

**Study on Molecular Assemblies Anchored to Silicon Surfaces
via Silicon-Carbon Covalent Bonds**

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Chapter
General Introduction

Much attention has been paid to organic monolayers as a promising and convenient method of molecular assemblies to construct functional organic surfaces reproducibly with well-defined compositions, structure, and thickness [1-3]. Monolayers such as organosilane molecules on hydroxylated surfaces (silicon oxide [4-9], mica [10-12], glass [9], *etc.*) and organosulfur molecules on metals (silver [13-17], copper [15-18], platinum [19], gold [20-26], *etc.*) have been investigated by infrared spectroscopy, ellipsometry, wetting measurement, X-ray photoelectron spectroscopy, and scanning probe microscopy. The interest in organic monolayers lies not only in basic research but also in applications to control of wetting, chemical resistance, molecular recognition for sensor applications, and many others. It is possible to change wetting properties of surfaces by coating the surface with organic monolayers [27,28]. Reversible control of wettability by light [29,30] or electrical potential [31] has recently been reported. Monolayers of metal complexes have the activity as catalytic surfaces [32-34]. Organic monolayers have been also used for the modification of surfaces with bio molecules such as DNA [35-37] and protein [38,39], to fabricate bio-interfaces. In the field of molecular electronics, sensors [40,41], photovoltaic cells [42,43], and memories [44] have been reported. Alkylsilane monolayers were used as a gate insulator of field effect transistors because of large barriers for electron tunneling [45,46]. The electronic properties, such as conductivity [47,48], switching [49], single electron tunneling [50] of single molecules or clusters have also been investigated using organic monolayers especially of the Au-S system.

Organic monolayers on inorganic semiconductors including silicon via covalent bonds such as silicon-carbon (Si-C) have attracted a growing interest as one of the most promising ways to assemble organic molecules with well-defined interfaces. Basically, silicon is not well suited for some functions such as light emission, light detection, and chemical sensing. These functions can be introduced to silicon by the assembly of organic molecules. Hence, the molecular assembly on silicon is expected to incorporate the functions of organic materials into silicon technologies and to make new devices.

Historically, a number of dry processes to fabricate Si-C bonds have been examined [51,52] since ultrahigh vacuum conditions are required to maintain clean surfaces of silicon. Wet processes [53,54] have received considerable attention to provide organic/inorganic systems based on Si-C covalent bonds because of the wide range of applications. Organic monolayers anchored to silicon via Si-C covalent bonds can be prepared through the reaction between molecules and silicon surfaces by thermal reaction [53], UV irradiation [55], electrochemical reaction [56], and others [57-59]. The reaction between 1-alkenes and hydrogen-terminated silicon (H-Si) is a typical one.

The reaction scheme proposed [53,60] is shown in Fig. 1. A radical site formed on the silicon surface by heat, UV irradiation, or radicals reacts with a 1-alkene to form Si-C bonds. A radical transferred to the molecule abstracts a hydrogen atom from an adjacent H-Si. The surface reaction then proceeds as a chain reaction. Instead of alkyl chains, the surfaces modified with complex molecules such as DNA [61-65], protein [66], and conducting polymer [67,68] have been also prepared for bio and electronic applications. Porous silicon surfaces are of interest because of their potential properties such as tunable electro-, photo-, and chemo-luminescence [69].

The characteristics of Si-C system are summarized in Fig. 2 with those of Au-S and Si-O-C (silane coupling) systems. The advantages of the Si-C system are as follows:

1: The interface between Au and S atoms is unclear, and not stable against chemical and thermal treatment. Although the interface of the Si-O-C system is covalent and relatively stable, silicon oxide between molecules and silicon is dissolved easily by HF and NH_4F [70] to lead the desorption of molecules. This is the serious problem in wet etching processes following the lithography. In contrast, the interface of Si-C bonds between organic molecules and silicon is proven to be thermally and chemically stable due to the high strength and low polarity of the bond [53,70,71]. Organic monolayers anchored to Si covalently are stable up to 615 K [71] while alkanethiols on Au desorb at about 350 K in a vacuum [72]. The Si-C system also showed high resistivity to various chemicals [53] including HF and NH_4F solution [70].

2: The electronic and photonic properties of organic monolayers on metals and semiconductors are affected by the electronic states of interfaces between molecules and substrates. While, it is difficult to control the work function of gold, we can control the electric properties of silicon substrates by doping electron-donating (P, As, Sb: n-type) or –withdrawing (B: p-type) impurities.

3: Two dimensional patterning in micro- and nano-meter scale is important to prepare novel devices with molecular systems. Microcontact printing [73] and dip pen lithography [74] have been intensively studied using the Au-S system. These methods have high reproducibility of patterns. However, these techniques have not been established as the convenient method to put the molecule at the specific site in nanometer scale. In the Si-C system, micro- and nano-fabrication techniques established in the field of semiconductor devices are applicable. Recently, micro- and nano-meter scale patterning of monolayers anchored to silicon by using convenient lithography techniques such as UV lithography [75], e-beam lithography [76], *etc.* have been achieved. Well-developed silicon technology would allow us to construct complicated integrated circuit system.

In this thesis, my interest is focused on two dimensional (2D) and three dimensional (3D) molecular assemblies on silicon surfaces utilizing the characteristics above mentioned. I have studied thermal and chemical stability of monolayers anchored to silicon, and proposed useful methods for 2D and 3D molecular assemblies by wet process.

This thesis is composed of the following six chapters.

Chapter . General Introduction:

The background and purposes of this study are described. Comparison between the Si-C system, Au-S system and Si-O-C system are summarized.

Chapter . Characterization of Organic Monolayers Anchored Covalently to Silicon (111) Surfaces:

Molecular structure and stability of the monolayers anchored to silicon via covalent bonds were investigated. Organic monolayers anchored to Si(111) surfaces were prepared through the reaction between 1-alkene molecules and hydrogen-terminated silicon by thermal treatment. The monolayers were characterized by infrared spectroscopy, sum-frequency generation spectroscopy, atomic force microscopy (AFM), and so on.

Chapter . Nanopatterning of Organic Monolayers Anchored Covalently to Si (111) with An Atomic Force Microscope:

Nanopatterning was applied to the alkyl monolayers on Si(111) for nanofabrication of organic/inorganic interfaces based on Si-C covalent bonds. Organic monolayers anchored to silicon via covalent bonds is expected to be good resists for lithography since the Si-C system shows high stability against HF and NH₄F compared to the Si-O-C system. Local oxidation of the silicon surface covered with the alkyl monolayer was performed in nanometer scale with a contact-mode AFM by applying positive bias voltage to the surface with respect to a conducting cantilever under ambient conditions. Following the local oxidation, patterned areas were selectively modified by chemical etching and coating with different molecules.

Chapter . Fluorescence from Dye Molecules Anchored Covalently to Silicon Surfaces:

The effect of conductivity of silicon substrates onto fluorescence of organic dyes anchored was investigated. Amino-terminated monolayers prepared on N-type (1300

cm), N-type (1-10 cm), and P-type (8.4-8.9 cm) Si(111) substrates. The fluorescence of the surfaces modified with fluorescein-4-isothiocyanate covalently was measured.

Chapter .Chemical Force Microscopy Using Silicon Cantilevers Covered with Organic Monolayers via Silicon-Carbon Covalent Bonds:

Cantilevers covered with organic monolayers anchored via Si-C bonds were prepared by an UV induced reaction and used for chemical force microscopy (CFM). It is possible to distinguish various surfaces by the modification of the AFM cantilever with organic monolayers. The desorption of molecules from the cantilever surface should be avoided for stable and reliable CFM measurement. The cantilevers covered with molecules via Si-C bonds are suitable since Si-C covalent bonds are stable. Hydrocarbon surfaces and fluorocarbon surfaces were discriminated by adhesion force microscopy and friction force microscopy using the cantilevers covered with monolayers. The cantilevers covered with monolayers were also used to observe TiO₂(110)-(1x1) surfaces by non-contact AFM.

Chapter . Conclusion:

Finally, the conclusions of this thesis are summarized in this chapter.

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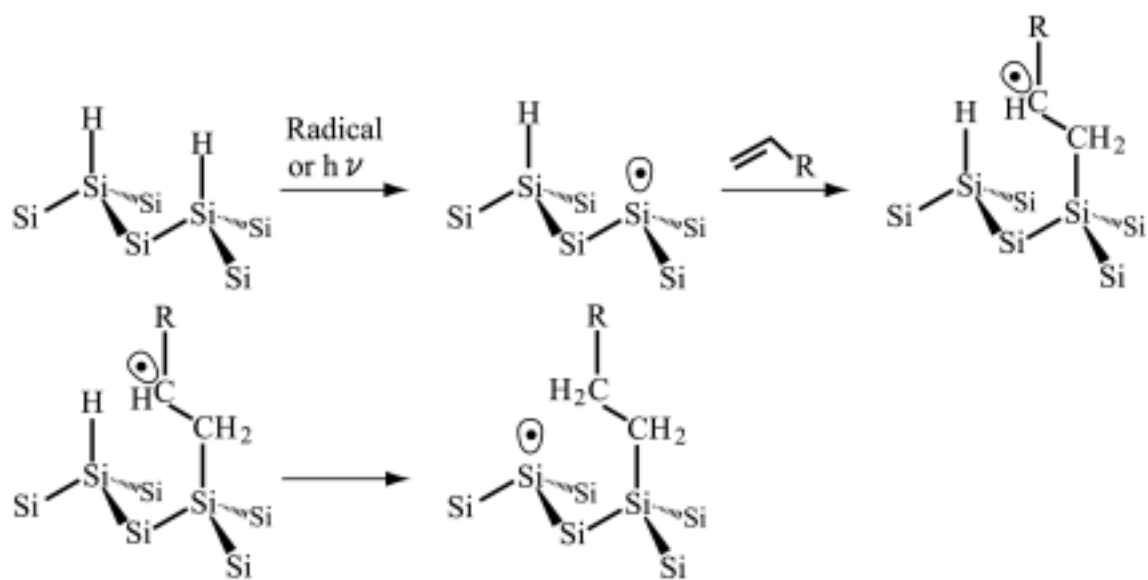


Fig. 1. Scheme of the reaction between an alkene and H-Si.

Si-C bond

- Interface Stable (covalent bond)
- Electrical properties Controllable
(p-type, n-type, heavily doped, slightly doped)
- Selective growth Possible
(micro- and nano-lithography)

Au-S bond

- Interface Unstable
- Electrical properties Uncontrollable
- Selective growth Possible
(micro-lithography)

Silane coupling (Si-O-C bond)

- Interface Stable (covalent bond)
- Electrical properties Controllable
(p-type, n-type, heavily doped, slightly doped)
Molecules are isolated from silicon.
- Selective growth Possible
(micro- and nano-lithography)

Fig. 2. Comparison between the Si-C system, the Au-S system and the Si-O-C system.

Chapter
Characterization of Organic Monolayers
Anchored Covalently to Silicon (111) Surfaces

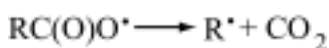
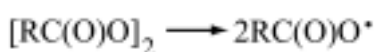
Japanese Journal of Applied Physics, **41**, 4894 (2002).

Journal of The Surface Science Society of Japan, **23**, 622 (2002).

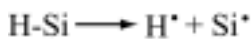
Chemical Physics Letters, **367**, 376 (2003).

.1 Introduction

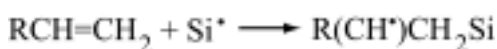
Recently, there is a growing interest in the preparation of organic monolayers covalently bound to silicon because of their potential applications to resist materials for lithography and to anchors for three dimensional molecular assemblies [1,2]. Organic monolayers anchored covalently to silicon surfaces were prepared through the reaction between diacetyl peroxide and hydrogen-terminated silicon (H-Si) by Linford and Chidsey [1]. The free radicals formed by cleavage of diacetyl peroxide molecules initiate the reaction as follows:



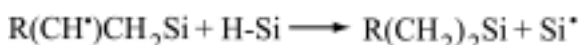
The monolayers prepared by this reaction are the mixture of Si-R and Si-O(O)CR. Instead of radical initiators such as diacetyl peroxide, heat [2] or UV irradiation [3] effectively produces silicon radicals.



Silicon radicals react with 1-alkene molecules to form Si-C covalent bonds. The advantage of this method is that the monolayers produced consist only of Si-R.



Molecules anchored to silicon having radicals abstract the hydrogen atoms from the other molecules or neighbor H-Si to be neutralized.



Besides the thermal and UV induced reaction, electrochemical reaction [4], Grignard reaction [5], Lewis acid mediated reaction [6], and the reaction using organolithium

reagent [7] to prepare monolayer anchored to Si have been reported.

Alkyl monolayers anchored to silicon covalently have been intensively characterized as typical monolayers by contact angle measurement, ellipsometry, infrared (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and so on [2]. IR spectroscopy has revealed the initial stage of alkyl monolayer formation [8,9]. The process consists of the fast adsorption step and the slow ordering step. The alkyl chains are tilted toward the silicon surface at the initial stage and arise with increasing the molecules adsorbed to form the densely packed monolayer.

It has been estimated that 50 % of hydrogen atoms on a Si surface are substituted for alkene molecules [10,11] as shown in Fig. 1. Linford *et al.* hypothesized that residual H-Si sites were terminated OH groups [2]. It is reported that alkyl chains are tilted around 28-36° and 28° from the surface normal based on the analysis by IR [2] and X-ray reflectivity [12], respectively. The molecule twists by 53° at the stem of the chain [2].

Molecularly resolved images of aromatic compounds anchored to the Si (111) surface were obtained by scanning tunneling microscopy [13,14]. Allongue *et al.* observed the (1x2) structure of the bromobenzene monolayer with respect to the silicon lattice and confirmed the coverage of 50 % [13]. However, molecularly resolved images have been observed in a limited area. It is expected that formation of lattice structure is difficult since the reconstruction of molecules anchored to surfaces through covalent bonds is unlikely.

It was found that the oxidation of the silicon surface was inhibited by the formation of alkyl monolayer on silicon by XPS investigation. Organic monolayers anchored to silicon surfaces also exhibit the high stability to various chemicals: hot solvents, acids, bases and so on [2]. It was also revealed that organic monolayers were stable up to 615K [15].

Although a variety of analytical techniques have been used to characterize the alkyl monolayers as cited above, the monolayer structure has not yet been well defined. This is partly because the film structure varies depending upon the preparation condition. It is thus important to characterize the film used in the present study and compare the properties with those reported elsewhere. In this Chapter, I describe the preparation and characterization of organic monolayers anchored to silicon (111) surfaces to discuss the molecular structure, surface property and stability.

.2 Experimental

Preparation of Organic Monolayers Anchored to Si(111) Surfaces vis Si-C Bonds

Organic monolayers were prepared through the reaction between 1-alkenes and H-Si. Medium doped (1-10 cm) n-type Si (111) wafers were used as substrates. Silicon substrates were cleaned and oxidized in boiled mixture of H₂SO₄ and H₂O₂. Hydrogen terminated Si (111) surfaces was prepared by dipping into a 5 % HF solution for 1 min and a deoxygenated 40 % NH₄F solution for 7 min [16,17]. H-Si substrates were transferred into neat or mesitylene-diluted 1-alkene [18], which was deoxygenated by argon bubbling prior to the reaction. The solution was then heated under continuous argon bubbling and it was cooled down to room temperature. The sample was taken out of the solution and rinsed with petroleum ether, ethanol, and dichloromethane.

Attenuated Total Reflectance (ATR) Fourier Transform Infrared Spectroscopy

ATR IR spectra were taken *in vacuo* (ca. 10 Pa) with a Fourier transform infrared spectrometer (JASCO, FT/IR-670 Plus) (Fig. 2) equipped with an ATR unit (SPECAC, P/N11000). Figure 3 shows the configuration of the P/N 11.000 multiple ATR unit and the optical path diagram. MCT (HgCdTe) detector was used.

Double-side polished silicon (111) substrates (9 × 48 × 0.5 mm³) with 45° bevels on each of the short sides were used as ATR crystals. Organic monolayers were prepared on ATR crystals. Infrared rays were internally reflected 95 times in the ATR substrate. Background reference spectra were measured using Si (111) oxidized chemically with the mixture of H₂SO₄ and H₂O₂.

The temperature of ATR crystals was raised by the resistive ceramic heater to investigate the thermal phase behavior.

Sum-Frequency Generation (SFG) Spectroscopy

SF spectra were measured by Ishibashi et al, at KAST in Kawasaki, for the samples I prepared in Okazaki [19]. SF spectra of alkyl monolayers were measured 1-2 days after their preparation. It is confirmed that the spectra were identical to those observed one month after the preparation.

Alkyl monolayers were prepared by thermal reaction in mesitylene solution of 1-alkene (40 vol%) at 160 °C for 24 h under argon bubbling. Medium doped (1-10 cm) n-type Si(111) was used as the substrate.

SF spectra were measured in air with a multiplex SF spectrometer with a 1-kHz laser system [20,21]. A picosecond narrow-bandwidth (7 cm⁻¹) visible pulse of a 633 nm

wavelength and a femtosecond broad-bandwidth (280 cm^{-1}) IR pulse of a $3.4 \mu\text{m}$ wavelength were used as probes of SF process. Geometry of the incidence plane with respect to the sample orientation is shown in Fig. 4. The visible ($2 \mu\text{J}$) and IR ($3 \mu\text{J}$) pulses were focused on a sample with incident angles of 70 and 50 degrees from the surface normal of the sample, respectively. We defined the azimuth angle (γ) of a sample as the angle between the incidence plane of the probe beams and the $[\bar{1}21]$ direction of the Si (111) surface. The SF signal generated in the direction of reflection was observed. Polarization of the signal and probes were selected to be p-polarized. The signal was analyzed by a spectrograph with a 4 cm^{-1} slit width and a multi-channel CCD detector. Sensitivity of the spectrometer was calibrated by dividing the SF spectrum of a sample by the SF spectrum of a GaAs(110) wafer.

XPS

Compositions of the alkyl monolayer surfaces were analyzed by XPS. Photoelectrons excited by the Al K line (1487 eV) and emitted at a take-off angle of 35° from the surface plane were analyzed by an ESCA 2703 spectrometer (Surface Science Instruments).

Force-Displacement Curve, Contact Mode AFM, Water Contact Angle Measurement

1-dodecene ($\text{CH}_2=\text{CH}-(\text{CH}_2)_9-\text{CH}_3$, C12), 1-octadecene ($\text{CH}_2=\text{CH}-(\text{CH}_2)_{15}-\text{CH}_3$, C18), and methyl 10-undecenoate ($\text{CH}_2=\text{CH}-(\text{CH}_2)_8-\text{COOCH}_3$, C10-COOCH₃) were used in the present study. The H-Si (111) substrates were transferred into a 4:6 mixture (v/v) of 1-alkene and mesitylene. Then the solution was heated at 160°C for 24 h. Force curve measurement and contact-mode AFM measurement of the monolayer surface were performed using an AFM (JEOL, JSPM-1300) under ambient conditions. Si_3N_4 cantilevers (NT-MDT, spring constant 0.6 N/m) were used. The water contact angle was measured using an optical microscope under ambient conditions.

