# Area-selective deposition of self-assembled monolayers on a synchrotron radiation etching pattern

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Patterning of self-assembled monolayer (SAM) was demonstrated by area-selective deposition of SAMs on a pattern made by synchrotron radiation (SR) stimulated etching $SiO_2$ thin films. The etching was conducted by exposing the $SiO_2$ films to SR through a Co contact mask with $SF_6 + O_2$ as the reaction gas. A dodecene SAM was deposited on the etched surface and an octadecyltrichlorosilane SAM was deposited on the $SiO_2$ surface. The deposited SAMs were densely packed and well ordered, which were characterized by infrared spectroscopy, ellipsometer, and water contact angle.

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A pre-patterned surface of hydrophobic or hydrophilic alkyl self-assembled monolayer (SAM) has been found to yield promising results for area selective deposition of biomaterials[1]. Micro-fabrication technology, a new and powerful tool in the manufacturing of various types of silicon-based biomedical micro-devices, has also made a considerable impact on the recent biotechnological researches[2]. Synchrotron radiation (SR) stimulated etching of $SiO_2$ thin films on Si substrates is considered to be a suitable micro-fabrication technology to make a template for area-selective deposition of SAMs, because it has several unique features such as high spatial resolution, high material selectivity between Si and $SiO_2$, anisotropy etching, and clean etching atmosphere[3−5]. A great number of studies have been conducted on SAMs from the aspects of the structure, formation process, and physical properties, for it is one of the promising candidates in such applications as adhesion promoters, surface modifications, surface protective films, and the fabrication of field effect transistors[6−10]. And the area-selective deposition of SAMs is one of the important topics in this field[11,12]. However, the investigations into the area-selective deposition of SAMs on a patterned Si substrate are sparse. In this work, SR stimulated etching is conducted to fabricate a pattern of $SiO_2$ thin film on the Si substrate, and patterning of SAMs for biosensor device fabrication is demonstrated by area-selective deposition of SAMs on the pattern of $SiO_2$ thin films.

A single-crystal Si(100) wafer was pre-cleaned in acetone, ethanol, and deionized water with an ultrasonic bath for 5 minutes, respectively, then immersed into a solution of concentrated $H_2SO_4$ and 30% $H_2O_2$ (70:30 v/v) at 110 °C for 10 minutes, and finally treated with 2.5% HF solution for 1 minute to remove the native oxide. The $SiO_2$ thin film was formed on the freshly cleaned Si surface by annealing at 1000 °C for 12 hours in a dry oxygen atmosphere. The thickness of the $SiO_2$ film measured with an ellipsometer was about 260 ± 10 nm. The cobalt contact mask on the $SiO_2$ surface was fabricated by the combination of conventional photolithography and sputtering technique. First, spin-coating a photo resist on the $SiO_2$ surface, irradiating ultraviolet (UV) light through a pattern mask, developing the wafer to get a photo resist pattern on the $SiO_2$ surface; then, depositing Co using a sputtering machine on the photo resist pattern; finally, washing the substrate with acetone in an ultrasonic bath. The thickness of the Co mask measured with a step profile meter was about 145 nm. A portion of the Co mask on $SiO_2$ surface was shown in Fig. 1.

SR etching of $SiO_2$/Si(100) substrate was conducted at the beam line 4A2 of the SR facility (UVSOR, the Institute for Molecular Science of Japan). A large pressure difference between the etching chamber and the beam line was sustained by using a differential vacuum pumping system. The SR etching of $SiO_2$/Si(100) was conducted using a mixture of $SF_6$ and $O_2$ as the reaction gas at room temperature. The sample was set normal to the incident SR beam. The beam diameter on the sample surface was about 9 mm and the beam current of the storage ring was about 200 mA.

