

Construction of Polymers by RAFT Polymerization on Hydrogen-terminated Si (111) Surface

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RAFT (reversible addition-fragmentation chain transfer) agents of dithiobenzoate capping were immobilized onto silicon (111) surfaces from hydrogen-terminated Si (111) through three steps. Polymerization of styrene initiated by AIBN was performed using this RAFT agent to obtain rigid polystyrene layers on semiconductor chips. The RAFT agent and polystyrene on Si (111) were characterized with AFM and optical microscope.

Key words: polystyrene layers on Si (111), hydrogen-terminated silicon (111), RAFT polymerization

1. INTRODUCTION

Technology of self-assembled monolayer (SAM) is widely used for immobilization of organic functional molecules on solid surfaces. Some types of SAM technology are already known; for example, the fixation of organic thiols through sulfide bond on noble metals such as Au and Pt [1], and the immobilization using silane coupling reagents on oxide layers of metallic substrates such as silicon, etc [2].

Particularly, thiol monolayer on Au surface has been used for the modification of the fixation of peptides, enzymes, antibodies, nucleic acids, etc. offering some bio-active sensors. However, sulfide bond on Au is comparatively labile; the organic layer is easily washed out from Au surface. In the case of the use of silane coupling reagents immobilized on the surface oxide layer of metals, the organic layer is detached from the metal surfaces for less stability under high temperature.

Recently, it was reported that alkyl-termination of the dangling bonds on silicon wafers through radical reaction of alkene with hydrogen-terminated Si surface [3, 4]. Such the alkyl monolayer on Si surface is very stable, because the alkyl monolayer was strongly combined by silicon-carbon covalent linkage.

This type of SAM technology has much attention to develop new sensing devices, because this method can be utilized for direct modification of semiconductor devices by organic components having sensing and actuating function. We have already investigated the reaction of ω -alkenyl Ni (II) complexes onto a hydrogen-terminated Si surface [5]. Then we attempted that the SAM technology could be used for the development of polymer layers on Si (111) surface. Stable polymer layers covalently bonded on Si surface can provide mechanical and chemical protection to the substrate, alter the electrochemical characteristics of the interface, and provide new pathways for the functionalization of silicon surfaces [6].

As a synthetic method of polymers, reversible addition-fragmentation chain transfer (RAFT) polymerization, one of living radical polymerization methods can give several polymers of very narrow polydispersity [7]. Additionally, major advantages of the RAFT polymerization are compatible with a wide

range of monomers and indication of living characteristics under various conditions. Moreover, this process is useful method to access for complex materials, such as block copolymers [8, 9]. Thus, we tried to prepare a polystyrene layers on Si (111) surface by RAFT polymerization.

2. EXPERIMENTAL SECTION

2.1 Measurements

Quantitative analysis and distribution images of the elements on Si surface were observed using a HORIBA X-ray Guide Tube Microscope XGT-2700. Optical-microscope images were obtained with a KEYENCE VHX-100. Atomic Force Microscopic (AFM) images were obtained using a SHIMADZU SPM-9500J scanning probe microscopy.

2.2. Preparation of hydrogen-terminated Si(111) [H-Si (111), chip 1] surface.

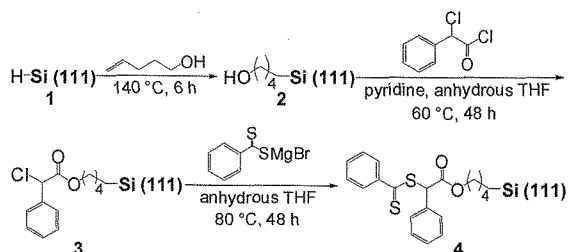
Hydrogen-terminated Si (111) [H-Si (111)] chips were prepared as following. Small cuts (10 mm×10 mm) of superficially oxidized silicon (111) wafer (11CN711-06, Shin-Etsu Semiconductor, Co. Ltd.) were treated with 10% aqueous HF for 20 min and etched twice with 40% aqueous NH₄F for 20 min, successively. The obtained chips were rinsed twice with distilled water under an irradiation of ultrasound.

