

## Formation of Polystyrene Layer by RAFT Agent Immobilized on Si (111) Surface

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Formation of polystyrene layer on Si (111) surface from hydrogen-terminated Si (111) was reported. Styrene was polymerized from RAFT (reversible addition-fragmentation chain transfer) agent immobilized Si (111) with AIBN and cumyl dithiobenzoate. The Si (111) chips obtained were estimated by water droplet contact angle, and XGT microscope. The contact angle was increased up to 101° by the change to hydrophobicity. Polystyrene layer was detached from Si (111) with hydrolysis and the polymer obtained was analyzed by GPC.

Key words: hydrogen-terminated Si (111), self-assembled monolayer, RAFT polymerization, polystyrene layer

### 1. INTRODUCTION

Technology of self-assembled monolayer (SAM) is widely used for immobilization of organic functional molecules on inorganic solid surfaces. In 1995, alkyl-termination of the dangling bonds on Si wafers through radical reaction of 1-alkene with hydrogen-terminated Si was reported [1]. This type of SAM offers direct modification of organic substances having sensing and actuating functions on semiconductor chips. Thus, the alkyl-termination of SAM has been regarded to develop new sensing devices, such as bioactive sensors [2]. The surface and interface of materials has much contribute to develop a fine control of a precision instrument, the SAM technology might be brought new materials.

We have already reported the construction of polystyrene layer on Si (111) surface by using RAFT agent immobilized onto Si (111) from hydroxypentyl-terminated Si (111) [3]. RAFT polymerization is one of the controlled living radical polymerization methods. Major advantages of RAFT polymerization are compatible with a wide range of monomers and the reaction conditions are mild in comparison with other radical polymerization methods [4, 5].

The long alkyl chain as a spacer let the RAFT agent away from the surface to avoid overlapping [6]. Consequently, well-defined polymer layer might be induced on Si (111) surface. The polymer layer on Si surface by covalent bond can provide the mechanical and chemical protection. Furthermore, the electrochemical properties of Si surface will be changeable. In this work, we investigated to immobilize the RAFT agents connected at the end of the long alkyl chain and to prepare a polystyrene layer on Si (111) surface using the immobilized RAFT agents. Additionally RAFT polymerization of the surface should provide new pathways for the

functionalization [7].

### 2. EXPERIMENTAL SECTION

#### 2. 1. Measurements.

Qualitative analysis and distribution images of the elements on Si surfaces were observed using a HORIBA X-ray Guide Tube Microscope XGT-2700. Atomic Force Microscopic (AFM) images were obtained using a SHIMADZU SPM-9500J scanning probe microscopy. <sup>1</sup>H-NMR spectra were recorded with a Varian UNITY300 (300 MHz) spectrometer. Gel permeation chromatographic analyses (GPC) were carried out on a TOSOH HLC8020 (DMF as eluent) using polystyrene standards.

#### 2. 2. Materials.

Superficially oxidized silicon (111) wafer was obtained from Shin-Etsu Semiconductor, Co. Ltd (11CN711-06). Cumyl dithiobenzoate (CDBA) was prepared by reported method [8]. Tetrahydrofuran (THF) was dried over sodium and distilled under nitrogen. Other reagents and solvents were directly used without further purification.

#### 2. 3. Preparation of hydrogen-terminated Si (111) [H-Si (111), chip 1].

Hydrogen-terminated Si (111) [H-Si (111)] chips 1 were prepared as following. Small cuts (10 mm × 10 mm) of Si (111) wafer were treated with 10% aqueous HF for 20 min and etched twice with 40% aqueous NH<sub>4</sub>F for 20 min, successively. The obtained chips were rinsed twice with distilled water under an irradiation of ultrasound.

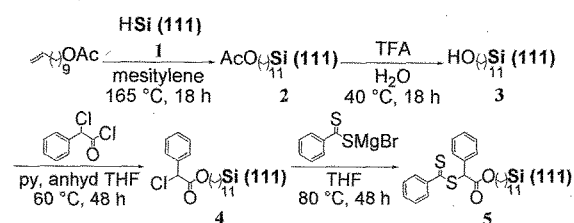
#### 2. 4. Immobilization of RAFT agent on Si (111) surface [9].