.3 Results and Discussion

Contact Mode AFM

Figure 5 (a) shows a contact-mode AFM image of a H-Si surface. Atomically flat and etch-pit free terraces with monoatomic steps are clearly seen. Etch pits usually exist on H-Si surfaces prepared in NH_4F solution without deoxygenation. It is known that

etch-pits is caused by $O_2^- \cdot$ [16]. These radicals abstract hydrogen to form silicon radicals. It is expected that silicon radicals react with either F^- or OH^- to form the F-Si or O-Si [22]. These bonds activate the cleavage of the adjacent Si-Si bonds [23] to lead etch-pits growth. In the present work, etch-pits were not grown as shown in Fig. 5 (a) since NH_4F solution was deoxygenated sufficiently. Figures 5 (b) and 5 (c) show AFM images of a C12 monolayer and a C10-COOCH₃ monolayer. Flat and etch-pit free terraces with monoatomic steps were seen in each image. It is difficult to discriminate between AFM images of H-Si and monolayers. Similar AFM images of octadecyl [24] and decyl [25] monolayers were reported by other groups. It was expected that highly ordered monolayers were formed on silicon.

ATR Infrared Spectroscopy

Hydrogen-Terminated Silicon (111)

ATR-IR spectroscopy is a powerful tool to identify the structure of molecules on silicon surfaces sensitively. Figure 6 shows ATR spectra of hydrogen-terminated silicon (111). While a vibrational peak derived from Si-H stretch at 2075 cm^{-1} was observed with p-polarized configuration (solid curve), the peak was not observed with s-polarized configuration (dashed curve). It was concluded that the Si(111) surface was terminated with H atoms uniformly and Si-H bond was oriented perpendicular to the surface.

Dependence on Reaction Temperature

ATR spectra of monolayers prepared in 1-dodecene at 50 °C, 100 °C, 150 °C, 200 °C for 2 h are shown in Fig. 7. The vibrational peak of Si-H stretch disappeared after the reaction. The peak intensity of spectra for monolayers prepared at higher reaction temperature became stronger and saturated at 150 °C. Peak positions of symmetric and asymmetric CH₂ stretch also shifted to lower frequency as the reaction temperature increased. It was suggested that the structure of monolayers became solid like as the reaction temperature increased. These results were in agreement with the report by Linford *et al* [2].

Temperature Dependence

The thermal phase behavior was investigated by ATR-IR [26]. Figures 8 (a) and 8 (b) show the peak shift of the asymmetric stretch of CH₂ groups and its normalized intensity as a function of the temperature, respectively, for C12, C14, C16 and C18 monolayer. The peak shifted to higher frequency continuously as the temperature increased for each monolayer. The peak intensity started to decrease above 490 K. Once

the monolayer was heated above 440 K, the position and intensity of the peak did not revert after the cooling to room temperature. Thermal phase behaviors were independent of the chain length. Similar behaviors were observed for the symmetric stretch of CH₂ as shown in Fig. 9 (a) and 9 (b). The peak shift to higher frequency was due to the increase of disorder in a monolayer as reported for the monolayers on Au [27,28]. The decrease of peak intensity above 440 K was due to the chain untilting [27]. The coupling between lower and higher frequency modes [29] was also the reason. In addition, the unreverted conformational disorder was introduced in the monolayer by heating above 440 K.

Solvent Effect

Large amount of 1-alkene molecules is used in the preparation of organic monolayers on Si by use of neat 1-alkene, while only a small amount of molecules reacts with silicon surfaces. In addition, it is required to dissolve molecules in solvent when target molecules are solid at room temperature due to the high melting point. An improved method for the monolayer preparation by the dilution of 1-alkene with various solvent has been proposed [18]. It is reported that mesitylene, cumene, xylene and *tert*-butylbenzene are useful to dilute 1-alkene, since the solvent molecules are too large to be intercalated in the monolayer. Organic monolayers prepared in 1-alkene diluted with mesitylene showed water contact angles comparable to the monolayers prepared in neat 1-alkene [18]. However, the difference between two films was detected in ATR-IR spectra in the present work. Figure 10 shows ATR spectra of C12 monolayers prepared in neat 1-dodecene and 40 % (v/v) 1-dodecene diluted in mesitylene. The peak intensity of the ATR spectrum of the monolayer prepared in 40 % 1-dodecene was weaker than that prepared in neat 1-dodecene. This was probably because the reaction H-Si and 1-dodecene was interfered by mesitylene molecules. It was found that order of monolayers in diluted solution was worse than that prepared in neat alkene by ATR. However, it is considered the method is useful when target materials are expensive and/or solid.

Exchange Reaction

It is known that the exchange process occurs in the Au-S system [30]. Possibility of the exchange reaction in the Si-C system was examined. Figure 11 shows the spectrum change of C12 monolayer treated in methyl undecenoate (C10-COOCH₃). Dashed curve shows the C=O stretch peak of C10-COOCH₃ for comparison. Curve (a) shows the spectrum of the C12 monolayer freshly prepared. Nothing is seen in the C=O stretch

region. After heating the C12 monolayer in neat C10-COOCH₃ for 12h, slight increase in the intensity of the C=O peak was observed (Fig. 11 (b)). The intensity of the C=O peak was not enhanced for further heating for 12 h (total 24 h) (Fig. 11 (c)). The increase in peak intensity of the C=O stretch was presumably caused by the physisorption of C10-COOCH₃ molecules on the C12 monolayer and the intercalation of C10-COOCH₃ in the monolayer. It was indicated that no exchange reaction of C12 molecules with C10-COOCH₃ molecules on the silicon occurred. The exchange reaction was suppressed because molecules were strongly anchored to silicon surfaces via covalent bonds.

Stability Test

Organic monolayers show high stability against hot solvent, acid and base [2]. The stability of the monolayer to NH₄F is especially important for the technological application of silicon. ATR spectra (CH₂ and CH₃ vibrational peak region) of the C12 monolayer before and after immersion in 40 % NH₄F for 10 min are shown in Fig. 12 (a). The intensity of symmetric CH₂ and asymmetric CH₂ peaks decreased. This decrease in the intensity is consistent with the result by Boukherroub *et al* [25]. On the other hand, no decrease in the intensity was observed through the 8 % NH₄F treatment for 10 min (Fig. 12 (b)). The monolayer showed the high stability to 8 % NH₄F. Therefore, it was possible to remove SiO_x and terminate with hydrogen without the degradation of the molecules using 8 % NH₄F as will be shown in Chapter .

Reaction by UV Irradiation

The reaction between 1-dodecene molecules and H-Si was induced by UV irradiation (Hg-Xe lamp, 200 W, Hamamatsu Photonics) for 2 h. The ATR spectrum is shown in Fig. 13. The wettability of area (ca. ϕ 8 mm) irradiated was changed compared with surroundings apparently. The intensity of the spectrum of the monolayer prepared by UV irradiation was weaker than that prepared by thermal reaction. This was because the UV-induced reaction did not occur at the surrounding area and at the backside of the substrate. This means that the selective growth can be done using UV-irradiation.

XPS

C10, C11, C12, C13, and C18 monolayers were analyzed by XPS. A sharp C(1s) peak appeared in the spectrum of each monolayers. Chain density estimated for each monolayer, ranged from 0.5-0.6 ML and independent of the chain length and parity. The result was consistent with the estimation by Sieval *et al.* [10,11].

SFG Spectroscopy

Azimuth-Orientation Dependence in SF Spectra

Several vibrational bands of alkyl chains were observed at 2965, 2938, 2914, 2877, and 2850 cm^{-1} . 2965 and 2877 cm^{-1} bands were assigned to the asymmetric and the symmetric stretch of the CH_3 group, and the 2938 cm^{-1} band to the Fermi resonance. The 2850 cm^{-1} band was assigned to the symmetric stretch of the CH_2 group. A broad band at 2914 cm^{-1} was assigned to the asymmetric stretch of the CH_2 group and/or the Fermi resonance. Observation of the CH_2 vibrational bands suggested that *gauche* defects exist in the monolayer, since the CH_2 bands are symmetrically forbidden in all-*trans* conformations in the SF generation process [31,32]. The spectra depended on the azimuth angle (γ) which reflected the C_{3v} symmetry of the Si(111) surface, indicating the monolayers were formed epitaxially on the Si(111) substrate (Fig. 14). The structure of the alkyl chains was controlled by the atom geometry of the Si surface through the Si-C covalent bonds. Alkyl chains fixed on quartz via silane coupling, which were derived from alkyltrichlorosilanes, presented SF spectra independently of the azimuth angle [33], showing that the epitaxial relationship was broken at the interface.

Chain Length Dependence in SF spectra

SF spectra of C10, C11, C12, C13 and C18 at $\gamma = 60^\circ$ are compared in Fig. 15. The two CH_2 bands as well as the three CH_3 bands were observed for all species, suggesting that alkyl chains with *gauche* defects were included in the monolayers. The 2965 cm^{-1} band was much larger than the 2877 cm^{-1} band for the C_n monolayers with even n , whereas these two bands had comparable intensities for the C_n monolayers with odd n . The two distinct intensity patterns depending on the parity of n indicate that the majority of the CH_3 groups are alternately oriented in two distinct directions depending on the parity. The alternate feature of the CH_3 bands was rationalized with an alternate orientation of the CH_3 terminal controlled by the parity of chain length since the chain densities of these monolayers were constant.

Molecular Conformation of n -Alkyl Chains

The conformation of the n -alkyl chains is considered on the basis of the results of SFG spectra. Figure 16 shows the structure proposed for the C18 monolayer based on molecular modeling with molecular mechanics force fields by Zhang *et al.* [34]. It has been predicted that the conformation of the monolayer is all-*trans* except around the first and second nearest C-C bonds to the silicon surface. This conformation is

consistent with the parity dependence observed by SFG spectroscopy. The twisted stem probably contributed to the CH₂ appearance in SF spectra.

Force-Displacement Curve Measurement

Figures 17 (a), 17 (b), and 17 (c) show force curves measured on a H-Si surface, a C12 monolayer, and a C10-COOCH₃ monolayer, respectively. A very small adhesion force between the cantilever and the H-Si surface was observed. On the other hand, larger adhesion force due to van der Waals interactions between the cantilever and molecules were observed in force curve measurement on monolayers. This indicates the possibility to distinguish chemical species on the surface with chemical force microscopy as will be shown in Chapter .

Water Contact Angle

The surface composition is very sensitive to the wetting behavior. Figures 18 (a), 18 (b), and 18 (c) show water droplets on a H-Si surface, a C12 monolayer, and a C10-COOCH₃ monolayer, respectively. The water contact angle measured on H-Si was consistent with the value of 88° reported by Sung *et al.* [15]. The contact angle of a C12 monolayer became higher than that of the H-Si surface and similar to the angles (over 100°) reported for alkyl monolayers [15,18]. In contrast, the C10-COOCH₃ monolayer was very hydrophilic. These results show that the wetting properties of silicon surfaces can be modified by highly ordered organic monolayers.

.4 Summary

In this chapter, organic monolayers anchored to Si (111) were prepared by wet process and characterized. It is confirmed that monolayer surfaces are atomically flat and defect-free using a contact-mode AFM. SFG spectroscopy revealed that alkyl monolayers anchored to Si(111) consist of alkyl chains with an all-*trans* head part and a twisted stem. Surface properties of monolayers were also characterized by ATR-IR spectroscopy, contact angle measurement and force curve measurement. In addition, monolayers show stability against NH₄F, which enables us to use monolayers as resists for lithography.

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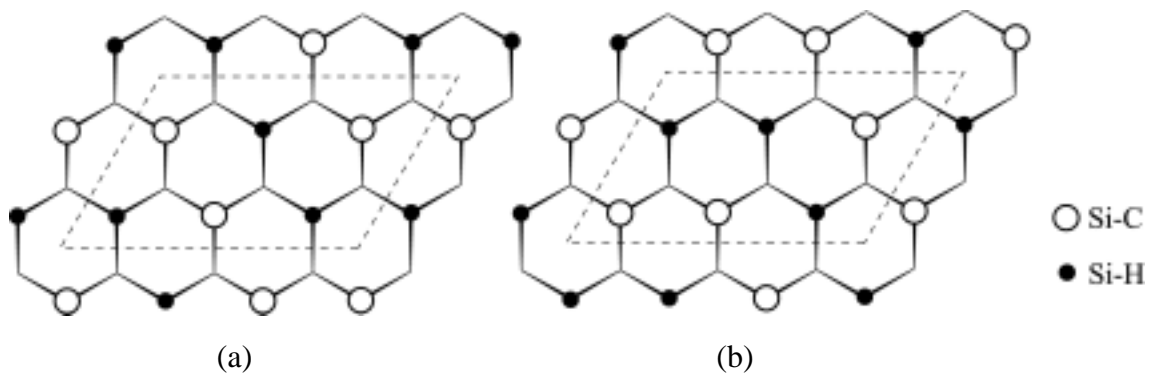


Fig. 1. Proposed unit cells with a substitution of 50 %.

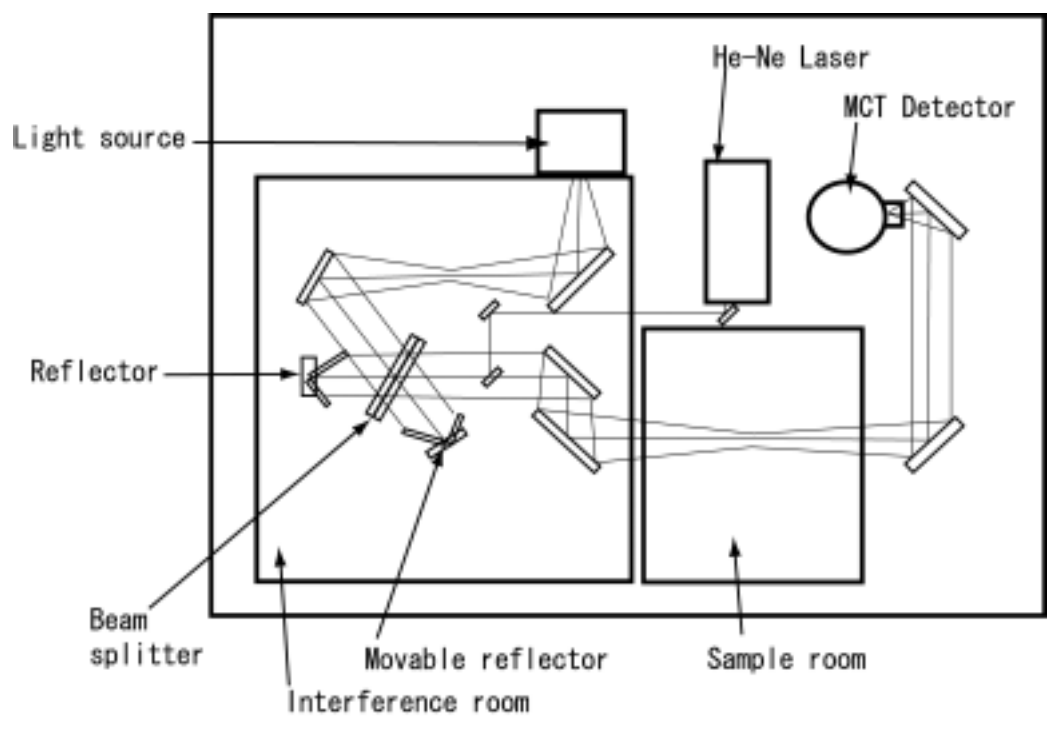
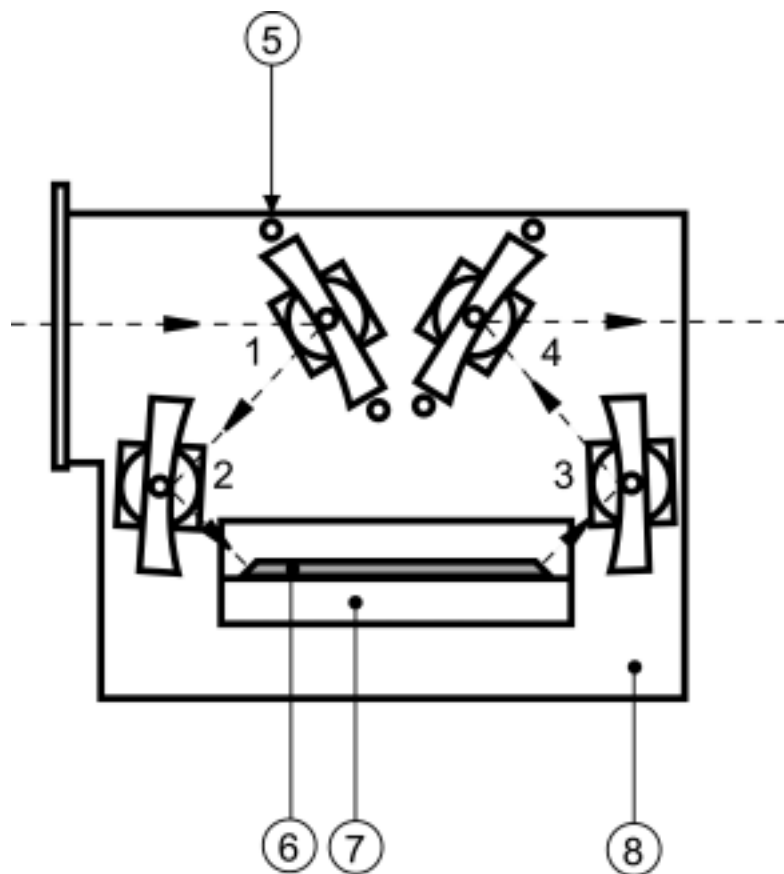


Fig. 2. Schematic view of a Fourier transform infrared spectrometer.



- 1 - 4. Mirror
- 5. Fiducial marks
- 6. ATR crystal
- 7. Sample holder
- 8. Base plate

Fig. 3. The scheme of the multiple attenuated total reflectance unit and the optical path diagram.