2.3. Immobilization of RAFT agent on Si (111) surface [10].

Detailed procedure is represented in the following Scheme 1. Chip 1 was immersed into 4-penten-1-ol (3 mL) at 140 °C for 6 h under N₂ atmosphere to give hydroxypentyl-terminated Si (111), chip 2. Then the chip was washed twice with acetone, methanol, and distilled water under an irradiation of ultrasound. The chip 2 was then immersed into the solution of pyridine (19.2 mmol) in anhydrous THF (20 mL). 2-chloro-2-phenylacetyl chloride (9.6 mmol) was added dropwise to the solution and the solution was heated to 60 °C for 48 h. After the reaction, the chloro-terminated Si (111), chip 3 was washed twice with THF, THF: distilled water (1:1), acetone, methanol, and distilled water under an irradiation of ultrasound.

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 was transferred to a test tube containing the chip 3. The reaction mixture was heated to 80 °C for 48 h. The obtained Si (111) chip having RAFT agent with dithiobenzoate capping, chip 4, was washed twice with THF, THF: distilled water (1:1), acetone, methanol, and distilled water under an irradiation of ultrasound.

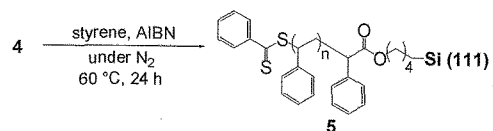
Scheme 1. Immobilization of RAFT agent on Si (111) surface.



2.4. Polymerization of styrene by RAFT agent immobilized Si (111) surface.

RAFT agent-terminated Si (111) chip 4, styrene (14.4 mmol) and AIBN (0.0487 mmol) were put into a 5 mL round bottomed flask. The reaction mixture was degassed with N₂ for 1 h and was heated at 60 °C for 24 h as shown in Scheme 2. After the cooling, the polystyrene-immobilized silicon chip 5 was washed twice with chloroform, THF, acetone, methanol, and distilled water under an irradiation of ultrasound.

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



3. Results and Discussion

3.1. Immobilization of RAFT agent on Si (111) surface.

To construct a foothold of RAFT agent, 4-penten-1-ol was reacted with H-Si (111) to give hydroxypentyl-terminated Si (111) (chip 2). Usually, the formation of SAM on Si (111) surface was performed in organic solvents such as mesitylene, however, the reaction of 4-penten-1-ol on Si (111) was carried out under bulk condition to remove the influence of solvents. The contact angles of chip 1 and 2 were measured by optical microscope as shown in Fig. 1. The contact angle of chip 2 was increased as 74° comparing to chip 1 (40°), which resulted from an increase of the hydrophobicity of the surface of chip 2 comparing to chip 1. The contact angle was evaluated by the average of the measurements repeated three times. Thus, immobilization of the organic molecules on Si (111) was fairly confirmed by the increase of hydrophobicity in chip 2.

The hydroxypentyl-terminated Si (111) (chip 2) was esterified with 2-chloro-2-phenylacetyl chloride to give active chloro-terminal, chip 3. The X-ray guide tube (XGT) microscope analysis indicated that chlorine was distributing homogeneously over the whole surface of the chip 3 as shown in Figures 2 and 3.

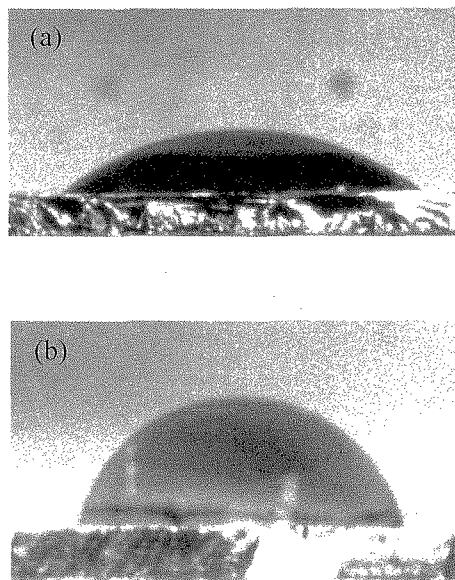


Figure 1. Water droplet on (a) original H-Si (111) (chip 1) surface, and (b) hydroxypentyl-terminated Si (111) (chip 2) surface.