Detailed procedure was shown in scheme 1. Chip 1 was immersed into the mesitylene (2 mL)

solution of  $\omega$ -undecylenyl acetate (1 mL) at 165 °C for 18 h under  $N_2$  atmosphere to give acetyl-terminated Si (111) **2**. The chip **2** was washed with methanol, *n*-hexane, and acetone. The chip **2** was immersed into the solution of trifluoroacetic acid (TFA) (3 mL) in  $H_2O$  (1.5 mL) at 40 °C for 18 h to give hydroxyl-terminated Si (111) **3**. Then the chip **3** was washed twice with water and methanol. The chip **3** obtained was immersed into pyridine (py) (20.0 mmol) in anhydrous THF (20 mL), and  $\alpha$ -chlorophenylacetyl chloride (10.0 mmol) was added dropwise to the solution. The solution mixture was heated to 60 °C for 48 h. After the reaction, the chloro-terminated Si (111) **4** was washed with THF, THF: methanol (1:1), methanol, and acetone.

To a separately prepared THF solution of phenylmagnesium bromide (20 mmol), carbon disulfide (20 mmol) was added dropwise at 0 °C with stirring. After the addition, the reaction mixture was heated to 40 °C for 3 h. Then the dark brown solution (magnesium bromide dithiobenzoate) was transferred to a side-arm flask containing the chip **4**. The reaction mixture was heated to 80 °C for 48 h. The obtained Si (111) chip having RAFT agent, chip **5**, was washed with THF overnight by soxlet extractor.

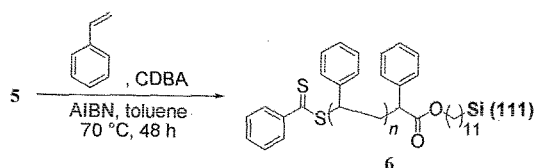
Scheme. 1 Immobilization of RAFT agent on Si (111) surface.



2. 5. Polymerization of styrene by RAFT agent immobilized on Si (111) surface.

Styrene (19.2 mmol), AIBN (0.0960 mmol), CDBA (0.240 mmol), chip **5**, and toluene (0.5 mL) were put into a 5 mL round bottomed flask. The reaction mixture was degassed with  $N_2$  for 30 min and was heated at 70 °C for 48 h as shown in scheme 2. After the reaction, the polystyrene-immobilized Si (111) **6** was washed with THF overnight by soxhlet extractor. Polystyrene from the polymerization solution was isolated by reprecipitation with methanol (0.93 g, 86% yield).

Scheme. 2 Polymerization of styrene from RAFT agent immobilized on Si (111) surface.



2. 6. Detachment of polystyrene chains from Si

(111) surface.

Polystyrene layer immobilized Si (111) **6**, THF (5 mL), and trifluoroacetic acid (TFA) (5 mL) were put into a test tube. The reaction mixture was placed at 35 °C for 3 days. Then, the solvent was roughly removed by rotary evaporator and chloroform (30 mL) was added. The organic layer was washed with  $NaHCO_3$  aq and brine, successively. The organic layer was dried *in vacuo* (yield: 6.8 mg). The residue was dissolved in chloroform-*d* and measured by  $^1H$ -NMR. Then, the solvent was evaporated and the sample was used for GPC analysis.

### 3. RESULTS & DISCUSSION

3. 1. Immobilization of RAFT agent on Si (111) surface.

To construct a foothold of RAFT agent,  $\omega$ -undecylenyl acetate was reacted with H-Si (111) **1** to give acetyl-terminated Si (111) **2**. The water droplet contact angle of chip **2** was similar to that of chip **1** measured by optical microscope. (Table I).

The acetyl group of chip **2** was hydrolyzed with TFA to give hydroxyl-terminated Si (111) **3**. The contact angle of chip **3** was approximately half of chips **1** or **2**, which were resulted from the increase of the hydrophilicity of the surface of chip **3**.

The chip **3** was esterified with  $\alpha$ -chlorophenylacetyl chloride to give chloro-terminated Si (111) **4**. The contact angle of chip **4** was increased up to 58° comparing to chip **3** (36°), which were resulted from an increase of the hydrophobicity of the surface.

