Preparation of Self-Assembled Monolayers in scCO\textsubscript{2} and Their Application to Fabrication and Patterning of Polymer Thin Films

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Abstract: A thin film of polymer was fabricated on functionalized silicon wafer through self-assembled monolayers (SAMs) of perfluorophenyl azide derivatives (PFPA-silane) with covalent bonds by photochemical reaction. The SAMs were formed in supercritical carbon dioxide (scCO\textsubscript{2}), and the immobilization of polymers was performed by UV irradiation. The results indicate that scCO\textsubscript{2} is a good solvent for silylation reactions, better than common organic solvent such as toluene. Compared with the optimum conditions for silylation, reactions are faster and optimum concentration of PFPA-silane is lower in scCO\textsubscript{2}. The SAMs formed in scCO\textsubscript{2} are more uniform than SAMs formed in toluene. The immobilization of polymers is based on photoreactive azido groups of PFPA-silane which is bound to SiO\textsubscript{2} surface via silane anchor. Furthermore, the combination of immobilization chemistry with photolithography, which generated patterned polymer films and hybrid arrays with unique surface topographies is also reported.

Keywords: self-assembled monolayers, supercritical carbon dioxide, perfluorophenyl azide derivatives, photochemical reaction, photolithography, immobilization

Introduction

Recent reports have indicated that monolayer systems can be targeted for a variety of applications, including cell adhesion [1], patterning [2-4], sensors [5], molecular electronics [6,7], biocompatible surfaces [8] and inhibiting corrosion [9]. Modification of surfaces with polymer thin films has emerged as an important method to control the physical and chemical properties and to introduce functional groups to the surface layer. Solution casting is a commonly used method to prepare polymer thin films, with spin coating the most popular technique when a flat substrate is used. However, these films are physisorbed and can be easily removed from the substrate by just rinsing with a solvent. Covalently immobilized films are firmly attached to the substrate and are therefore more robust toward environmental and processing conditions. Most covalent immobilization methods involve chemical derivation of the substrate and/or the polymer, and sometimes, the synthetic chemistry can be complicated and challenging.

We have employed functionalized perfluorophenyl azides (PFPA-silane) to immobilize thin polymer films to silicon wafers. The approach is based on the photochemistry of PFPA-silane. Upon UV irradiation, highly reactive nitrenes are generated that undergo C-H insertion reaction to the adjacent polymer chains. An attractive feature of this method is its versatility, as no special functional groups are needed on the polymer. In addition, patterned polymer films can be readily generated by a photochemical activation. In our previous experiment, we used toluene for SAM formation on silicon wafers as a depositing medium [10].

Traditionally, typical organic solvents such as ethanol, hexane, toluene and chloroform have been used for SAM formation because of their availability and ease of use in the laboratory. As society raises concerns about environmental issues, research on reducing the use of volatile organic compounds and reducing the generation of aqueous waste has become important. Because of this, there has been a significant increase in the use of liquid and supercritical carbon dioxide as alternative solvents and processing tools [11-16]. CO\textsubscript{2} is a small molecule that has lit-
Figure 1. The structure of PFPA-silane.

tle affinity with either the substrate or the adsorbate. In addition, the self-diffusion coefficient of CO$_2$ is greater than that of traditional solvents [17], which might enable SAMs to form more rapidly in CO$_2$. Material transport in compressed CO$_2$ should also be increased because of the low viscosity of CO$_2$. The viscosity of compressed CO$_2$ is lower than that of traditional liquid solvents [18,19]. In addition, pressurized CO$_2$ is environmentally benign, nontoxic, inexpensive, and nonflammable.

In this paper, we used scCO$_2$ for formation of SAM on silicon wafers as a depositing medium and compared these films with those assembled in toluene as conventional solvent medium. Besides, we describe the fabrication of patterned polymer arrays with unique surface topography.

**Experimental**

**Materials**

*N*-Succinimidyl-4-azidotetrafluorobenzoate and *N*-(3-triethoxysilylpropyl)-4-azidotetra-fluorobenzoate (1, PFPA-silane) were prepared according to the literature [20,10]. (3-Aminopropyl)triethoxysilane, PEOX ($M_w$ 50,000, 200,000, and 500,000) and PS ($M_w$ 382,100) were purchased from Aldrich. Research-grade CO$_2$ (Daeyoung Co., 99.99 %) was used. Unless otherwise stated, all other chemicals and solvents were used as received.

**Substrates**

Silicon wafers were first treated with piranha solution (concentrated sulfuric acid: 30 % hydrogen peroxide = 7:3 v/v) for 90 min at 80 ~ 90 °C. Later, it was washed thoroughly with boiling deionized (DI) water (18.2 MΩ, Elga Maxima Scientific) for 90 min and dried by stream of nitrogen. This cleaning procedure creates a surface rich in hydroxyl groups on the oxide surface to facilitate the subsequent silanization process [21].