We examined the deposition of the dodecene SAM on the Si surface after SR etching. Approximately 3 ml of the neat dodecene was placed in a small glass flask and was deoxygenated with dry nitrogen for about 30 minutes. After the SR etching, a thin $SiO_2$ layer covered the etched surface. The sample substrate was washed by ethanol, acetone and deionized water, then it was treated with a dilute HF solution (∼2.5%) for 30 seconds to remove the thin oxide layer, blown dry with nitrogen, and immediately placed in the deoxygenated dodecene liquid for 2 hours at about 200 °C, while slowly bubbling nitrogen through the dodecene liquid. Subsequently, the sample was taken out from the flask, rinsed 3 times in petroleum ether and ethanol, sonicated for 5 minutes in dichloromethane and dried in the stream of nitrogen. Then, we deposited octadecyltrichlorosilane (OTS) on the $SiO_2$ surface beneath the Co mask as follows. The Co mask was removed by dipping the sample into a dilute $HNO_3$ solution for several minutes before the deposition. The deposition was performed by immersing the substrate coated partially with the dodecene monolayer in a 2-mmol/L solution of OTS/toluene for 1 hour below

Fig. 1. CCD image of a portion of the Co mask on $SiO_2$ surface.

29 °C, followed by washing thoroughly with toluene, ethanol and deionized water.

The $SiO_2$ was found to be effectively etched by SR with $SF_6 + O_2$ as the reaction gas at room temperature. The etching took place only in the area irradiated with SR and proceeding in the direction of incident beam, as shown in Fig. 2. In this figure, the $SiO_2$ thin film on the Si substrate was directly irradiated with SR in the atmosphere of $SF_6 + O_2$ mixture gas without mask.

Figure 3 shows a scanning electron microscopy (SEM) image of the SR-etched micro-pattern with cobalt mask. In the etching experiment, the irradiation dose of the SR beam was about 10000 mA·min and the gas pressures of $SF_6$ and $O_2$ were about 0.05 and 0.002 torr, respectively. From this pattern, an etching rate of 2.6 nm per 100 mA·min measured with a step profile meter was obtained. After the SR etching, the Co surface looked flat and uniform, indicating that the material of Co possessed large resistibility against the SR etching. Moreover, the etching process stopped completely on the interface of $SiO_2/Si$. The SR irradiation with flowing $SF_6 + O_2$ did not etch the Si crystal, which was the same as the previous report[3].

The dodecene SAM was deposited on the etched region by the reaction of dodecene molecules with the hydrogen-terminated silicon surface at 200 °C. This hydrosilylation reaction resulted in the formation of very stable silicon-carbon bonds. OTS monolayer was deposited on the $SiO_2$ beneath the Co mask by the silanization reaction of alkyltricholorosilanes with the OH-terminated $SiO_2$ surface. The process of removing Co mask did not destroy the dodecene SAM, for it was known to be stable in contact with aqueous acid at room temperature[6].

The deposited SAMs was characterized with a Fourier transform infrared spectrometer in the transmission mode using a tri-glycine-sulfate (TGS) detector at 4-$cm^{-1}$ resolution, an ellipsometer, and water contact angle (WCA) measurements. Figure 4 shows the infrared transmission spectra in the region of $CH_2$ stretching vibration measured for the sample of area-selective deposition on the etched pattern. The $CH_2$ vibration peaks, the thickness ($d$), and the WCA of the deposited monolayer are listed in Table 1. These results are in good agreement with data published by other groups. The observed peak positions (2850±1 and 2918±1 $cm^{-1}$) assigned to the symmetric ($\nu_s$) and antisymmetric ($\nu_a$) stretching vibrations of the methylene ($-CH_2$) groups, respectively, are close to the values measured on alkane crystals (well-ordered) but far below the positions for liquid alkanes, which are at 2856 and 2928 $cm^{-1}$, respectively[9]. Ellipsometer measurement showed that the films were composed of a single monolayer with thickness $d = 2.5$ and 1.4(±0.1)nm for the OTS and dodecene, respectively. In the measurement of the SAM thickness with ellipsometer, a value of 1.46 was used for the SAM refractive index at 633 nm. Considering the small incline of SAM on the substrate surface, these values are in good agreement with the formula $d(C_n) = 0.126(n-1) + 0.478$ nm, where $n$ is the number of carbon atoms in the alkyl chain, valid for hydrocarbon chains oriented perpendicular to the solid substrate and extended in their all-trans conformation. The WCAs were found to be 110(±2) degrees for the deposited monolayer of OTS and dodecene, respectively, consistent with a top layer of methyl ($-CH_3$) or vinyl ($-CH{=}CH_2$) groups as it should be if the alkyl chains are densely packed[6,10]. Combining these characteristics, we concluded that the deposited SAMs were made of alkyl chains in their all-trans conformation, and they were nearly perpendicular to the substrate and had a densely packed molecular architecture.