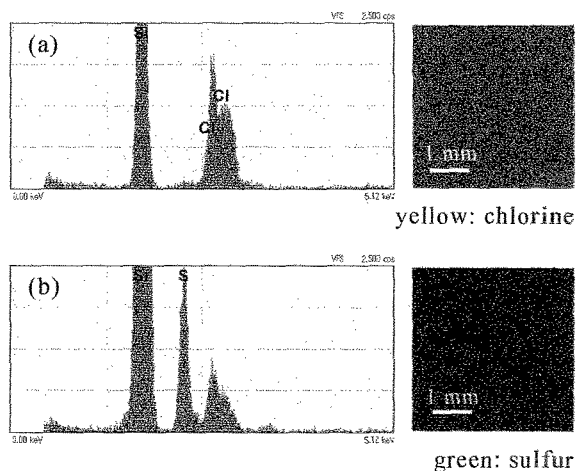


Fig. 1 Elemental analyses and distribution images of elements on (a) chloro-terminated Si (111) **4** and (b) RAFT agent immobilized Si (111) **5** surface.

The X-ray guide tube (XGT) microscope analysis indicated that the chlorine was distributing homogeneously over the whole surface of the chip **4** as shown in fig. 1a. Further the resulted terminal chloride was converted to dithioester by the reaction of chip **3** with magnesium bromide dithiobenzoate. The contact

angle of **5** ( $62^\circ$ ) was similar to that of **4**. The RAFT agent immobilized Si (111) **5** was confirmed by XGT microscope. The element of sulfur was detected and was densely distributed on the surface of chip **5** (Fig. 1b).

### 3. 2. Polymerization of styrene by RAFT agent immobilized on Si (111) surface.

To induce a polystyrene layer on Si (111) surface, chip **5** was reacted with styrene, CDBA, and AIBN as an initiation at  $70^\circ\text{C}$  for 48 h to obtain polystyrene layer immobilized Si (111) **6**. In this case, CDBA was added to the polymerization system because of (i) the advantage of the growth of polystyrene SAM by the exchange of terminal benzenecarbodithioate group on Si (111) surface and CDBA, (ii) the low concentration of the immobilized RAFT agent on Si (111) in solution, and (iii) inhibition of the termination reaction of styrene for coupling of growing terminal [10].

The contact angle of chip **6** was changed from  $62^\circ$  to  $101^\circ$  compared to chip **5** (Table I). The contact angle of chip **6** is the highest among all of the chips studied in this work.

Table. I Water droplet contact angles on Si (111) surfaces

chip	contact angle / $^\circ$ <sup>a</sup>	chip	contact angle / $^\circ$ <sup>a</sup>
<b>1</b>	69	<b>4</b>	58
<b>2</b>	67	<b>5</b>	62
<b>3</b>	36	<b>6</b>	101

<sup>a</sup> The contact angle values were shown by the average of the measurements repeated three times.

The XGT microscope analysis of chip **6** indicated that the sulfur was detected on the surface as shown in fig. 2. This result shows the growing end of polystyrene, *i.e.*, the dithioester groups were remaining.

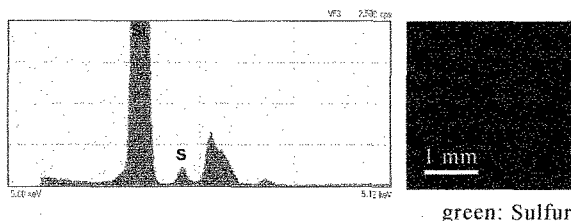


Fig. 2 Elemental analyses and distribution images of elements on polystyrene layer immobilized Si (111) **6** surface.

The AFM images on the surface of chips **1** and **6** were shown in fig. 3. Both images were scanned to  $40\ \mu\text{m} \times 40\ \mu\text{m}$  and adjusted the Z scales to 55 nm. The surface of chip **1** was appreciated to flat plane. The surface of chip **6** was observed by the changes of topography by the construction of polystyrene layer on Si (111) surface. Polystyrene layer from immobilized Si (111) **6** surface was observed a lot of projection. Therefore, polystyrene layer was formed densely arrayed on Si (111) surface. Thus,

polymerization reaction of styrene was developed on chip **5** surface and polystyrene layer was confirmed on Si (111) surface.

The molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of polystyrene isolated from the polymerization solution was estimated by GPC ( $M_n=5.3 \times 10^3$ ,  $M_w/M_n=1.16$ ).