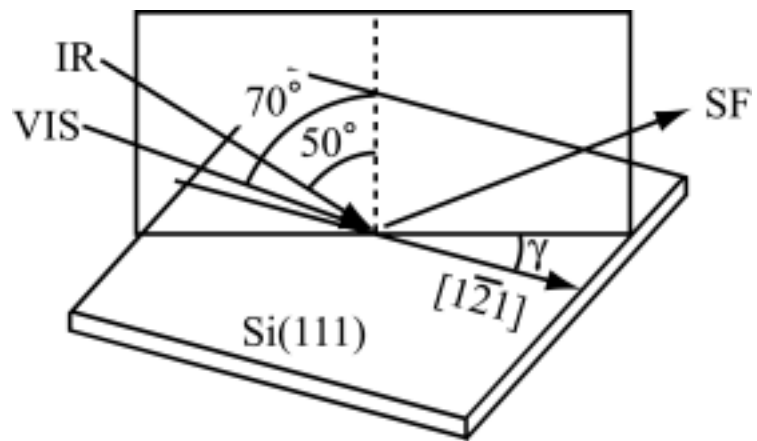
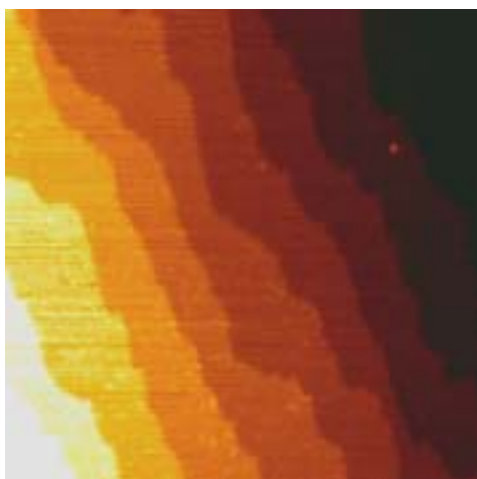


Fig. 4. Geometry of the incidence plane with respect to a sample orientation.



(a)



(b)



(c)

Fig.5. Topographic AFM images ($1 \mu\text{m} \times 1 \mu\text{m}$) of (a) H-Si, (b) a C12 monolayer and (c) a C10-COOCH₃ monolayer.

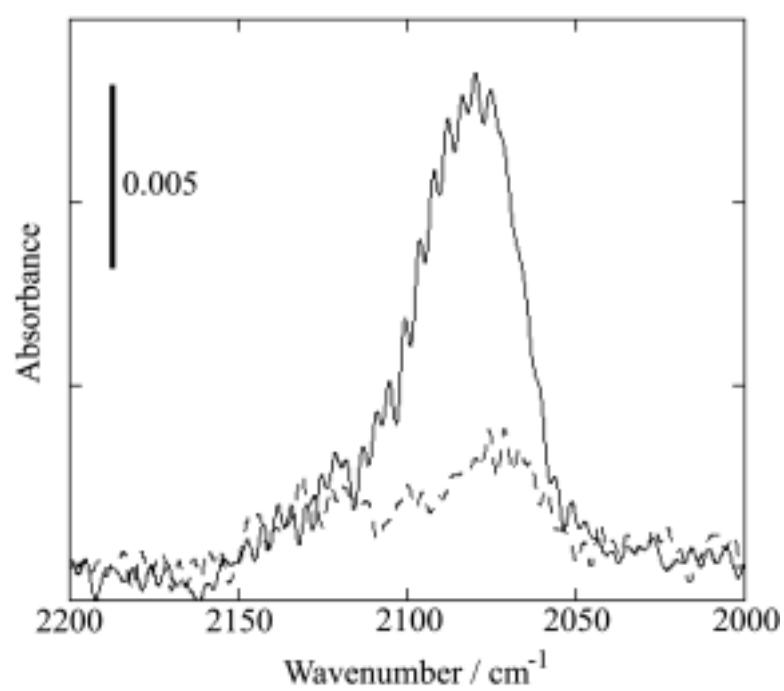


Fig. 6. ATR spectra of H-Si with s-polarized (dashed curve) and p-polarized (solid curve) infrared light.

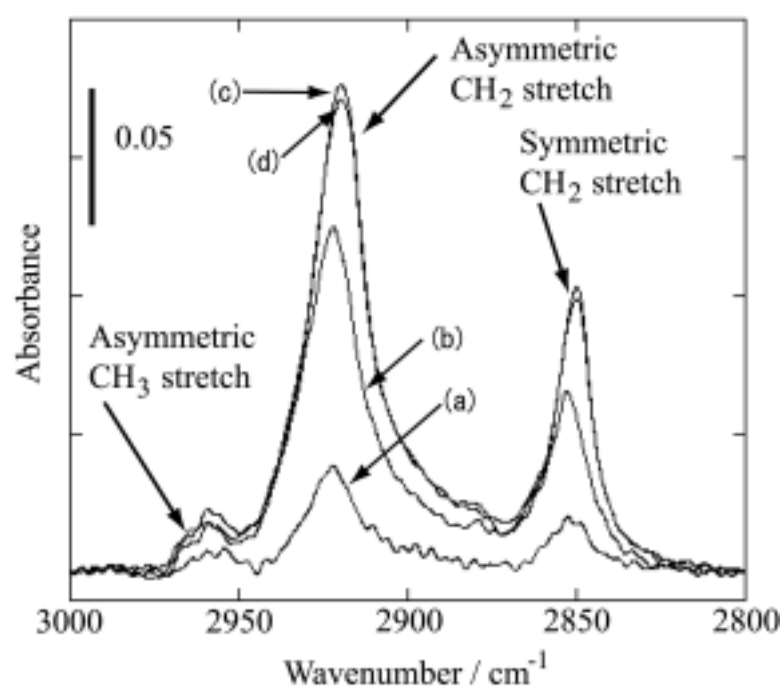


Fig. 7. ATR spectra of C12 monolayers prepared at 50 °C (a), 100 °C (b), 150 °C (c), and 200 °C (d).

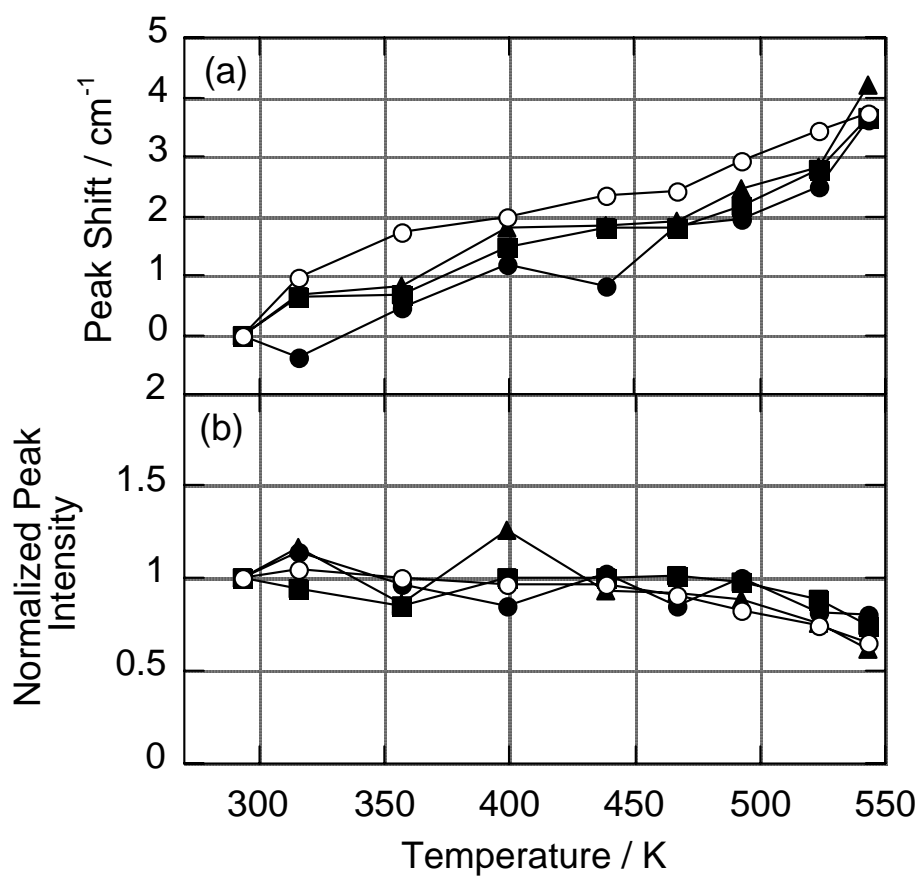


Fig. 8. Peak shift (a) and normalized peak intensity (b) of asymmetric stretch of CH₂ groups as a function of the temperature: C12 (□), C14 (○), C16 (■) and C18 (●) monolayers.

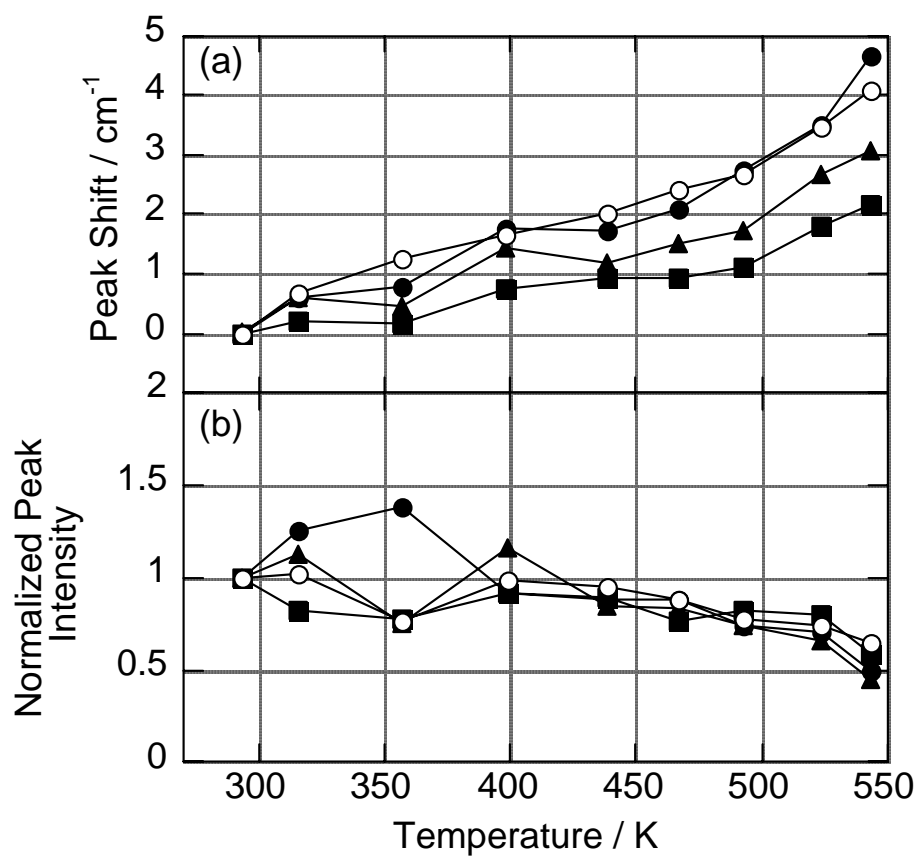


Fig. 9. Peak shift (a) and normalized peak intensity (b) of symmetric stretch of CH₂ groups as a function of the temperature: C12 (○), C14 (△), C16 (□) and C18 (●) monolayers.

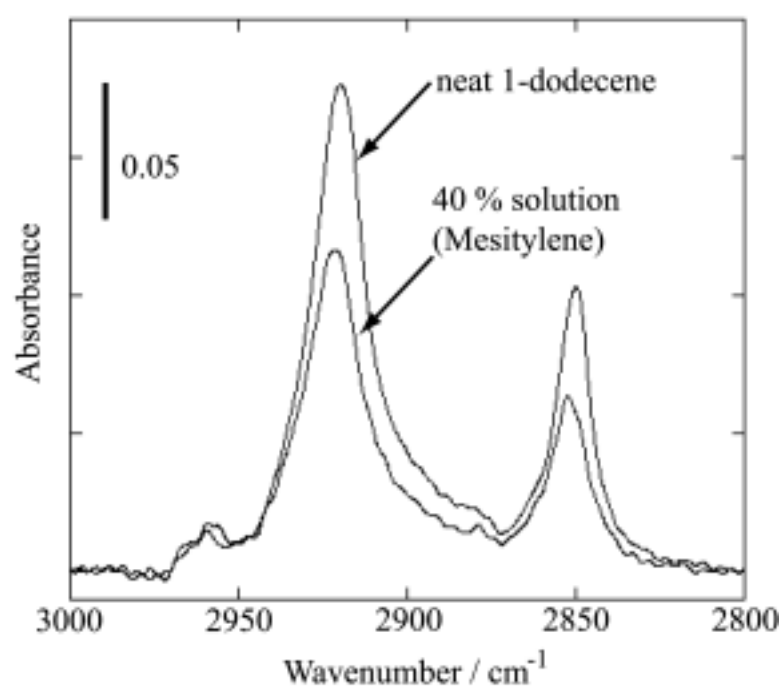


Fig. 10. ATR spectra of C12 monolayers prepared in neat and mesitylene-diluted 1-dodecene.

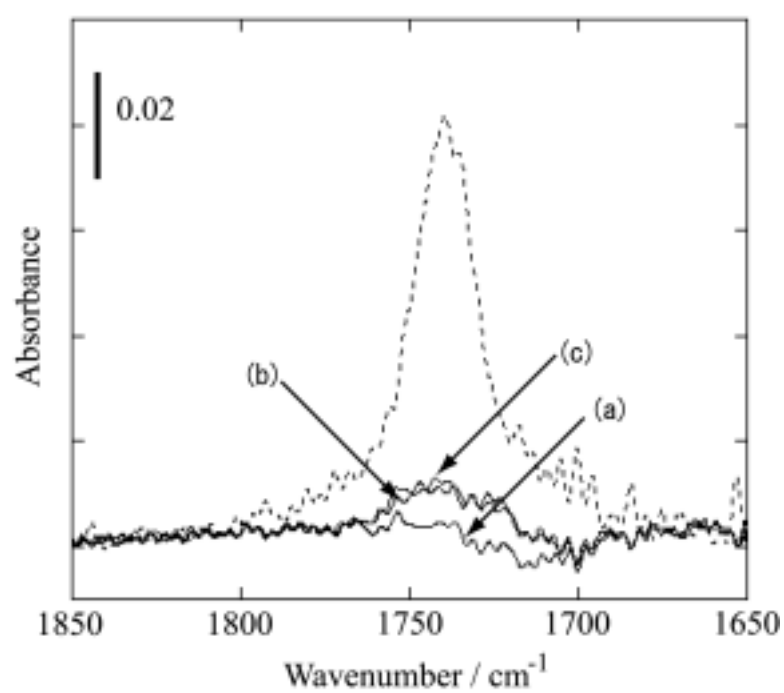
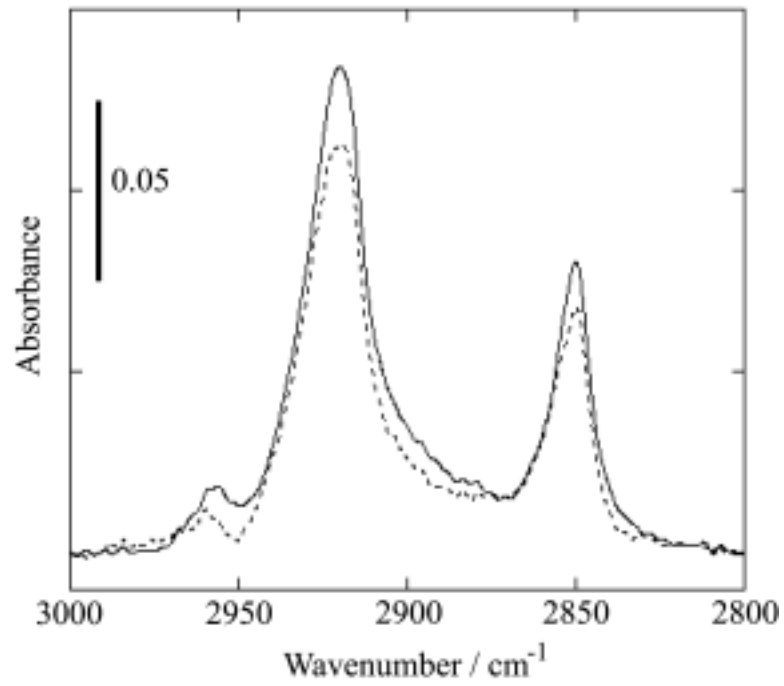
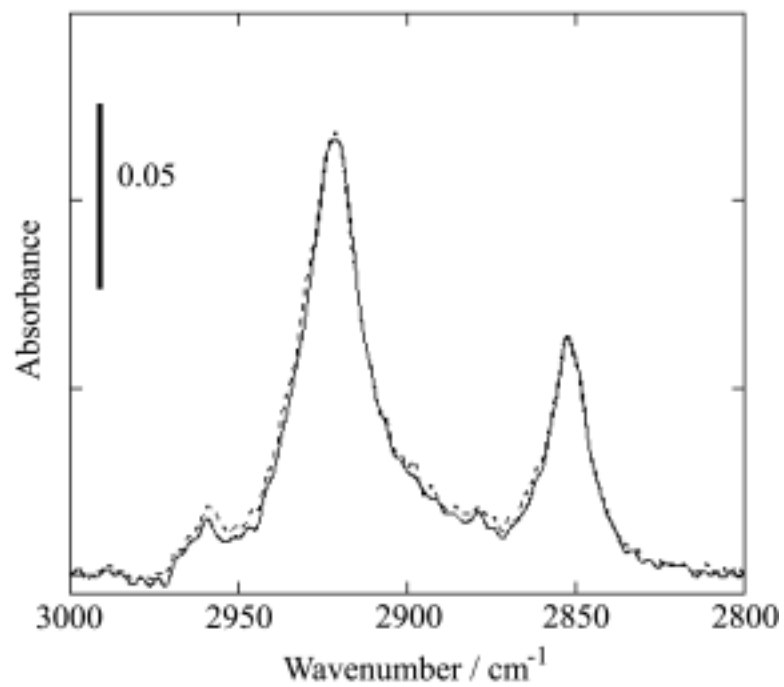


Fig. 11. ATR spectra of C=O region of a C12 monolayer heated in C10-COOCH₃ for 0 h (a), 12 h (b), and 24 h (c). Dashed curve is an ATR spectrum of a C10-COOCH₃ monolayer for comparison.



(a)



(b)

Fig. 12. ATR spectra of CH region of C12 monolayers; (a) Before (solid curve) and after (dashed curve) the 40 % NH₄F treatment for 10 min; (b) Before (solid curve) and after (dashed curve) the 8 % NH₄F treatment for 10 min.

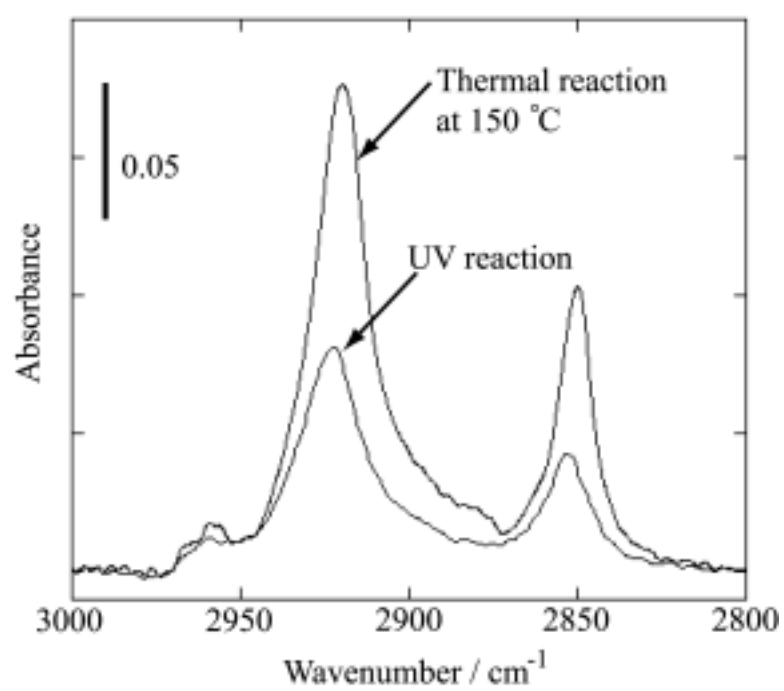


Fig. 13. ATR spectra of CH region of C12 monolayers prepared by the UV induced reaction and thermal reaction.