**SAM Formation in CO$_2$**

SAMs from CO$_2$ were prepared in a 10 mL stainless steel reactor. The cleaned silicon wafer was placed in the reactor with depositing species 1. Once the temperature was reached at 40 °C, an ISCO syringe pump (260D) was used to pressurize the reactor with CO$_2$ (15 MPa). The reaction was carried out for the required time. Then the sample was removed and rinsed with methylene chloride, acetone, and methanol sequentially. Finally, the silicon wafer was dried by a stream of nitrogen.

**Immobilization of Polymer Thin Films**

Thick overcoats of the polymers were prepared by spin-coating solutions of the polymers at a typical spin speed of 2000 rpm for 60 s. Toluene and chloroform were used as a solvent for PS and PEOX respectively at a concentration of 10 mg/mL. The samples dried by a stream of nitrogen and used directly for irradiation experiments. These experiments have been performed at room temperature using a Karl Suss MJB 3 mask aligner with a high pressure Hg lamp (200 W, Osram). After irradiation for the desired period of time, we sonicated the samples in good solvent (PS: toluene, PEOX: chloroform) for at least 3 min to remove unbound polymers. The thickness of the resulting polymer layers were again determined by ellipsometry.

**Fabrication of Surface Topography**

The wafer spin-coated with PEOX (10 mg/mL in CHCl$_3$) was placed in direct contact with a quartz photomask when subjected to UV irradiation. After extraction in CHCl$_3$, the wafer was spin coated with the second polymer (10 mg/mL PS/toluene) at 2000 rpm for 60 s. And then it was irradiated with UV light, extracted in toluene to remove unattached polymer and dried by stream of nitrogen. The formation of the PEOX/PS polymer array was confirmed by AFM and SEM.

**Instruments and Measurements**

Spin coating was performed using a E. H. C SC-300. Film thicknesses were measured using a Gaertner L2W830 ellipsometer at an incident angle of 70°. The following refractive indices: SiO$_2$ 1.465, PFPA-silane 1.503, PS 1.592, and PEOX 1.520 were used to determine the thicknesses of various film layers. The refractive index of 1 was determined using a Bausch & Lomb Abbe 3 L refractometer. The measurements were performed at six different spots of a given sample. The surface topography of the films was examined by atomic force microscopy (Nanoscope IIIa, Digital Instruments) and scanning electron microscope (JSM-6700F, JEOL).

**Results and Discussion**

We have synthesized a PFPA-silane, *N*-(3-triethoxysilylpropyl)-4-azidotetrafluorobenzoate (1), for the photochemical immobilization of polymer films to silicon wa-
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Scheme 1. Formation of SAM on silicon wafer and Immobilization of PS thin film.

Figure 2. PFPA-silane film thickness as a function of concentration.

Figure 3. PFPA-silane film thickness as a function of deposition time.

Figure 4. Comparison of average surface roughness for SAM formed in scCO$_2$ and toluene. (a) AFM image of SAM formed in scCO$_2$ ($R_{\text{rms}}$: 0.177 nm), (b) AFM image of SAM formed in toluene ($R_{\text{rms}}$: 0.225 nm).

The film immobilization process was started with the functionalization of silicon wafers with PFPA-silane to introduce a monolayer of azido groups on the wafer surface. Figure 2 shows the thicknesses of SAM as a function of concentration of PFPA-silane. The thickness of SAM was measured to be about 13 Å, assuming the refractive index is 1.503.

Figure 3 shows the thickness of SAM as a function of deposition time with 0.55 mg/mL. It seems to be increased up to 4 h and reached a constant value after deposition for about 4 h. In case of toluene, optimum deposition time was 9 h and optimum concentration of PFPA-silane was 2.2 mg/mL [10]. The root-mean-square average surface roughness ($R_{\text{rms}}$) of the SAMs is compared in Figure 4 for scCO$_2$ and toluene. The $R_{\text{rms}}$ value of SAM formed in scCO$_2$ (0.177 nm) is lower than $R_{\text{rms}}$ value of SAM formed in toluene (0.225 nm). These $R_{\text{rms}}$ values were obtained from AFM sectional analysis.

These results indicate that scCO$_2$ is superior solvent for SAM formation compared to conventional solvent such as toluene. This can be attributed to the advantageous solubility, density, and transport properties of supercritical CO$_2$.

The polymer solution was then spin coated on the treated wafer and the sample was irradiated with UV light. Photolysis activated the azido group and generated the highly reactive singlet nitrene intermediate which underwent C-H insertion reaction to the adjacent polymer chains (Scheme 1) [22-26]. Removal of the unattached polymer by solvent extraction resulted in a thin film that was covalently immobilized on the wafer surface.

We have performed various sets of experiments each for PS and PEOX to study this procedure for the photochemical attachment of thin polymer coatings to wafer surfaces. All experiments were carried out at comparable light intensities.

For time-dependent studies, we varied the UV irradiation times of PS and PEOX layers deposited on treated wafers to check the optimal time needed to successfully immobilize the polymer on the surface. These studies were performed using a PS ($M_w$ 382,100) and PEOX ($M_w$ 200,000). The polymer solution concentration of 10 mg/mL was used for spin coating. Figures 5 and 6 show...
Scheme 2. Fabrication procedure for patterning of polymer thin film on a SAM surface.