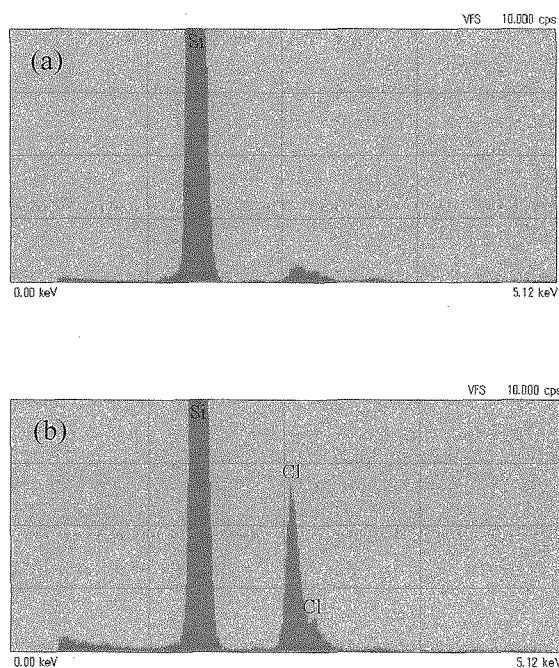


Figure 2. Elemental analysis of (a) original H-Si (111) (chip 1) surface, and (b) chloro-terminated Si (111) (chip 2) surface.

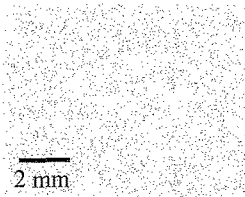


Figure 3. Distribution image of chlorine on chloro-terminated Si (111) (chip 3) surface.

The contact angle value of chip 3 was 68° shown in Figure 4. The contact angle of chip 3 is similar to the chip 2.

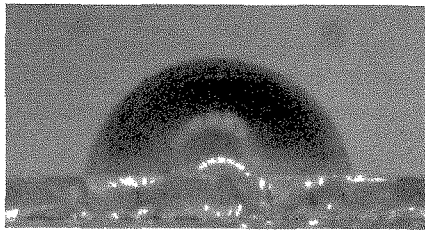


Figure 4. Water droplet on chloro-terminated Si (111) (chip 3) surface.

Further the resulted terminal chloride was converted to dithioester by the reaction of chip 3 with magnesium benzenecarbodithioate bromide. The RAFT agent immobilized Si (111) surface 4 was confirmed by XGT microscope (Figure 5). The element of sulfur was detected and was densely distributed on the surface of 4 (Figure 6).

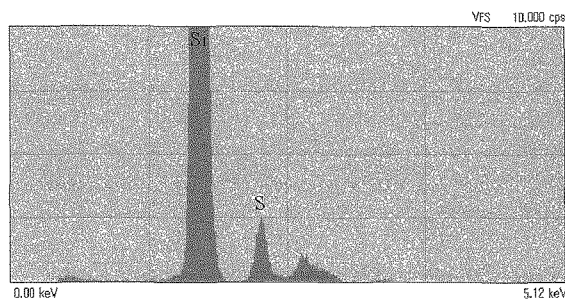


Figure 5. Elemental analysis of RAFT agent-terminated Si (111) (chip 4) surface.

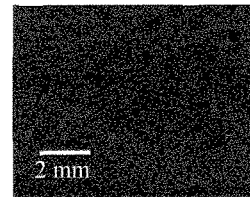


Figure 6. Distribution image of sulfur on RAFT agent-terminated Si (111) (chip 4) surface.