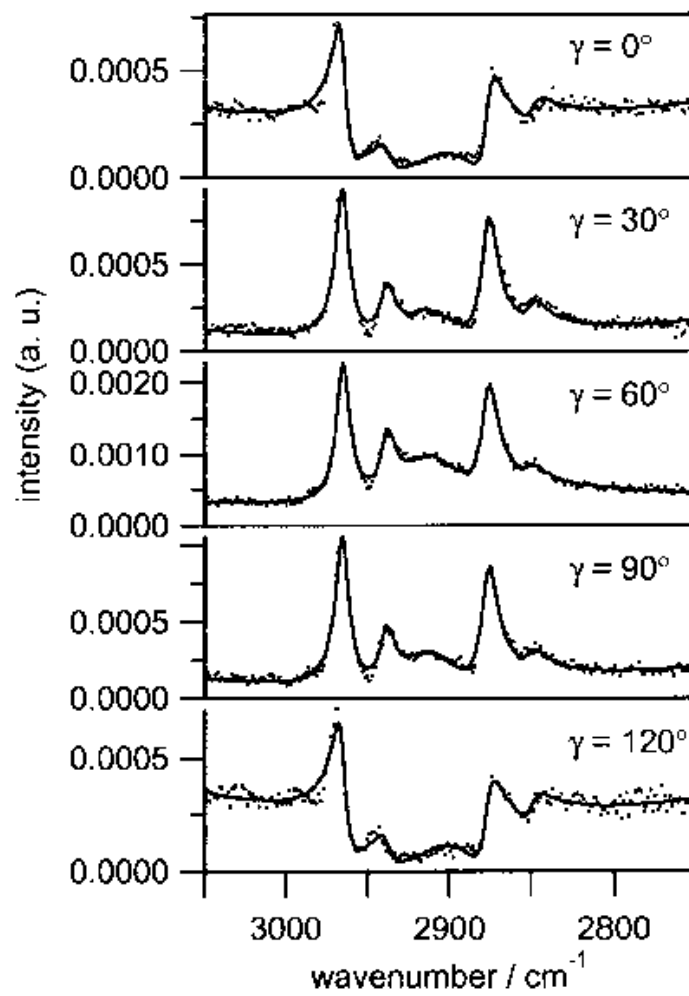


Fig. 14. Azimuth dependence of SF spectra of tridecyl ($C_{13}H_{27}$) monolayer on Si(111). Sample azimuths (γ) are shown. The solid lines were derived from a numerical fit. The spectra were measured at room temperature.

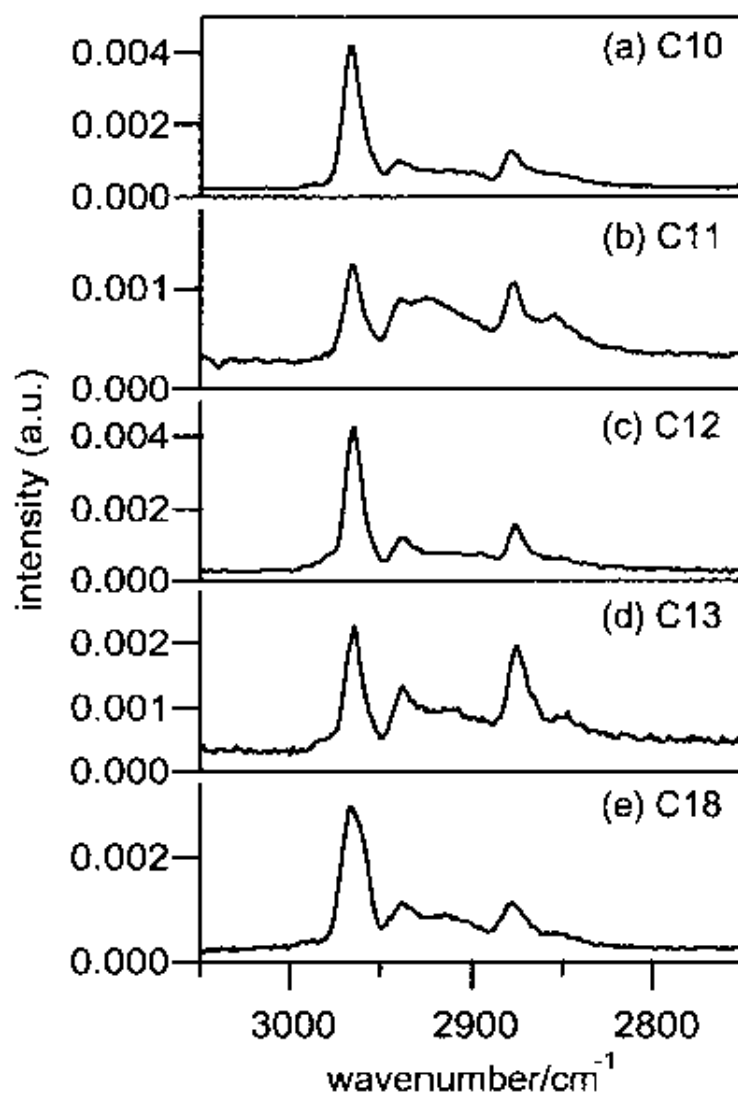


Fig. 15. SF spectra of n -alkyl (C_nH_{2n+1} ; $n = 10-13, 18$) monolayers on Si(111) measured at the azimuth $\gamma = 60^\circ$. The spectra were measured at room temperature.

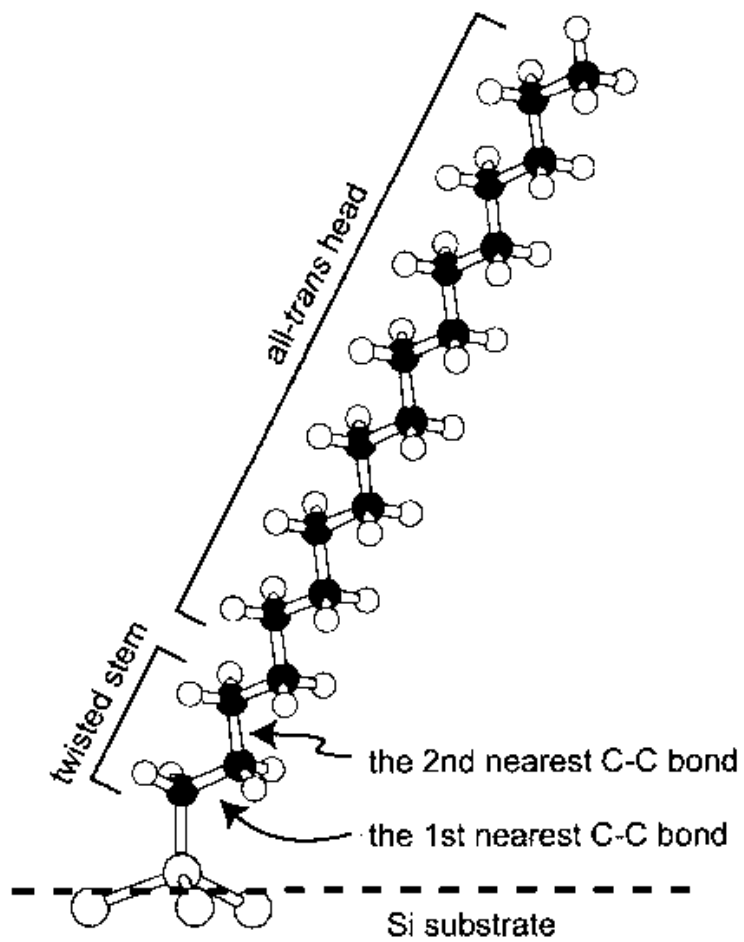


Fig. 16. Octadecyl molecule on Si(111) determined by the molecular mechanics simulation [34].

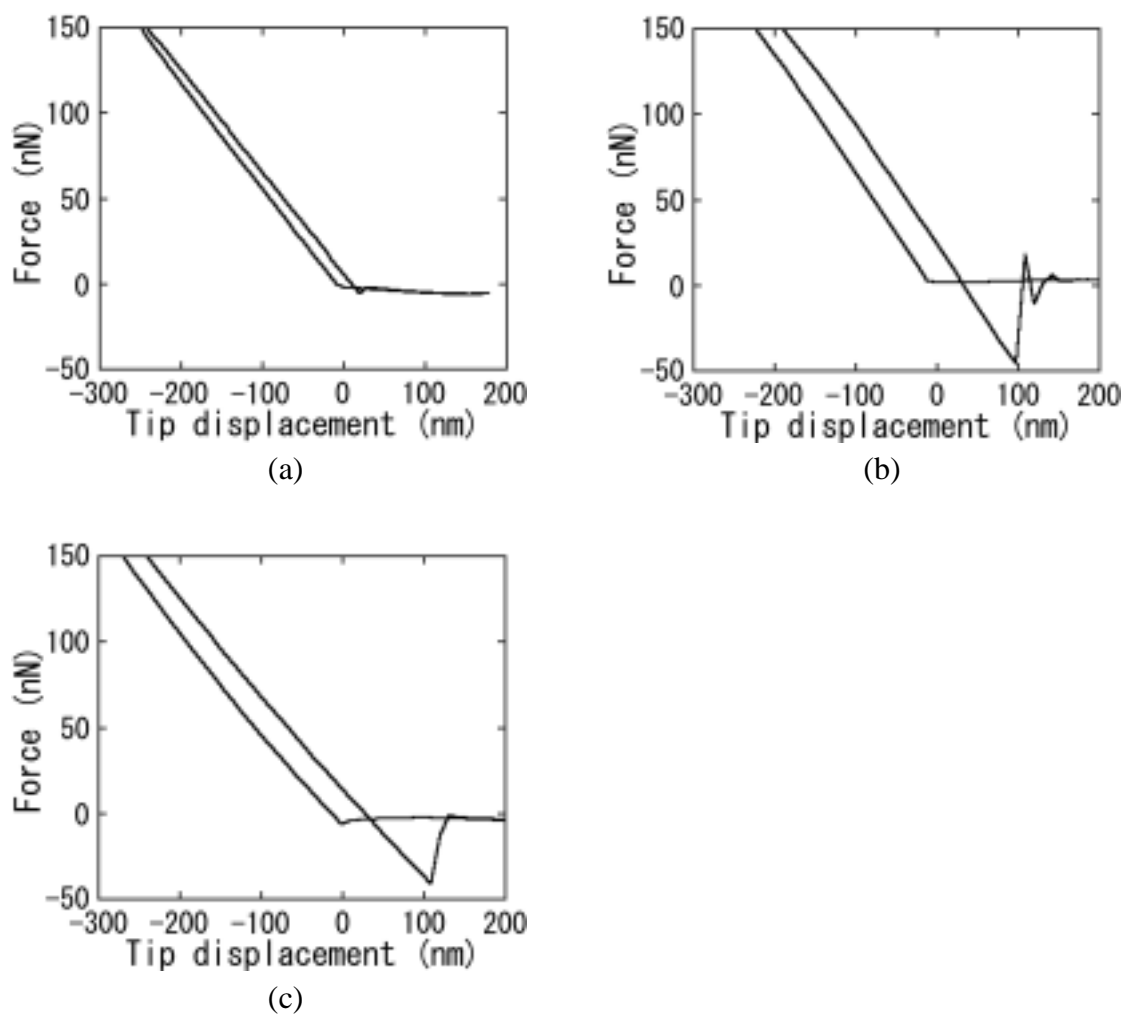
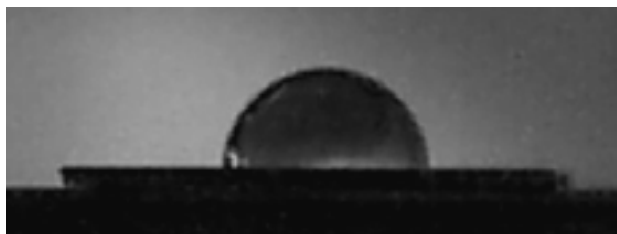


Fig. 17. Force curves on (a) H-Si, (b) a C12 monolayer and (c) a C10-COOCH₃ monolayer.



(a)



(b)



(c)

Fig. 18. Water droplets on (a) H-Si, (b) a C12 monolayer and (c) a C10-COOCH₃ monolayer.

Chapter
Nanopatterning of Organic Monolayers
Anchored Covalently to Si (111) with An Atomic
Force Microscope

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Japanese Journal of Applied Physics, **41**, 4894 (2002).

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.1 Introduction

The surface modification with scanning probe microscopes (SPMs) has received considerable attention as a predominant technique to fabricate nanometer-scale structures on metals [1-3], semiconductors [4-13] and organic materials [14-18]. Among various techniques proposed so far, the field-induced oxidation (FIO) with conducting SPM probes has been intensively studied since the report by Dagata *et al.* in 1990 [4]. They demonstrated the nanometer-scale patterning of H-Si surfaces with scanning tunneling microscope (STM) tips.

The atomic force microscope (AFM) with metal-coated cantilevers was also used as a promising tool for local oxidation, since AFM has an advantage that the voltage applied to the cantilever for local oxidation is independent of the feedback control. The mechanism and kinetics of local oxidation by scanning probe microscopes was revealed by Snow *et al.* [5,6] and Avouris *et al.* [10,11]. Hydroxide ion (OH^-), produced by the electric field between the surface and conducting probe, combine with silicon atom to form Si-O bonds. OH^- is supplied from the water film condensed on the surface. The oxidation process strongly depends on the electric field, humidity, and duration time. Nanometer-scale electronic devices such as field effect transistors were also fabricated from H-Si by the AFM local oxidation [8]. The surface of H-Si is, however, not so stable against oxidation that whole area of the surface is oxidized gradually in air [19]. In addition, friction during the scanning on silicon strips the metal coatings away from cantilever surfaces.

In order to protect both surfaces from these problems, one approach is to use organic monolayers as resist materials for chemical modifications. Silicon surfaces covered with organic monolayers inhibit the oxidation of the silicon surfaces compared to H-Si even in electrolyte solution [20]. It has been proven that organic monolayers are available for ultrathin uniform resists of lithography with UV [21] and electron-beam [22]. Scanning probe lithography using organic monolayers has been performed and was reviewed by Krämer *et al.* [23]. Organosilane monolayers were patterned with AFM [16,17]. Monolayers based on the large molecules such as dendrimers were also used as resists for SPM-FIO [24]. Nanofabrication was performed using organic monolayers patterned as templates for monolayers stack and the metal deposition by Maoz *et al.* [25].

In this chapter, I describe nanometer-scale modification of alkyl monolayers on Si(111) by FIO with platinum coated AFM cantilevers. Alkylation of silicon is of growing interest since it provides the novel organic/inorganic system based on Si-C covalent bonds [19,20,26-32]. Nanometer-scale patterning of this system will become a

key technology for assemblies of both inorganic and organic nanometer scale devices.

.2 Experimental

Preparation of Alkyl Monolayers

Medium doped (1-10 Ωcm) n-type Si (111) wafers were used as substrates. Hydrogen termination of Si (111) surfaces was carried out according to the literature by Wade *et al.* [33]. Alkyl monolayers were prepared through the reaction between 1-alkenes and H-Si. We used 1-dodecene ($\text{CH}_2=\text{CH}-(\text{CH}_2)_9-\text{CH}_3$) in the present experiment. H-Si (111) substrates were transferred into a 4:6 mixture (v/v) of 1-dodecene and mesitylene, which was deoxygenated by argon bubbling for at least 1 hour prior to the reaction. The solution was then heated at 433 K for 24 hours under the continuous argon bubbling and it was cooled down to room temperature. The sample was taken out of the solution and rinsed with petroleum ether, ethanol and dichloromethane.

Oxidation of Silicon Covered with Organic Monolayers in Nanometer Scale with An AFM

Oxidation of the monolayer surface in nanometer-scale was done using a contact-mode AFM (Jeol, JSPM-1300) with platinum coated cantilevers (NT-MDT, spring constant 0.6 N/m) under ambient conditions. Typical bias voltage applied to the surface was +5V with respect to the cantilever. The scan speed was adjusted to 200 nm/sec.

Surface Modification of Organic Monolayers after Local Oxidation

Following the AFM anodization, chemical modifications illustrated in Fig. 1 were carried out. Anodized areas with AFM were etched by 8 % NH_4F for 5 min at room temperature, and were rinsed with ultrapure water. The etched surface was terminated with hydrogen as illustrated in Fig. 1, on which 1-alkene molecules were chemisorbed. I put 1-octadecene ($\text{CH}_2=\text{CH}-(\text{CH}_2)_{15}-\text{CH}_3$) on the etched areas in a similar manner to that for the preparation of 1-dodecene films. Anodized areas of a different sample were covered selectively with octadecyltrichlorosilane (OTS; $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$). It has been reported that OTS is adsorbed on oxide layers through the siloxane coupling, and siloxane monolayers are utilized as resist films for lithography [16,17]. This modification was carried out by immersing the patterned sample in mesitylene consisting of 2 mM OTS for 30 min under a nitrogen atmosphere. The sample was then sonicated in dichloromethane.

.3 Results and Discussion

Oxidation of Silicon Covered with Organic Monolayers in Nanometer Scale with An AFM

Figure 2 (a) shows a contact-mode AFM image of a patterned dodecyl monolayer. On unoxidized areas, atomically flat terraces with the monoatomic steps are clearly seen. It was expected that the highly ordered monolayers were formed on Si as shown in Chapter . Similar AFM images were reported for octadecyl [28] and decyl [29] monolayer. A cross section view along the line X-Y is shown in Fig. 2(b). The silicon surface was oxidized and protrusions appeared on the monolayer surface. The height and width of the oxidized line were about 1.1 nm and about 50 nm, respectively. The minimum width achieved in the present work was about 40 nm. The anodization process was strongly influenced by the electric field, the duration time as well as humidity. The height of the formed oxide showed voltage dependence as shown in Fig. 3. Within the error bars linear behavior of the height with the applied voltage can be estimated. Such a linear behavior was also clearly found for hydrogen-terminated silicon at various lithography speeds [13]. Comparing to the local oxidation using siloxane layer on SiO_x, the system of monolayers covalently bound to Si makes it possible to reduce the bias voltage required to local oxidation. The bias voltage applied in our system was, in fact, about 50 % lower than that for siloxane monolayers examined so far [17]. The reduction of the required bias voltage enables us to fabricate narrower line. The surface did not change over one week in air. Alkyl monolayers were available to protect the surface from oxidation.