The $SiO_2$ thin film pattern structure was fabricated on the silicon surface by the SR stimulated etching using $SF_6 + O_2$ as the reaction gas and a Co contact mask.

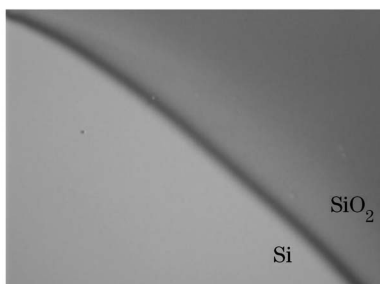


Fig. 2. CCD image of a portion of the SR etching $SiO_2$ thin films on Si substrate without mask.

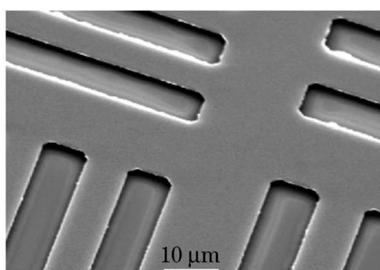


Fig. 3. SEM image of the micro-pattern after the SR etching with Co mask.

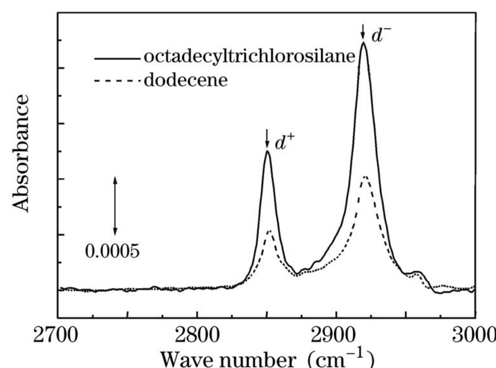


Fig. 4. Infrared spectra of the deposited SAMs of OTS and dodecene.

**Table 1. Infrared Peak Positions ($cm^{-1}$) for the Symmetric ($\nu_s$) and Antisymmetric ($\nu_a$) Methylene Stretching Vibrations, the Thickness ($d$), and the Water Contact Angles (WCA) of the Deposited Self-Assembled Monolayers**

| Monolayer | $\nu_s$–$CH_2$ | $\nu_a$–$CH_2$ | $d$ (nm) | WCA (deg.) |
|---|---|---|---|---|
| $CH_3(CH_2)_9CH{=}CH_2$ | 2851 | 2919 | 1.4±0.1 | 110±2 |
| $CH_3(CH_2)_{17}SiCl_3$ | 2850 | 2919 | 2.5±0.1 | 110±2 |

The etching stopped completely at the $SiO_2$/Si interface. Covalently bonded alkyl monolayer of dodecene on hydrogen-terminated Si surface after SR etching and trichlorosilane-derived SAM of OTS on the OH-terminated $SiO_2$ surface beneath the Co mask was deposited area-selectively. These SAMs of area-selective depositions were well ordered and densely packed, as evidenced from infrared spectroscopy, ellipsometer, and water contact angle measurements.

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