### 3.3 Detachment of polystyrene chains from Si (111) surface.

To detach the polystyrene layer from Si (111) surface, chip **6** was treated with TFA in THF at  $35^\circ\text{C}$  for 3 days. After the reaction, AFM image on the Si (111) surface was shown in fig. 3c. The Si (111) surface was observed by the change to flat surface compared to the chip **6**. However, polystyrene chains were still remained, because the projections on the surface were partially confirmed.

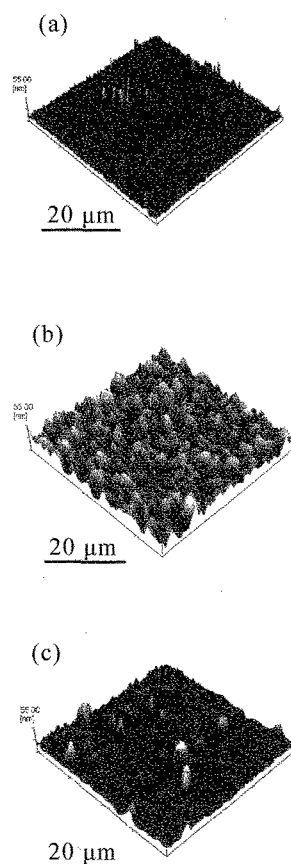


Fig. 3 AFM images of (a) H-Si (111) (chip **1**), (b) polystyrene layer immobilized Si (111) (chip **6**), and (c) polystyrene layer detached Si (111) surface [ $40\ \mu\text{m} \times 40\ \mu\text{m}$ , Z max=55 nm].

To analyze the polystyrene detached from Si (111) surface, the molecular weight and molecular weight distribution of detached polystyrene were estimated by GPC ( $M_n=4.5 \times 10^3$ ,  $M_w/M_n=1.31$ ). The molecular weight and molecular weight distribution of the detached polystyrene was similar to polystyrene isolated from

polymerization solution. Therefore, formation of polystyrene layer was effectively performed by the existence of CDBA in the polymerization system. The detached polystyrene was analyzed by  $^1\text{H-NMR}$  spectrum shown in fig. 4. The protons of methylene ( $\delta$  1.84 - 2.18 ppm) and aromatic rings of polystyrene ( $\delta$  6.59 - 7.26 ppm) were confirmed. In the case of the non-modified Si (111), the organic contaminant was observed at  $\delta$  0.9 - 1.5 ppm in fig. 4b. The area of the peaks should be neglected in fig. 4a [11].

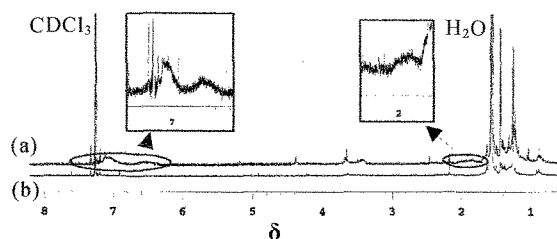


Fig. 4  $^1\text{H-NMR}$  spectra of (a) polystyrene detached from chip 6 and (b) the treatment by TFA for non-modified Si (111) surface

#### 4. CONCLUSIONS

Formation of polystyrene layers on Si (111) surface was carried out by the RAFT polymerization. RAFT agent was immobilized on the surface of hydrogen-terminated Si (111). The RAFT agent was densely distributed on Si (111) surface confirmed by XGT microscope images. Polymerization of styrene with CDBA was developed from RAFT immobilized Si (111). The terminal dithioester group of polystyrene layer was confirmed on the Si (111) surface. The AFM images of the surface were drastically changed from H-Si (111) surface. The contact angle of polystyrene immobilized Si surface was the highest (*i.e.*, the most hydrophobic) among all chips studied in this work. Polystyrene layer was cleaved by acid hydrolysis of ester group from RAFT agent immobilized Si (111). Polystyrene layer detached from Si (111) surface was observed by the change to smoothly. Detached polystyrene chains from Si (111) surface were confirmed by  $^1\text{H-NMR}$  spectra. The molecular weight and molecular weight distribution was estimated by GPC, which was similar to polystyrene isolated from polymerization solution.

#### 5. ACKNOWLEDGEMENT

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