Etching with NH₄F

Following the AFM anodization, chemical modifications illustrated in Fig. 1 were carried out. Anodized areas were etched by 8 % NH₄F for 5 min at room temperature and then rinsed with ultrapure water. Figure 4 (a) and the solid curve in Fig. 4 (b) show an AFM image and the cross section view of the patterned surface after etching by 8 % NH₄F, respectively. It was found that anodized areas were selectively etched. The width was approximately 50 nm, which was the same as that of anodized area. The depth was in the range from 1 to 3 nm. The aspect ratio (depth/width) in the present process was 0.02 - 0.06. The depth of the silicon oxide formed by anodization is directly related to the height of the silicon oxide; the height of the silicon oxide is normally about 60 % of the total thickness of the oxide [13] The percentage calculated from data (the height of the oxide, 1.1 nm; the depth of the oxide, 1-3 nm; total thickness of the oxide, 2.1-4.1

nm) was in the range from 48 % to 73 %, which agreed with the report by Fontaine *et al.* [13]. NH_4F dissolved not silicon but silicon oxides exclusively. Dodecyl monolayers showed high stability against 8 % NH_4F as demonstrated in Chapter . Comparing the images in Fig. 2 (a) and Fig. 4 (a), additional defects were not produced by NH_4F treatment. The defects were originating from the dusts produced by the scratching the surface to write marks for AFM observation at the same area.

1-Octadecene Growth

1-octadecene molecules were put on etched areas. The cross section view is shown by the dashed curve in Fig. 4 (b). As can be seen in the cross section, the grooves apparently became shallow after reaction. 1-octadecene molecules were found to react selectively to the hydrogen terminated surfaces in grooves. As shown in Chapter , 1-octadecene did not react at the surface covered with C12.

Etching with The Mixture of NH_4F and H_2O_2

Anodized areas were etched in the mixture of 40 % NH_4F (2 ml), H_2O_2 (0.5 ml), and H_2O (8ml) [17]. The etching depth is plotted as a function of the oxide height in Fig. 5. The etching depth was proportional to the oxide height, which could be controlled by the voltage applied for anodization. The groove was very deep compared with that formed only by NH_4F . This is because H_2O_2 oxidized silicon to form the silicon oxide, which is quickly removed by NH_4F . It was possible to form the deep groove, whose depth could be controlled, by the etching in NH_4F solution containing H_2O_2 .

OTS Growth on Silicon Oxide Formed by Local Oxidation

Anodized areas were covered selectively with octadecyltrichlorosilane (OTS; $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$). It has been reported that OTS is adsorbed on oxide layers through the siloxane coupling, and siloxane monolayers are utilized as resist films for lithography [16,17]. This modification was carried out by immersing the patterned sample in mesitylene consisting of 2 mM OTS for 30 min under a nitrogen atmosphere. The sample was then sonicated in dichloromethane.

Figures 6 (a) and 6 (b) show a topographic image and the cross section view of the surface after the treatment with the OTS solution, respectively. The dashed curve in Fig. 6 (b) indicates the height profile of the surface before reaction. The height of anodized areas increased by about 0.4 nm, indicating that OTS reacted selectively to anodized areas. This height difference was rather small comparing to the expected length of an OTS molecule (c.a. 2.6 nm). It is supposed that dodecene molecules were not totally

removed during the initial anodization process. The modified areas are thought to be covered with the mixture of dodecane and OTS molecules.

.4 Summary

In summary, local oxidation of dodecyl monolayers anchored to Si (111) was performed with a contact-mode AFM by applying positive bias voltage to the surface with respect to a conducting cantilever under ambient conditions. The monolayers showed high resistance against NH_4F etching and oxidation. Anodized areas were selectively modified with different molecules. The grooves, depth of which was controlled, were fabricated through the etching process. In the present study, alkyl chains reacted at the grooves etched by NH_4F . Instead of alkyl chains, the attachment of molecules with reactive terminal groups, such as amino, sulfide, sulfonamide, ester, alcohol, and aromatic compounds, in nanometer scale is the next steps for further attractive modification with DNA, protein, organic dyes, and metals. These modifications of alkyl monolayers will become of greatly useful for the nanofabrication of organic/inorganic interfaces based on Si-C covalent bond in nanometer scale.

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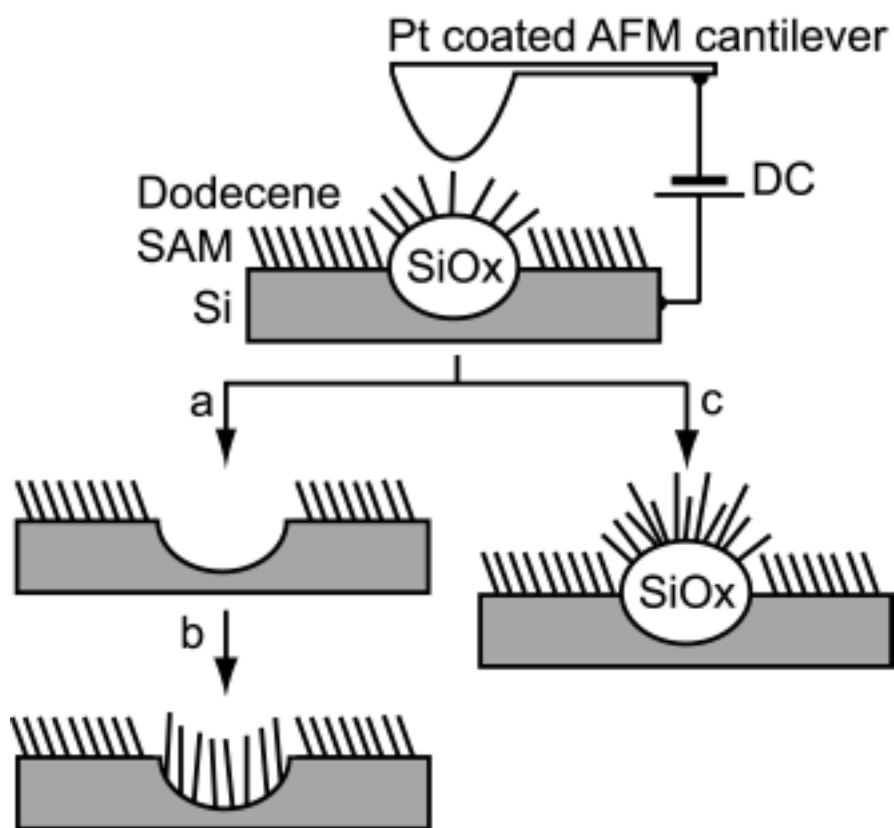


Fig. 1. Schematic view of chemical modification process: a) removing the silicon oxide and terminating the surface of grooves with hydrogen using NH₄F; b) covering the etched surface with 1-octadecene molecules; and c) covering the silicon oxide with octadecyltrichlorosilane molecules.

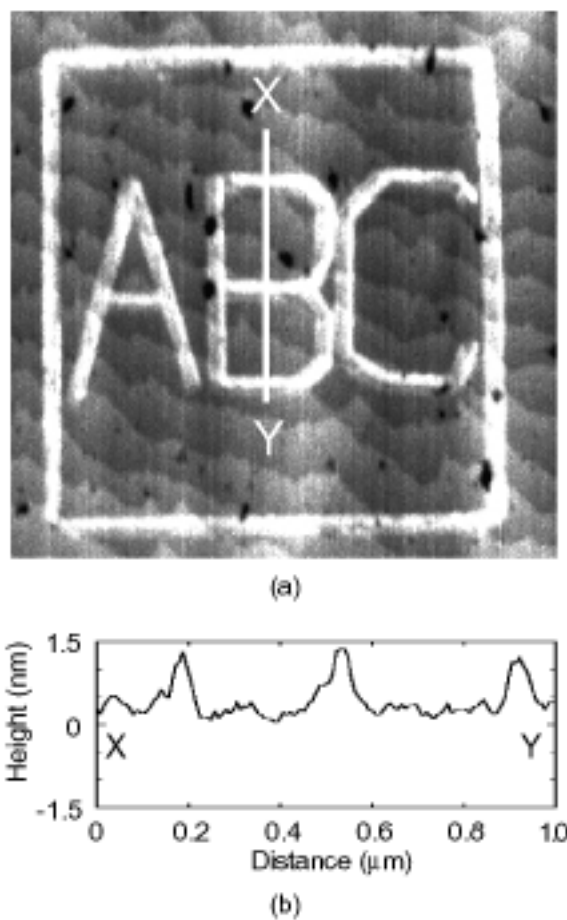


Fig. 2. (a) A topographic AFM image ($2\ \mu\text{m} \times 2\ \mu\text{m}$) and (b) the height profile of a dodecyl monolayer on Si (111) after anodization in air with the sample bias voltage of +5V.

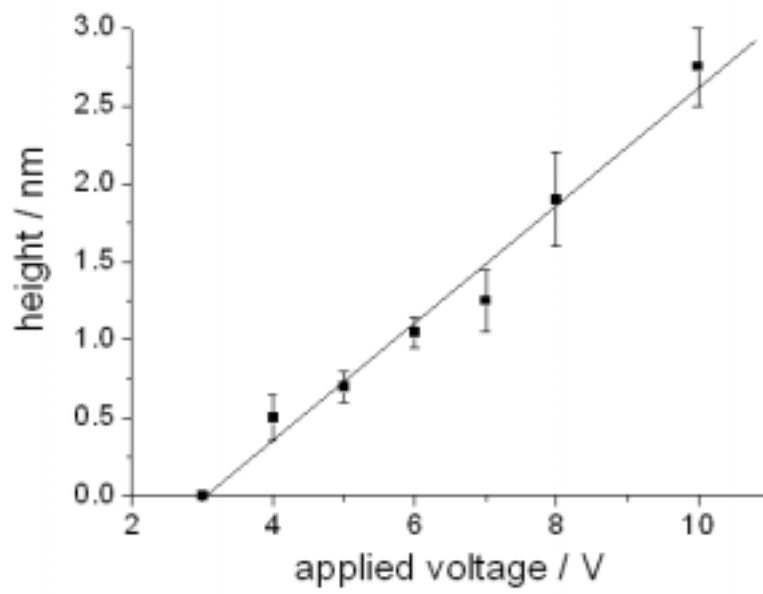
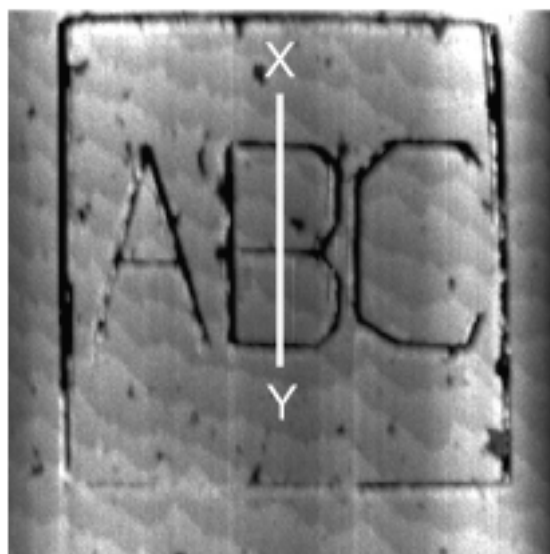
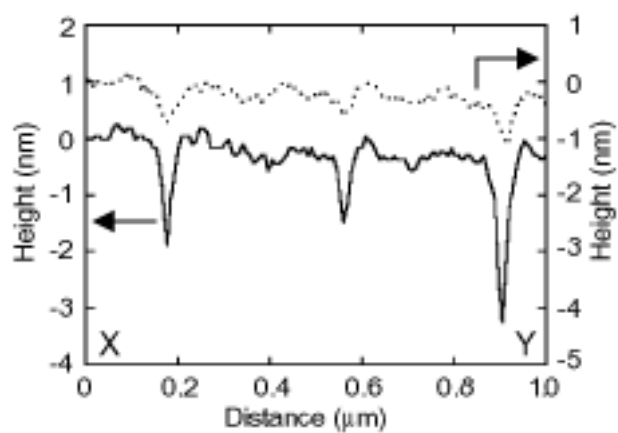


Fig. 3. Height of the silicon oxide formed by local oxidation with AFM on dodecene covered p-type silicon (111) at different applied voltages.



(a)



(b)

Fig. 4. (a) A topographic AFM image ($2 \mu\text{m} \times 2 \mu\text{m}$) and (b) the height profile of a dodecyl monolayer on Si (111) after etching by 8 % NH_4F for 5 min at room temperature. The dashed curve in (b) is the height profile of a dodecyl monolayer on Si (111) after treatment in 40 % 1-octadecene solution for 24 hours at 433 K.

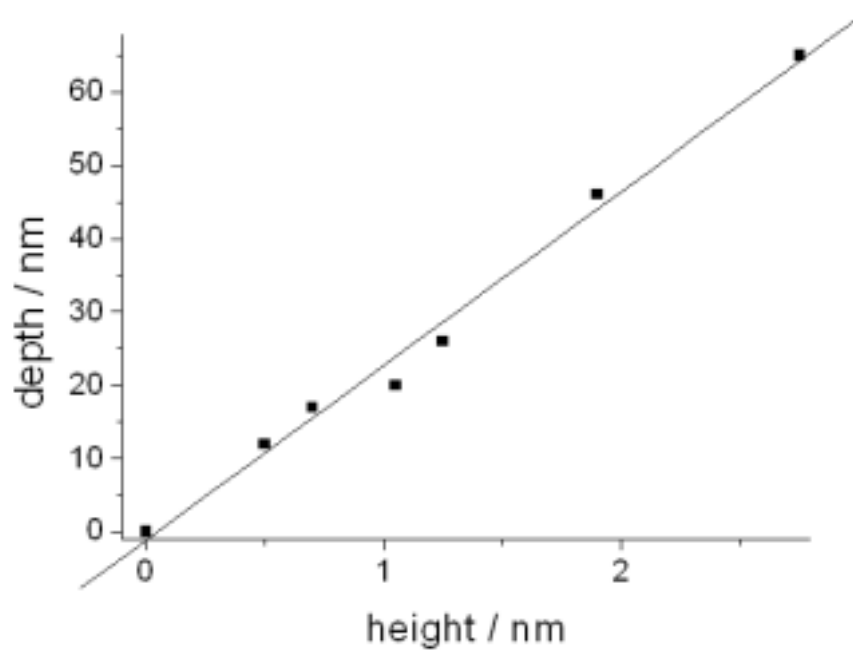
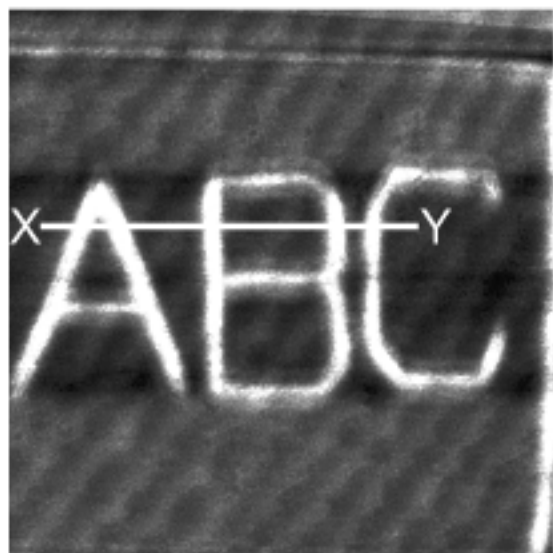
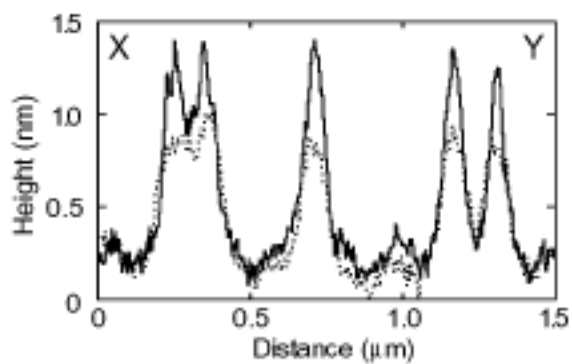


Fig. 5. Plot of the depth of the grooves formed by etching of the patterned p-type silicon with $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$ against the height of the formed silicon oxide. Etching time was 5 min.



(a)



(b)

Fig. 6. (a) A topographic AFM image ($2\ \mu\text{m} \times 2\ \mu\text{m}$) and (b) the height profile of a dodecyl monolayer on Si (111) after treatment in 2 mM OTS solution for 30 min at room temperature. The dashed curve is the height profile before reaction.

Chapter
Fluorescence from Dye Molecules Anchored
Covalently to Silicon Surfaces

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Material Research Society Symposium Proceedings, **739**, H7.37.1 (2003).

.1 Introduction

Functionalization of silicon surfaces by formation of Si-C bonds between 1-alken molecules and hydrogen-terminated silicon (H-Si) has been of growing interest as an approach for designing well-defined interface for numerous applications. These monolayers are so stable under a variety of conditions that they are available for resists of lithography [1]. The surface modification of monolayers on Si (111) in nanometer-scale was demonstrated in Chapter . It is possible to immobilize various functional molecules on Si by using anchor molecules. There have been some reports to immobilize DNA [2-6], protein [7] and conducting polymers [8,9] to silicon via anchor molecules.

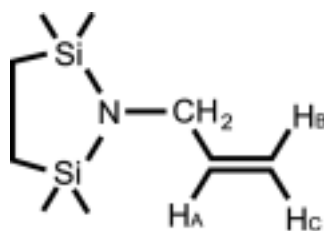
In this chapter, preparation of aminopropyl monolayers which serve as anchor layers to react with functional molecules will be demonstrated. Surfaces of aminopropyl monolayers were coupled with a fluorescent dye, fluorescein-4-isothiocyanate (FITC). It is known that fluorescence of organic molecules on metals and semiconductors is quenched. Kittredge *et al.* investigated the effect of spacer chain length on quenching of fluorescence using the self-assembled monolayer on Au [10]. It was reported that the quenching ratio of luminescence of thin tetraphenylporphyrin films on SnO₂ depends on the resistivity of substrates [11]. The conductivities (doping concentration) and Fermi-levels of semiconductor substrates are tunable while it is difficult to control the work function of gold. We found that the intensity of fluorescence from FITC films was affected by the conduction type and doping concentration of substrates. Electron transfer (ET) and excited energy transfer (EET) at interfaces between molecules and substrates are one of the important subjects in molecular science and engineering.

.2 Experimental

Synthesis of 1 - (3 - propenyl) - 2, 2, 5, 5 - tetramethyl - 2, 5 - disilazole (Protected-Aminopropene)

Figure 1 shows a schematic of immobilization of FITC dye molecules on aminopropyl layers. The direct reaction of amino groups with H-Si results in disordered layers [12,13]. To avoid the undesirable reaction, it is necessary to deactivate the amino groups [14]. 1-(3 - Propenyl) - 2, 2, 5, 5 - tetramethyl - 2, 5 - disilazole (protected-aminopropene) **1** is anchored to silicon by the thermal reaction. The protecting group of protected-aminopropene is removed in an acidic solution. Then FITC is anchored to the aminopropyl monolayer via covalent bonds.