Figure 5. Immobilized PS film thickness as a function of UV irradiation time. PS ($M_w$ 382,100) solution of 10 mg/mL was used for spin coating.

Figure 6. Immobilized PEOX film thickness as a function of UV irradiation time. PEOX ($M_w$ 200,000) solution of 10 mg/mL was used for spin coating.

the thickness of the immobilized polymer films after the unattached polymer was removed by sonication as a function of irradiation time. The thicknesses increased with increasing irradiation time and reached constant value after 20 and 10 min for PS and PEOX respectively. Since no change was observed over long irradiation time, the above values were optimized and maintained. The observed polymer film thickness was about 57 Å for PS and 23 Å for PEOX.

For concentration-dependent studies, we varied the concentration over a range from 5 to 30 mg/mL. The PS ($M_w$ 382,100) solution and PEOX ($M_w$ 200,000) solution of various concentrations were spin coated on 1-functionalized wafers. After that, the wafer was UV irradiated for 20 min (PS) and 10 min (PEOX), and sonicated in appropriate solvent. Figure 7 and 8 show that the higher concentration of polymer provides the thicker polymer film. But the finally immobilized polymer film thickness was uniform for all concentrations of the spin coated polymers. This result was consistent with the proposed mechanism given in Scheme 2. Since the C-H insertion reactions occurred at the interface between the azido groups and the adjacent polymer chains, thicker polymer films should have no effect on the thickness of the immobilized polymer film. Therefore, just a monolayer of polymer is attached to the surface after UV irradiation.

The effect of molecular weight on the thickness of the immobilized polymer films was also studied. This study was conducted using the PEOX of various molecular weights ($M_w$ 50,000, 200,000, and 500,000). The polymer solution of 10 mg/mL was spin coated on 1-functionalized wafers, irradiated for 10 min and sonicated in chloroform. Figure 9 shows that the immobilized film thickness increased with the molecular weight of the PEOX. Thicker films (about 28 Å) were generated using a higher molecular weight (500,000), while a lower mo-
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Figure 7. Immobilized PS ($M_w$ 382,100) film thickness as a function of concentrations.

Figure 8. Immobilized PEOX ($M_w$ 200,000) film thickness as a function of concentrations.

Figure 9. Immobilized PEOX film thickness as a function of molecular weight. PEOX solution of 10 mg/mL was used.

Figure 10. AFM image of patterned PEOX/PS array. Pattern Width = 10 µm.

Molecular weight (50,000) produced about 8 Å thick films. The thickness of the immobilized film is related to the radius of gyration ($R_g$) of the polymer coil which increases with the molecular weight of the polymer [27]. Therefore, higher the molecular weight of the polymer, larger the radius of gyration and thicker the immobilized polymer film.

These results indicate that the reactivity of SAMs formed in scCO$_2$ is the same in the case of toluene. However, about formation of SAMs, optimum deposition time is shorter and optimum concentration of 1 is lower than in the case of toluene.

This immobilization chemistry was employed to generate patterned polymer thin films. Scheme 2 indicates the fabrication procedure. To evaluate this procedure for use in patterning thin films, the 1-treated wafers spin coated with PEOX ($M_w$ 200,000) were placed in direct contact with a quartz photomask when subjected to UV irradiation. The photomask had a 10 µm L/S (Line/Space) pattern, the azido groups in transparent regions would be decomposed after irradiation. Fabrication of polymer arrays was possible after the unattached PEOX film was removed from the unexposed regions leaving unreacted azido groups on the wafer available for insertion into a second polymer (10 mg/mL, PS/toluene). This was conducted by spin coating a second polymer onto the surface of the PEOX patterned wafer followed by UV irradiation and solvent extraction of unattached polymer. The formation of the PEOX/PS polymer array was confirmed by AFM and SEM (Figures 10 and 11 respectively). The array is a good illustration of the sharp PEOX and PS interface, which define each polymer film boundary. An AFM cross-section image revealed that vertical distance was 3.576 nm (Figure 10 inset). The height of the micropatterns correlated well with the thickness of films immobilized under the same condition. These results demonstrated the ability of this immobilization method to create polymer arrays with unique surface topographies.
Conclusion

For SAMs formation studies, deposition time in scCO$_2$ is shorter than that in toluene. And also optimum concentration of 1 in scCO$_2$ is lower compared to toluene. Therefore, supercritical CO$_2$ is an effective solvent for the formation of self-assembled monolayers compared to traditional solvent such as toluene. These results are likely to be due to the favorable properties of the scCO$_2$ such as its small molecular size, low viscosity and high self-diffusivity. However, the reactivity of SAMs for polymer immobilization is the same.

This immobilization method can be used to create polymer arrays with unique surface topographies. This simple procedure is versatile due to the chemical reactivity of nitriles, which can covalently bond to a myriad of molecules and materials.

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