3.2. Polymerization of styrene from RAFT agent immobilized Si (111) surface.

To grow polystyrene on Si (111) surface, chip 4 was reacted with styrene and AIBN as an initiation at 60 °C for 24 h to obtain polystyrene-terminated Si (111), chip 5. After the reaction, chip 5 was washed with chloroform, THF, acetone, and distilled water. The contact angle of chip 5 was changed from 61° to 83° compared to chip 4 (Figure 7). Thus, polymerization reaction of styrene was developed on chip 4, and polystyrene was immobilized on Si (111) surface. The contact angle of chip 5 is the largest among all chips studied in this work and is twice as large as that of chip 1. The AFM images of the surface of chip 1, chip 4, and chip 5 were shown in Figure 8. The relief of top and bottom of the surface of chip 1 was 5.6 nm, and thus the surface was appreciated to flat plane by AFM image. The surface could be observed by the changes of every step, and the relief of top and bottom of surface of chip 4 and chip 5 were 5.3 nm and 8.1 nm, respectively. Thus, the polystyrene-terminated Si (111), the surface of chip 5 was relatively flat by AFM image. Therefore, polystyrene layers were formed well-defined and densely distributed on Si (111) surface [11].

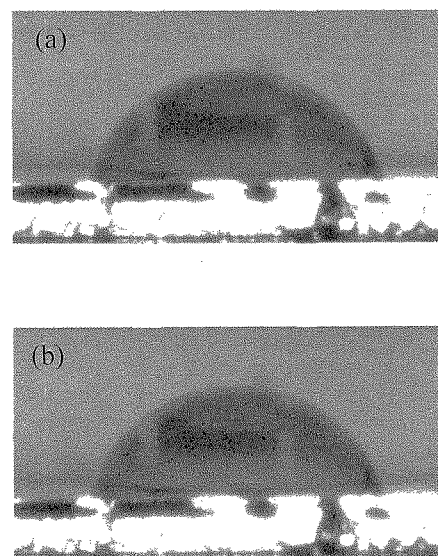


Figure 7. Water droplet on (a) RAFT agent-terminated Si (111) (chip 4) surface and (b) immobilization of polystyrene on Si (111) (chip 5) surface.

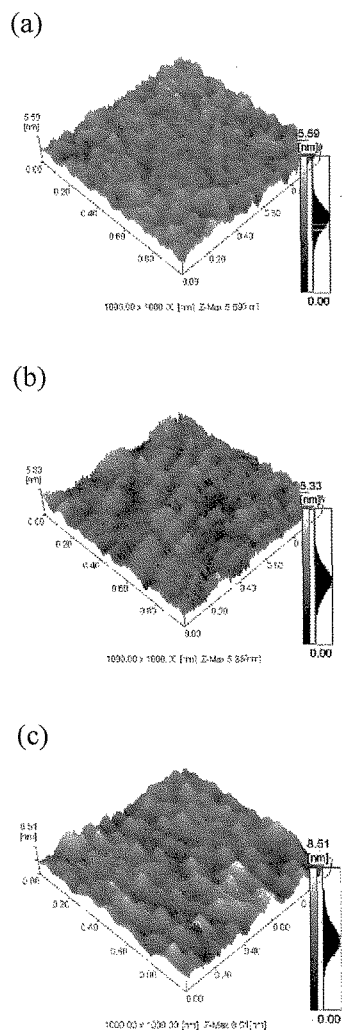


Figure 8. AFM image of (a) H-Si (111) (chip 1), (b) RAFT-terminated Si (111) (chip 4) and (c) polystyrene immobilized on Si (111) (chip 5) surface.

4. SUMMARY

A novel approach to construct the polystyrene layers on Si (111) surface was carried out with the RAFT polymerization. Immobilization of RAFT agent on the surface of Si (111) was applied using SAM technology. The RAFT agent was densely distributed on Si (111) surface confirmed by XGT microscope images. After the polymerization reaction of styrene with RAFT-terminated Si (111), the AFM images of the surface was changed at each reaction steps. Additionally, the surface was flat plane confirmed by AFM analysis.

Construction of polystyrene layers on Si (111) surface could be accomplished; however, the property of polystyrene isn't obtained yet. In future, we would try to investigate the detachment of polystyrene from Si (111) surface.

5. Acknowledgement

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