The schematic of the synthesis of protected-aminopropene are shown in Fig. 2. Protected-aminopropene was synthesized by the coupling of 3-amino-propene with 1,2-bis (chlorodimethylsilyl) ethane referring to the literature by Djuric *et al.* [15] (Fig. 1(b)). A solution of 1,2-bis (chlorodimethylsilyl) ethane (12.9 g, 60.1 mmol) in dichloromethane (30 ml) was added dropwise to the mixture of 3-amino-propene (6.7 ml, 89 mmol), triethylamine (16.7 ml, 120 mmol), and dichloromethane (45 ml) under argon. The solution was stirred for 2.5 h keeping the temperature below 300 K by cooling in water. Then the solution was added to a 2.7 M NaH₂PO₄ aqueous solution (500 ml) and extracted with hexane. The hexane-extract was dehydrated with Na₂SO₄ for 15 min. The product protected-aminopropene was obtained in 43 % yield (5.1 g) by distillation of the extracted solution and identified with nuclear magnetic resonance analysis (NMR). ¹H NMR (270.1 MHz, CDCl₃): (2H), 5.86-5.72 (m, 1H, [H_A]), 5.07 (ddt, *J* = 17.16, 1.65, 1.65 Hz, 1H, [H_B]), 4.93 (ddt, *J* = 9.90, 1.65, 1.65 Hz, 1H, [H_C]), 3.42 (ddd, *J* = 5.94, 1.32, 1.32 Hz, 2H, [N-CH₂]), 0.70 (s, 4 H, [Si-CH₂]), 0.03 (s, 12 H, [Si-CH₃]). ¹³C NMR (67.8 MHz, CDCl₃): 141.0, 113.4, 44.9, 8.1, -0.1.



1

Hydrogen termination of Si (111) surfaces was carried out according to the literature by Wade *et al.* [16]. The H-Si (111) substrates were transferred into a 4:6 mixture (v/v) of protected-aminopropene and mesitylene, which was deoxygenated by argon bubbling for at least 1 h prior to the reaction. The solution was then heated at 433 K for 24 hours under the continuous argon bubbling and it was cooled down to room temperature. The sample was taken out of the solution and rinsed with petroleum ether, ethanol and dichloromethane.

It is possible to remove protecting groups under acidic conditions. The removal was performed by immersing the sample for 1h in a 1:35 mixture (v/v) of acetic acid and dichloromethane at room temperature. This reaction was confirmed by ¹H NMR. Subsequently, the sample was rinsed in triethylamine to neutralize the surface.

FITC was purchased from Dojindo and used without further purification. FITC shows high reactivity with amino groups. The reaction of FITC with aminopropyl monolayer surface was performed by immersing the sample for 1h in 0.1mg/ml aqueous solution of FITC at room temperature. After reaction, the sample was sonicated thoroughly in

acetone to remove physical adsorbates.

Experimental Setup

The contact-mode AFM measurement was performed using an AFM (Jeol, JSPM-1300) under ambient conditions with Si₃N₄ cantilevers (NT-MDT, spring constant 0.6 N/m). Fluorescence spectra of FITC-aminopropyl monolayers were measured using a fluorometer (SPEX, Fluorolog-2) at an excitation wavelength of 450 nm. The fluorescence measurement was performed at room temperature in air. Aminopropyl monolayers without addition of FITC were used for references.

Sum-frequency generation (SFG) spectroscopy and X-ray photoelectron spectroscopy (XPS) were measured in the same manner as described in Chapter .

.3 Results and Discussion

AFM

Figures 3 (a) and 3 (b) show AFM images of a protected-aminopropyl monolayer surface and a FITC-aminopropyl monolayer surface, respectively. As compared with AFM images of alkyl monolayers on silicon shown in Chapter and those reported by other groups [2,17], corrugations were noticeable. It was reported steric hindrance due to shapes of protecting groups prevented the formation of closely packed monolayers [14,18]. Although corrugations were observed on terraces, steps were seen. Steps were not observed for monolayers prepared from 3-amino-1-propene without protection. It was expected that the protection of amino groups was essential for preparing ordered aminopropyl monolayers.

SFG

Figure 4 shows a SFG spectrum of protected-aminopropyl monolayers. Two vibrational peaks were observed at 2960 and 2905 cm⁻¹. The band at 2960 cm⁻¹ was assigned to the asymmetric stretch of CH₃ groups. The band at 2905 cm⁻¹ was assigned to the symmetric stretch of CH₃ groups or stretch of CH₂ bridging the two Si atoms in the protecting group. The results indicated that the protected-aminopropene molecules were anchored to silicon surfaces.

XPS

A N (1s) peak was observed around 400.5 eV in XPS spectra of a protected-aminopropyl monolayer. After the treatment of the monolayer in acetic acid

and in FITC solution, the N (1s) peak did not varied. The peak was not observed in the XPS spectrum of alkyl monolayers. XPS analysis indicated that aminopropyl molecules were anchored to the silicon and remained on the surface through a series of reactions. However, S peaks were not observed after the treatment in FITC solution. SFG spectra of protected-aminopropyl monolayers before and after the treatment in acetic acid were measured. Asymmetric CH₃ peaks derived from the protecting group were observed after the treatment in acetic acid. This result indicated that few protecting groups were removed. It was assumed that few protecting groups were removed due to the interference of the dissociative reaction on the monolayer surface by the effect of steric hindrance. Consequently, few FITC molecules could react to the monolayer surface.

Fluorescence Measurement

Figures 5 show fluorescence spectra of a FITC-aminopropyl monolayer prepared on N-type silicon with the resistivity of 1300 Ωcm (a), P-type silicon with the resistivity of 8.4-8.9 Ωcm (b), and N-type silicon with the resistivity of 1-10 Ωcm (c). The fluorescence intensity from monolayers on high conductive P-type (8.4-8.9 Ωcm) and N-type (1-10 Ωcm) silicon substrates was weaker than that from monolayers on low conductive N-type (1300 Ωcm) wafers. I examined three sets of experiments and confirmed the same tendency. The decrease in emission intensity is due to the electronic coupling or electron-transfer quenching [10]. The emission from thin tetraphenylporphyrin films on SnO₂ was also remarkably quenched when the resistivity of SnO₂ substrates was low [11]. This was caused by the relaxation of excited porphyrin molecules due to the electron transfer from molecules to SnO₂. Charge carriers in silicon substrates are thought to play an important role for the fluorescence quenching. Several studies have discussed the effect of linker chain length on electron transfer between molecules and substrates by monitoring absorption intensity, fluorescence intensity [19], photocurrent [20], *etc.* It is possible to use anchor molecules with various chain length in the Si-C system. Since the study of electron transfer process at the interface is interesting and important phenomenon for surface science, molecular science and the design of molecular-scale devices, the method presented in this chapter will be useful.

.4 Summary

In summary, aminopropyl monolayers on Si were prepared by using protecting groups. It was found that protecting groups were not removed on the surfaces perfectly,

as opposed in solution. This was probably caused by the effect of steric hindrance. It will be important to optimize the removal reaction on surfaces or to design the molecules with protecting groups, which can be removed on surfaces easily. The aminopropyl monolayer surfaces were then covered with FITC. The fluorescence of monolayers modified with FITC was measured. Fluorescence intensity depended on the dopant type and doping concentration of silicon substrates. This method will be useful to investigate electron and/or energy transfer between neighboring molecules, and molecules and substrates by controlling the distance between molecules and chain length of anchor molecules.

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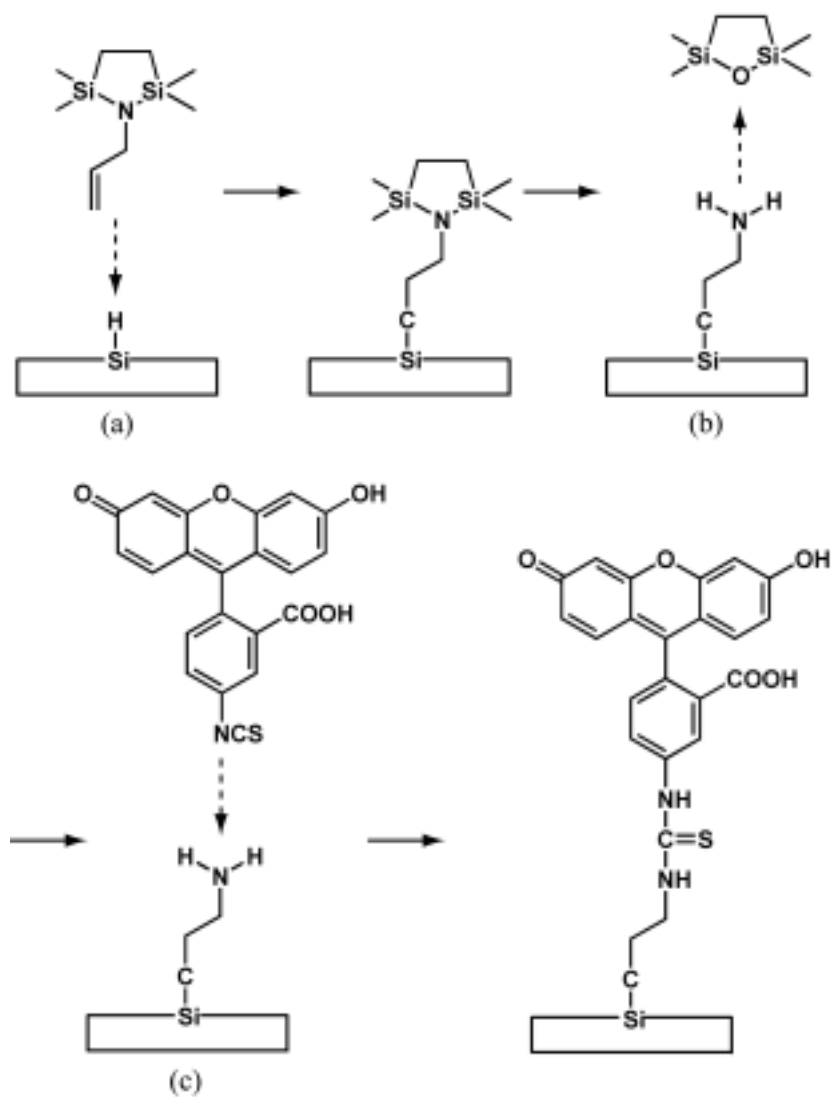


Fig. 1. Schematic view of the preparation of the FITC-aminopropene monolayer: (a) the thermal reaction between protected-aminopropene and H-Si, (b) the removal of the protecting group in an acidic solution, and (c) anchoring of FITC to the aminopropyl monolayer.

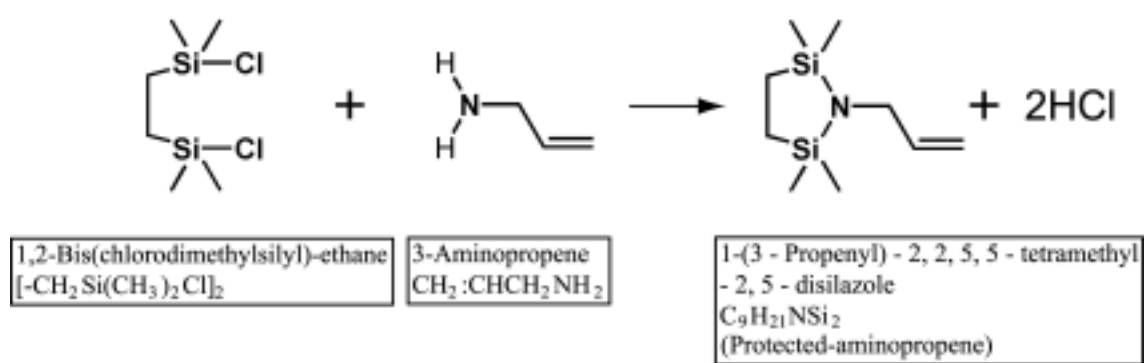
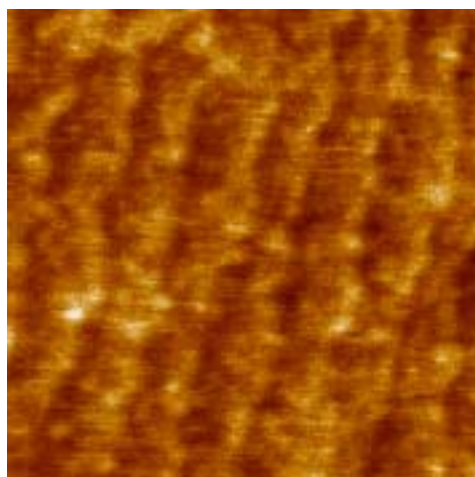
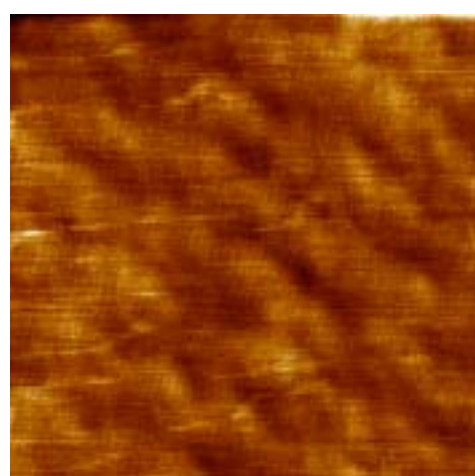


Fig. 2. Synthesis of protected-aminopropene.



(a)



(b)

Fig. 3. Topographic AFM images ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of (a) a protected-aminopropyl monolayer and (b) a FITC-aminopropyl monolayer.

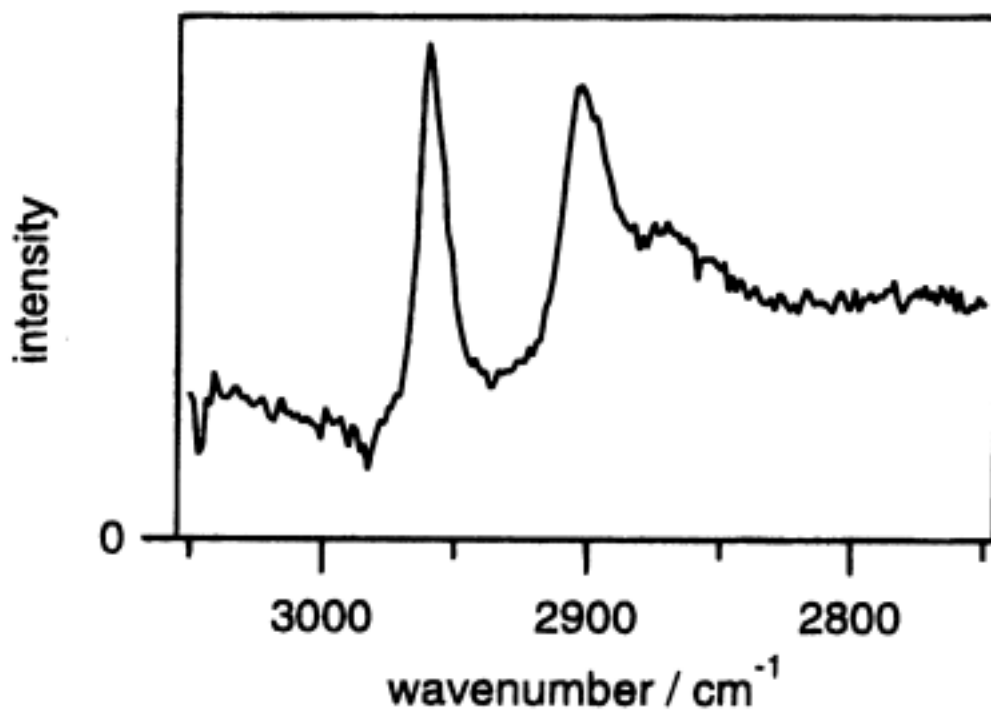


Fig. 4. SFG spectra of a protected-aminopropyl monolayer.

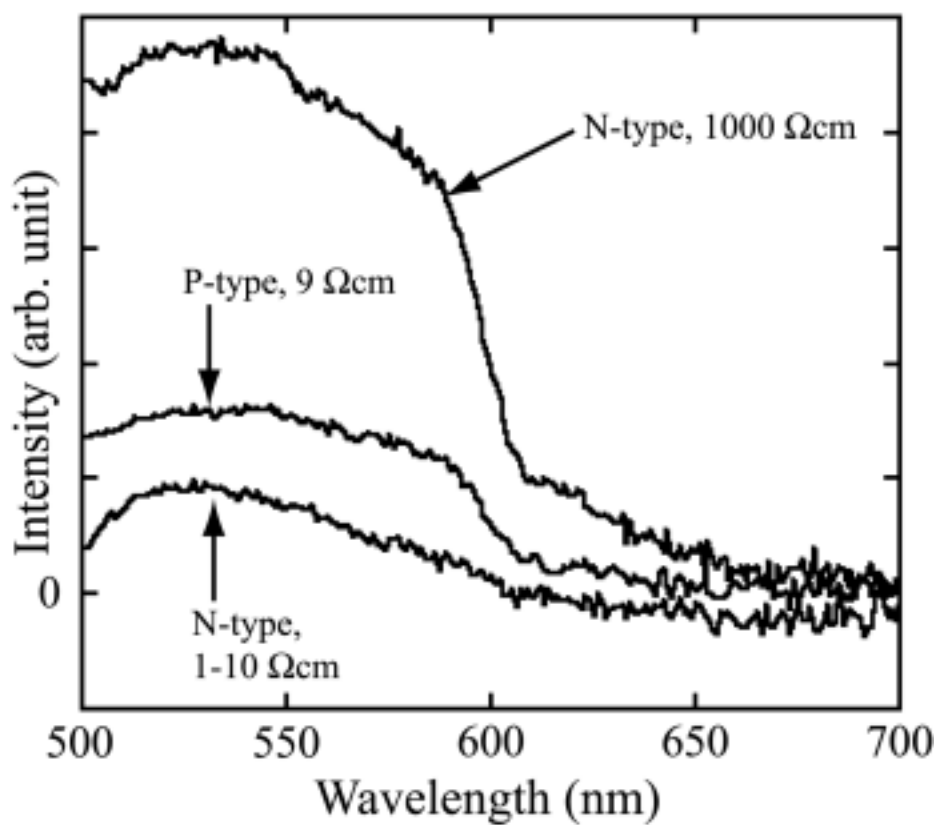


Fig. 5. Fluorescence spectra of the FITC-aminopropyl monolayers on Si; (a) 1300 Ωcm (N-type), (b) 9 Ωcm (P-type), and (c) 1-10 Ωcm (N-type).

