-disciplinary nature of the research presented here. I have no doubt that an increasingly intimate interaction among traditional fields, such as surface science, physical chemistry, organic chemistry, biotechnology, and engineering, will continue to yield fruitful research.

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Fig. 9 Fluorescence microscope images of Texas-Red labeled oligonucleotide(upper left) and Green fluorescent protein (lower left) covalently bonded to the PEG brush on Si(111). The images on the right are corresponding background, without linking chemistry

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硅表面有机单层膜：微印章、微加工与微阵列

朱晓阳

(Department of Chemistry, University of Minnesota Minneapolis, MN 55455 USA)

摘要 总结了作者的实验室在将有机物结合到硅表面方面的研究进展。发现并发展了将有机单层膜组装到硅、氧化硅和相关材料表面的新方法。这些方法简单、可重复，并可得到物理、化学性能良好的致密单层膜。这些单层膜在许多方面有令人鼓舞的应用，包括 (a) 应用于软印刷术，特别是微接触印章法；(b) 用作硅的微加工 (微机电系统, MEMS) 的单层膜润滑剂；(c) 用作 DNA 和蛋白质微阵列功能分子固定的基底。

关键词： 硅表面， 自组装单层膜， 微接触印章法， 微机电系统 (MEMS)， DNA 芯片， 蛋白质芯片

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