Chapter

**Chemical Force Microscopy Using Silicon
Cantilevers Covered with Organic Monolayers
via Silicon-Carbon Covalent Bonds**

Applied Physics Letters, **83**, 578 (2003).
Nanotechnology, **15**, S65-S68 (2004).

.1 Introduction

Chemical force microscopy (CFM) has been studied extensively as a tool to distinguish various chemical species on surfaces [1-10]. Cantilevers covered with thiols (Au-thiol system) and organosilane derivatives (Si-O-C system) have been widely used for CFM since the report by Nakagawa *et al.* [2]. They discriminated the chain lengths of organic molecules on the alkyl monolayers using cantilevers covered with alkyltrichlorosilanes. Frisbie *et al.* distinguished the difference between CH₃ and COOH functional groups by friction force microscopy (FFM) with chemically modified cantilevers [3]. Chiral discrimination was also demonstrated by McKendry *et al.*[5]. These pioneering works have pointed out the difficulties in CFM as well as the usefulness.

Figures 1(a)-(c) show a comparison of cantilevers covered with molecules via Au-S bonds (a), Si-O-C bonds (b) and Si-C bonds (c). The binding at the interface between sulfur and gold in the Au-thiol system is not so strong that thiols are easily stripped away from the cantilevers during the scanning. In addition, it was reported that the underlying gold-gold interaction in the Au-thiol system contributed remarkably to the interaction between cantilevers and samples [8]. One of difficulties in preparation of cantilevers covered with organosilane derivatives is high reactivity of silane coupling reagents with moisture in air. Octadecyltrichlorosilane (OTS), which is used frequently as a typical organosilane molecule, is easily hydrolyzed in air to polymerize [11]. Hence, the preparation should be done carefully in an inert atmosphere. Moreover, gold layers and silicon oxide layers used to bind molecules blunt the apex of cantilevers in each system.

In order to overcome these difficulties, organic monolayers anchored to silicon cantilever surfaces via silicon-carbon covalent bonds are promising candidates for CFM. Organic monolayers anchored to Si via Si-C bonds can be prepared easily and are thermally and chemically stable [12]. Therefore, organic monolayers anchored to silicon surfaces via Si-C covalent bonds are utilized for coating of atomic force microscope (AFM) cantilevers. The high stability of cantilevers covered with the monolayers anchored covalently enables us to perform stable CFM measurement under various conditions.

Non-contact atomic force microscopy (NC-AFM) in ultrahigh vacuum (UHV) is a useful tool to observe the topography of clean surfaces in atomic scale without destroying the surfaces. CFM combined with NC-AFM, such as Kelvin probe force microscopy, magnetic force microscopy, and scanning dissipation microscopy, occupies

a major part in the field of scanning probe microscopy. Cantilevers covered with organic molecules anchored via Si-C bonds are expected to be a promising way for the progress of CFM.

In this chapter, I demonstrate adhesion force measurement and FFM with silicon cantilevers with organic monolayers anchored covalently. Cantilevers covered with monolayers were also applied to NC-AFM of TiO₂ (110)-(1x1) surfaces.

.2 Experimental

Preparation of Silicon Cantilevers Covered with Organic Monolayers Anchored via Si-C Covalent Bonds

Cantilevers covered with monolayers of 1-dodecene [CH₃(CH₂)₉CH=CH₂, CH] and (perfluorodecyl)ethylene [CF₃(CF₂)₉CH=CH₂, CF] were prepared through the reaction between molecules and hydrogen-terminated silicon (H-Si) cantilevers by UV irradiation. The reaction is induced by UV irradiation as described in Chapter . The schematic view of the preparation of the cantilever covered with monolayers is shown in Fig. 2. Silicon cantilevers (NT-MDT) were dipped into 8% NH₄F solution for 1 min to prepare H-Si cantilevers. The H-Si cantilevers were transferred into neat CH- or CF-liquids and irradiated UV light (Hg-Xe lamp, 200 W, Hamamatsu Photonics) for 2 h under continuous argon bubbling to form organic monolayers on cantilevers. Gold layers (50 nm) were deposited onto the backsides of cantilevers *in vacuo* because aluminum coatings originally on surfaces were damaged in the etching process. We used two types of cantilevers with different spring constant: one was a soft type (0.03 N/m) and the other was a hard one (0.6 N/m). Soft ones were suitable for adhesion force measurement and hard ones for FFM to get better contrast in the images.

Preparation of The Patterned Surfaces of Si (111) Covered with CH- and CF-Monolayers

The patterned surfaces of Si (111) covered with CH- and CF-monolayers, which are called CH-areas and CF-areas hereafter, were prepared according to the process described in Chapter . A schematic view of a patterned monolayer surface and the process are illustrated in Fig. 3 (a) and 3 (b), respectively. The organic monolayers on Si (111) were prepared by thermal reaction. Medium-doped (1-10 Ωcm) n-type Si (111) wafers were used as substrates. H-Si substrates were heated at 433 K in neat CH-liquid for 8 h under argon bubbling. Anodization of surfaces was performed using an AFM (JEOL, JSPM-1300) under ambient conditions. Platinum-coated cantilevers (NT-MDT,

spring constant 0.6 N/m) were used for anodization. The bias voltage applied to the surface was +6 V with respect to the cantilever. The scan speed was adjusted to 200 nm/s. Following the AFM anodization, silicon oxide formed was removed by HF etching. Finally, silicon was dissolved by NH_4F etching in order to form flat large surfaces. The etched areas were covered with CF molecules by thermal reaction.

Experimental Setup

Adhesion force and FFM measurements were performed using an AFM (JEOL, JSPM-1300). Adhesion force was measured *in vacuo* (5×10^{-3} Pa) in order to reduce the effect of water. FFM was observed in air and *in vacuo* (5×10^{-3} Pa) at room temperature.

NC-AFM was performed using an UHV-AFM (JEOL, JSPM-4500A) with the base pressure of 2×10^{-8} Pa. Figure 4 shows a schematic view of the NC-AFM for frequency-modulation (FM) detection. The oscillation frequency (f_0) changes to $f_0 + \Delta f$ when the force between the apex of the cantilever and the sample surface changes as shown Fig. 5. The FM technique was used to detect the frequency shift of the oscillating cantilever due to force interaction. NC-AFM was operated by keeping the constant frequency shift constant. The TiO_2 (110)-(1x1) surface (Earth Chemicals Co., Ltd, Japan) was prepared by repeated argon ion sputtering (IG35, OCI) at room temperature and annealing at 900 K. LEED optics (SPECS, ErLEED 3000D) were used to obtain the diffraction pattern of the TiO_2 (110)-(1x1) surface. The surface was observed with a NC-AFM in a constant frequency shift mode. Cantilevers with a spring constant of 14 N/m and resonant frequency of 315 kHz were covered with dodecyl monolayers and used for NC-AFM. Scanning electron microscopy (SEM, JEOL, JSM-6700F) was used to observe the surface of cantilevers.

.3 Results and Discussion

SEM

Figures 6 (a) and 6 (b) show SEM images of the silicon cantilevers uncovered and covered with a dodecyl monolayer, respectively. The sharpness of the cantilever remained unchanged while surface structure of the cantilever was changed by chemical treatment, presumably by NH_4F etching.

Adhesion Force Measurement

Topographic images of a patterned surface were measured using a contact-mode

AFM with CH- and CF-cantilevers. There were not so drastic differences between topographic images measured with CH- and CF-cantilevers. The height of patterned areas was lower than that of surrounding areas and the height difference was about 30 nm. The large height difference was caused by the process of NH_4F etching.

Figures 7 (a) and 7 (b) show the scatter plots of adhesion force obtained by measurement of force-displacement curves with a CH- and CF-cantilever, respectively. Adhesion force on CF-areas was larger than those on CH-areas measured with all covered cantilevers used. Furthermore, the difference in adhesion force between CH-areas and CF-areas measured with a CF-cantilever was larger than that measured with a CH-cantilever. This indicates that cantilevers are covered with molecules and that the chemical species on the cantilever surfaces affect adhesion force.

FFM

Figures 8 (a)-(d) show FFM images (a and b) and the friction profiles (c and d) of the patterned dodecyl monolayer surface on Si(111) measured in air with hard CH- and CF-cantilevers. Solid curves are profiles measured in air and dashed ones are *in vacuo*. In both figures, dashed curves almost traced the solid curves. Little difference in friction force between in air and *in vacuo* could be detected. While a little contrast was observed between CH- and CF-areas with a CH-cantilever, the friction profile taken with a CF-cantilever showed clearer contrast. The results of FFM were consistent with those of the adhesion force measurement. It was reported that CF-areas show larger friction than CH-areas by FFM with Si_3N_4 cantilevers [1,6] and OH terminated cantilevers [9]. However, the origin of the enlargement of friction force on CF-areas is still not completely clear. Van der Waals force is thought to play an important role for adhesion and friction force. Polarizabilities of fluorocarbon molecules are larger than those of hydrocarbon molecules, e.g., 4.93 for ethane and 7.59 for hexafluoroethane (in units of $10^{-40} \text{ Cm}^2/\text{V}$) [13]. Ionization potentials of fluorocarbon molecules are also larger than those of hydrocarbon molecules. Consequently, these factors enlarged of van der Waals forces between CF-molecules, which resulted in large adhesion and friction force measured on CF-areas, especially with CF-cantilevers.

NC-AFM

Figure 9 shows a LEED pattern of the TiO_2 (110) surface after cleaning treatment. The clear spots with (1x1) rectangular lattices in the reciprocal space were observed.

Figure 10 (a) shows the NC-AFM image of TiO_2 (110)-(1x1) observed using the cantilever covered with the dodecyl monolayer. Many particles were seen on the surface.

Residual 1-dodecene molecules physisorbed to the cantilever are thought to move from the cantilever surface to the TiO₂ surface during observation. No particles were observed on the surface when the cantilever was annealed at 423 K for 15 h prior to observation [Fig. 10 (b)]. Since the covalent Si-C bonds are thermally stable up to 615 K [14], monolayers do not decompose in this annealing process.

Figures 11 (a), (b), and (c) show NC-AFM images of TiO₂ (110)-(1x1) using the covered cantilever at sample bias voltages of 0 V, 1.0 V, and 2.0 V, respectively. The image observed at 0V was unclear. Clear images of atomically flat terraces were obtained at the sample bias voltage around 2.0 V. In contrast, clear images were obtained at 0.9 V for original silicon cantilevers without organic monolayers. The surface potential of cantilevers is thought to be modified due to the coating with monolayers. This demonstrates the possibility that the surface potential can be controlled by using various organic molecules. Many groups have measured the contact potential difference by frequency shift vs. bias voltage curves [15], Kelvin probe force microscopy [16], *etc.* Cantilevers covered with monolayers are applicable to such kind of measurement to study the effect of chemical species on the cantilever surface onto the surface potential in detail.

Figure 12 shows a surface structure of TiO₂ (110)-(1x1) and Fig. 13 shows a high-resolution image of the surface with the sample bias voltage of 2.0 V. It is known that oxygen rows are protrusive over the surface as shown in Fig 11. It is reported titanium rows are imaged as bright lines by scanning tunneling microscopy (STM) with positive sample bias voltages [17]. In contrast, titanium and oxygen rows are imaged as dark and bright lines, respectively, with NC-AFM [18]. These results demonstrate clearly the difference in imaging mechanisms: STM detects surface electronic state and NC-AFM shows physical topography. Almost the same image as that reported in the previous paper [18] was observed in the present study using chemically modified cantilevers. The cantilevers with various organic materials make it possible to study the interaction between tip and surface in NC-AFM measurement.

.4 Summary

In this chapter, cantilevers covered with organic monolayers anchored via Si-C bonds were prepared by an UV induced reaction and used for adhesion force measurement and FFM. CH- and CF- areas patterned by the method described in Chapter were distinguished by adhesion force measurement and FFM. The adhesion force and friction force on CF-areas were larger than those on CH-areas, especially using CF-cantilevers.

Large polarizabilities of CF-molecules comparing to CH-molecules were found to enhance the contrast in adhesion and friction images.

Cantilevers covered with organic monolayers were also used for NC-AFM of TiO_2 (110)-(1x1) surfaces. Annealing treatment of cantilevers was found to improve images. The difference in surface potential between cantilevers uncovered and covered was observed. Clear images of atomic rows on atomically flat terraces were observed with the dodecyl-coated cantilevers when the samples were biased around 2.0 V with respect to the cantilevers. This is the first application of the cantilevers covered with molecules to NC-AFM. The cantilevers covered with organic monolayers via covalent bonds are useful for chemical force microscopy with contact and non-contact mode atomic force microscopy in various conditions since the interface between molecules and cantilevers is thermally and chemically stable.

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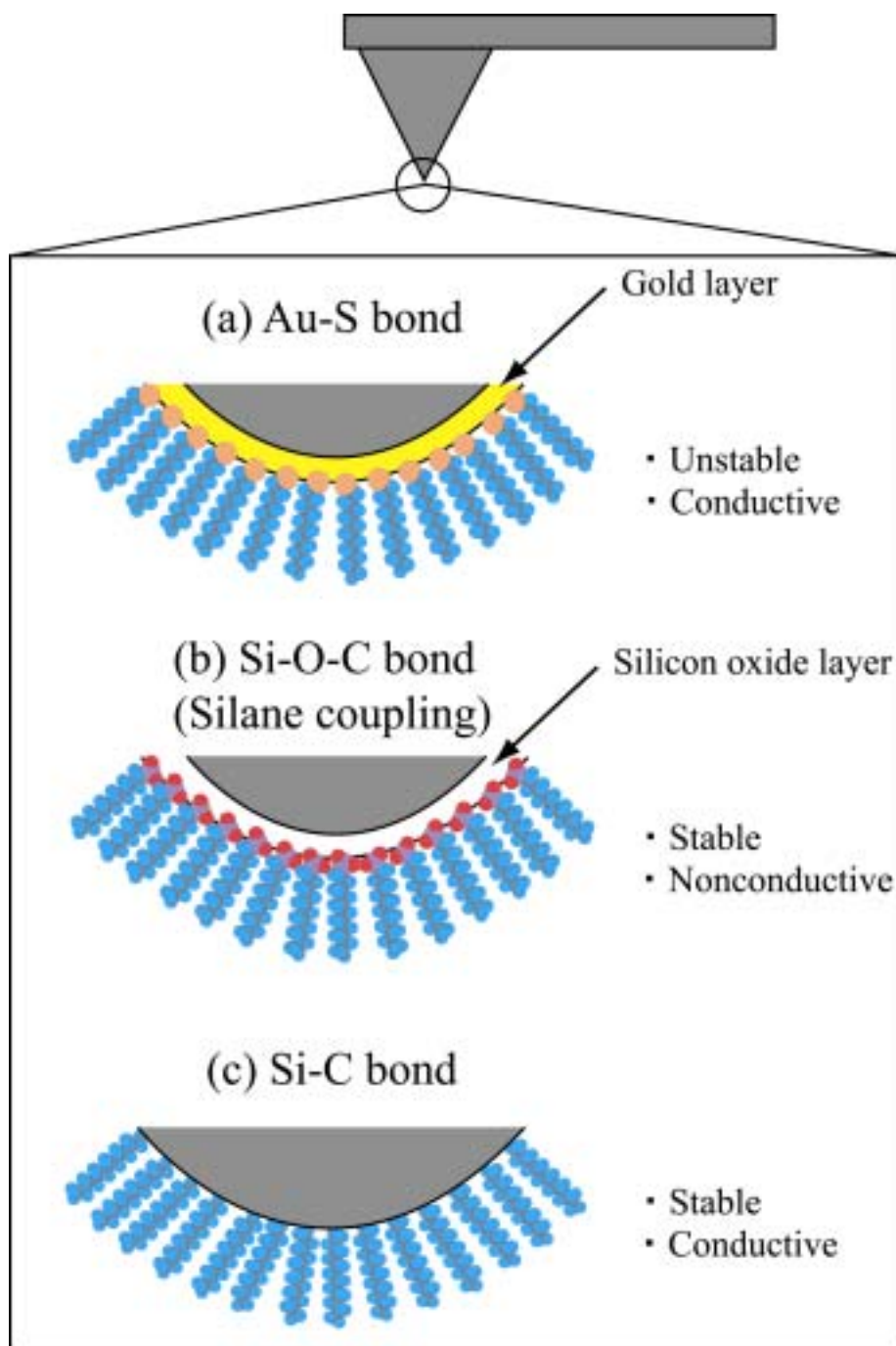
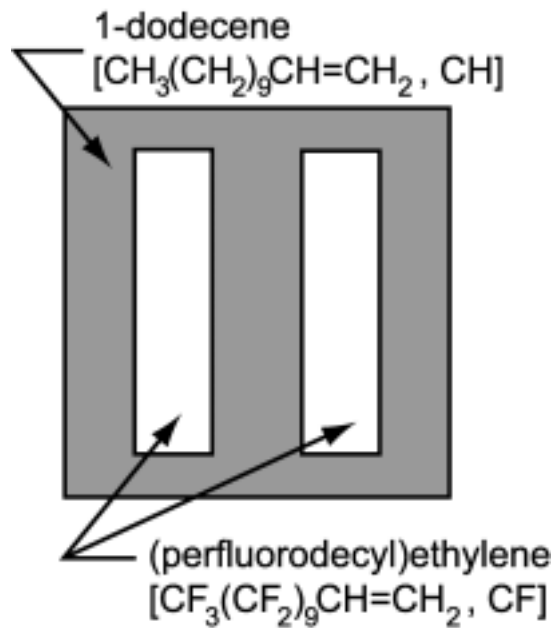
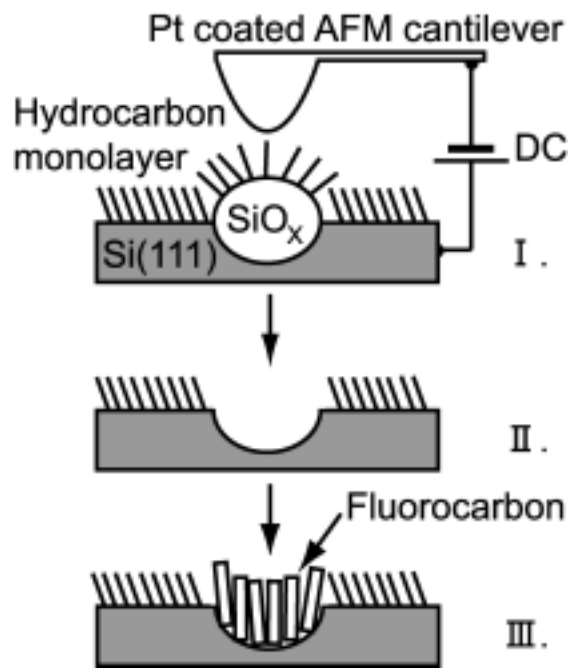


Fig. 1. Comparison between the cantilevers covered with molecules via Au-S bond (a), Si-O-C bond (b) and Si-C bond (c).



(a)



(b)

Fig. 3. Schematic view of a specimen (a) and the chemical modification process (b) : AFM anodization (), etching with HF (5%, 1 min) and NH₄F (8%, 10 min) to remove the silicon oxide and terminate the grooves with hydrogen atoms (), and covering the etched area with (perfluorodecyl)ethylene molecules ().

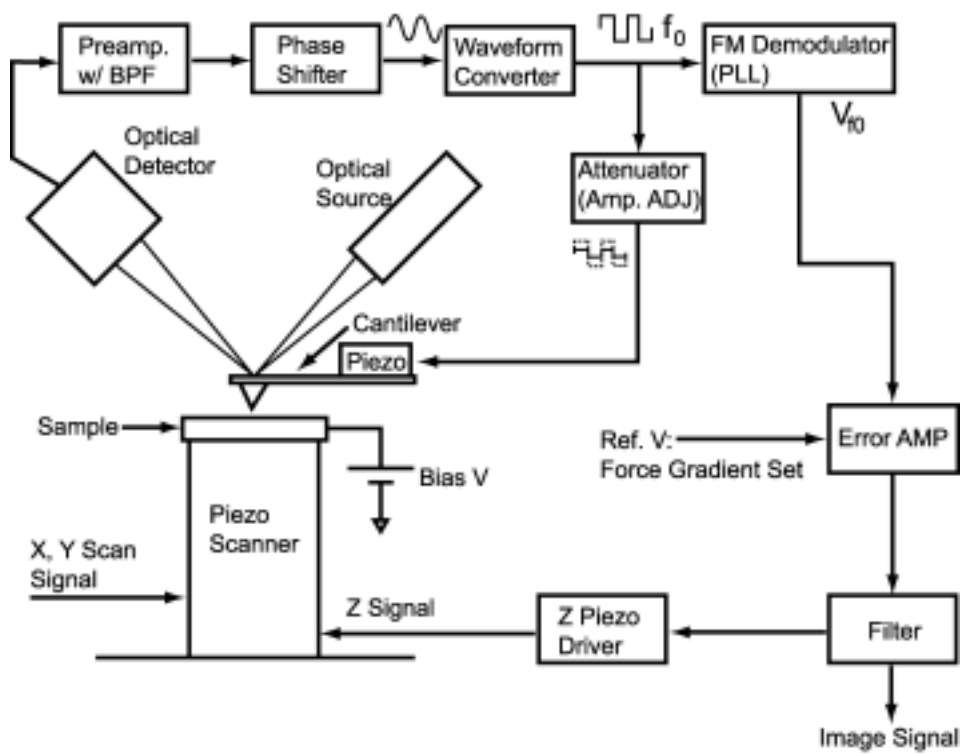


Fig. 4. Schematic view of NC- AFM using the FM detection method.

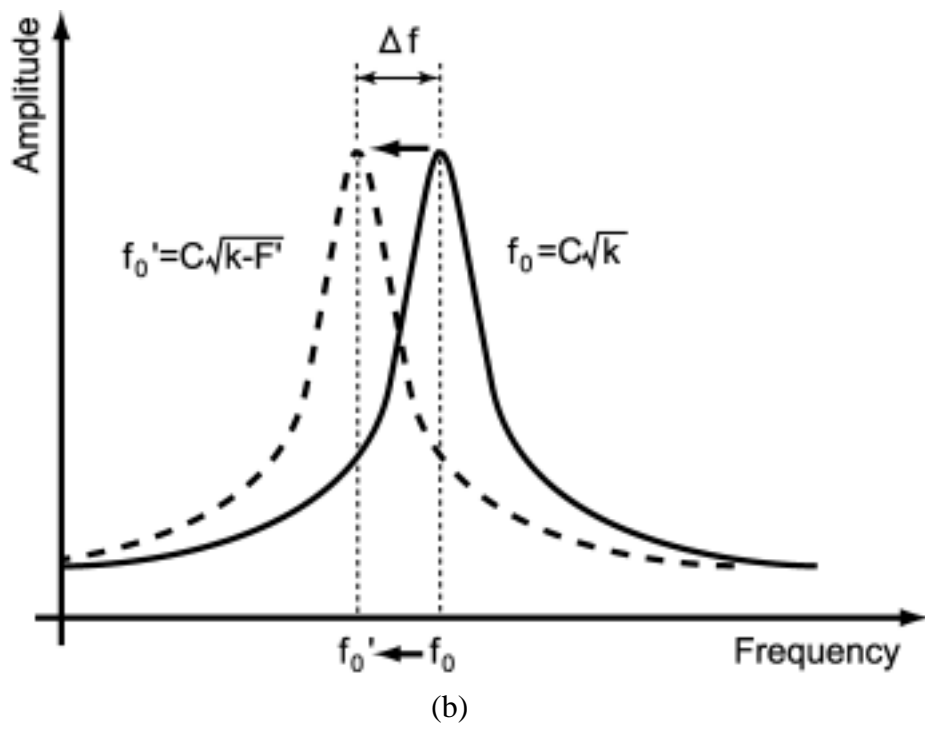
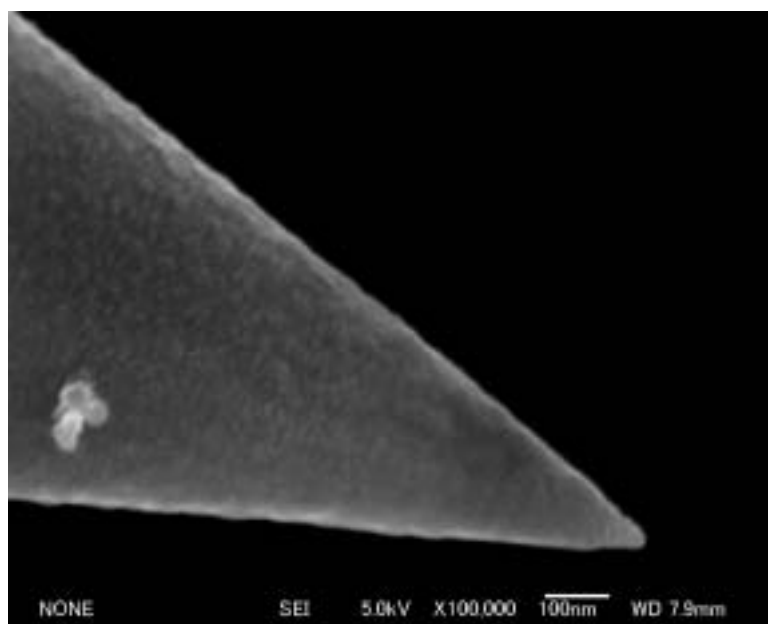
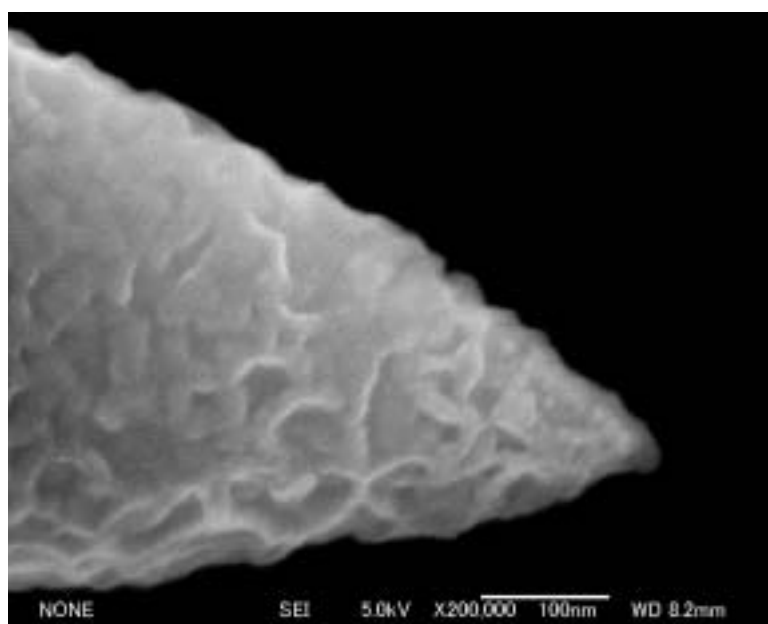


Fig. 5. Frequency response curve of the cantilever.

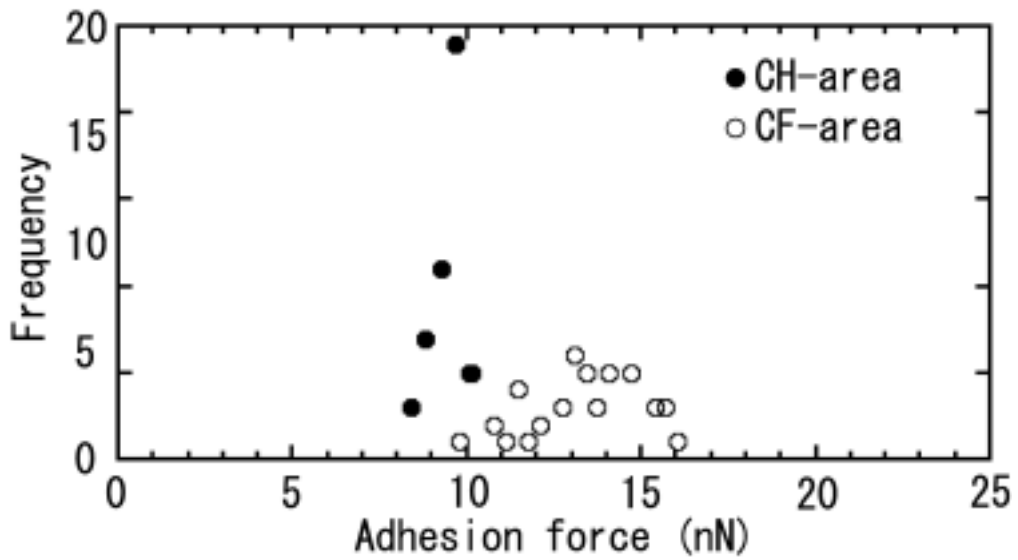


(a)

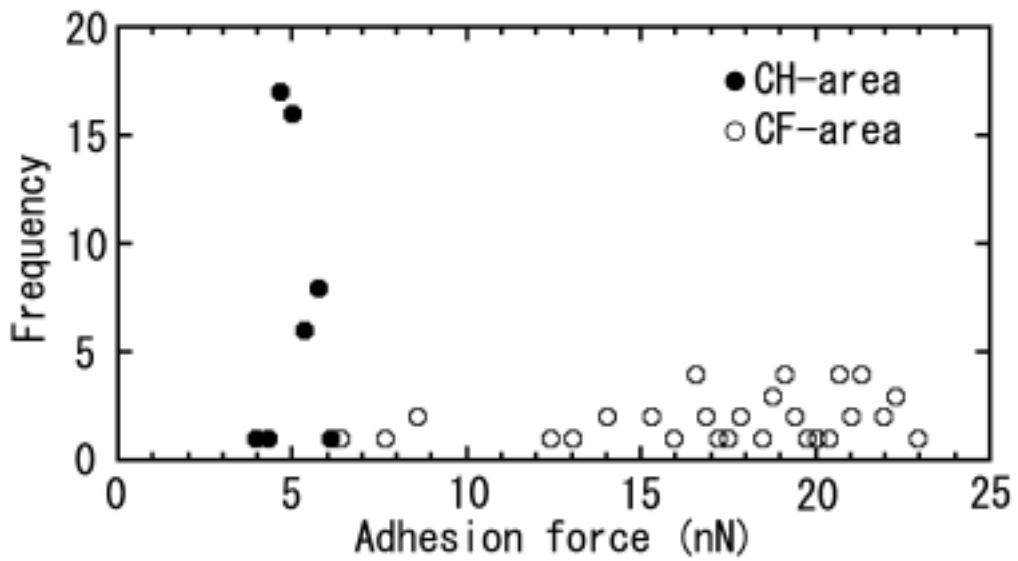


(b)

Fig. 6. SEM images of a silicon cantilever uncovered (a), and a cantilever covered with a dodecyl monolayer (b).



(a)



(b)

Fig. 7. Scatter plots of adhesion force based on force-displacement curves on CH- and CF-areas *in vacuo* with a soft CH- (a) and CF-cantilever (b). Spring constants of both cantilevers were 0.03 N/m.

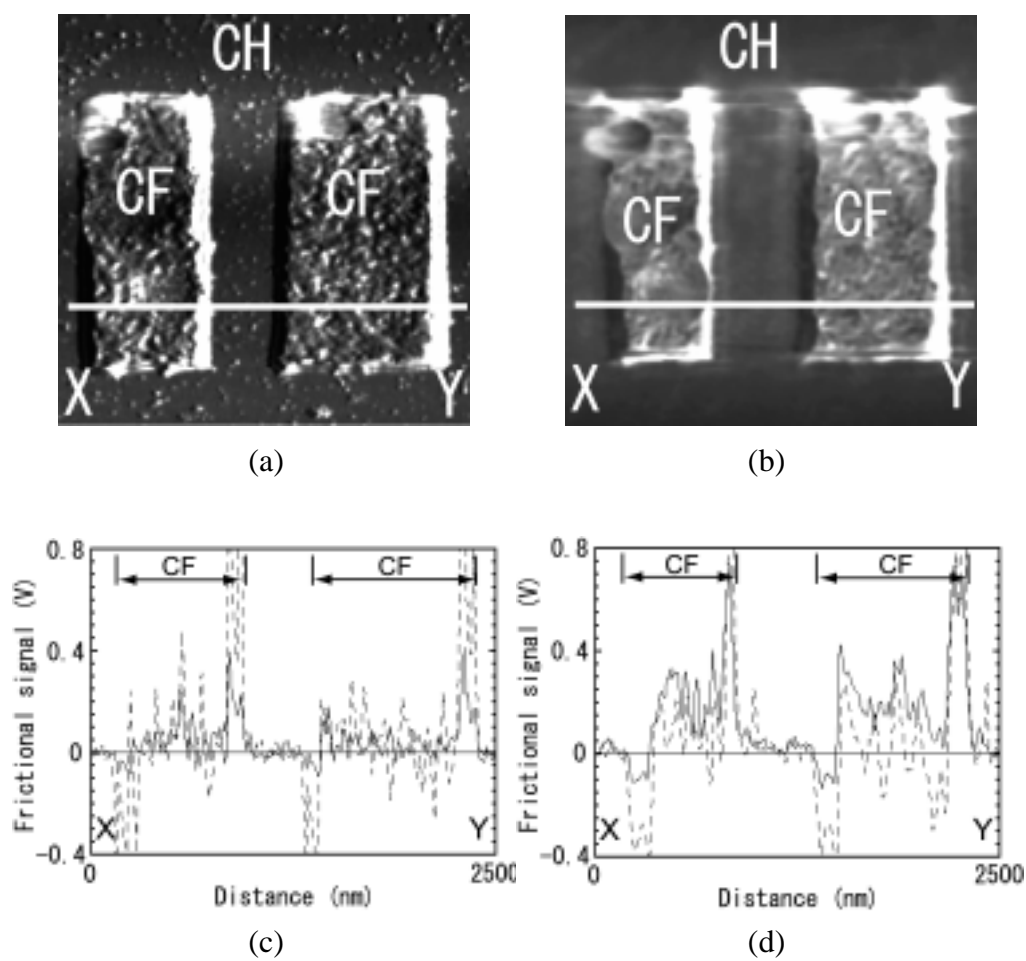


Fig. 8. FFM images (a and b) ($2.5 \mu\text{m} \times 2.5 \mu\text{m}$) and the friction profiles (c and d) of the patterned surface on Si (111) with a CH-cantilever and a CF-cantilever. Spring constants of both cantilevers were 0.6 N/m . Typical loads applied were 30 nN . Solid curves and dashed curves were the profiles measured in air and *in vacuo*, respectively.

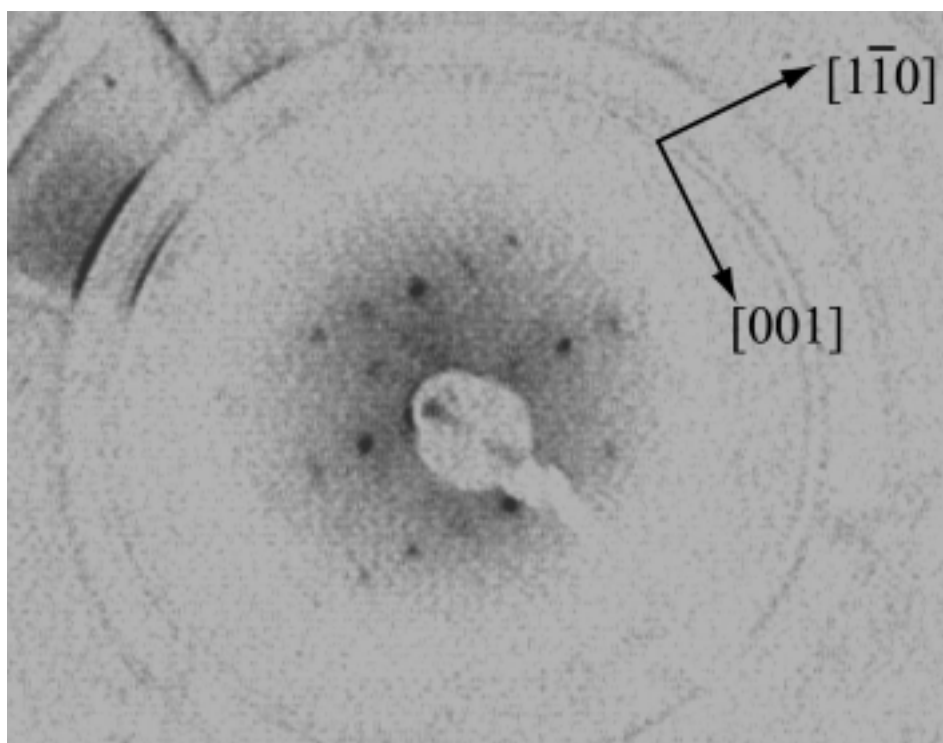
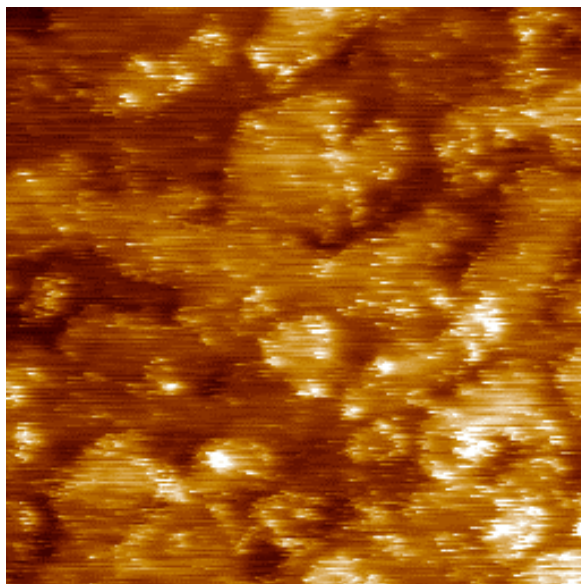
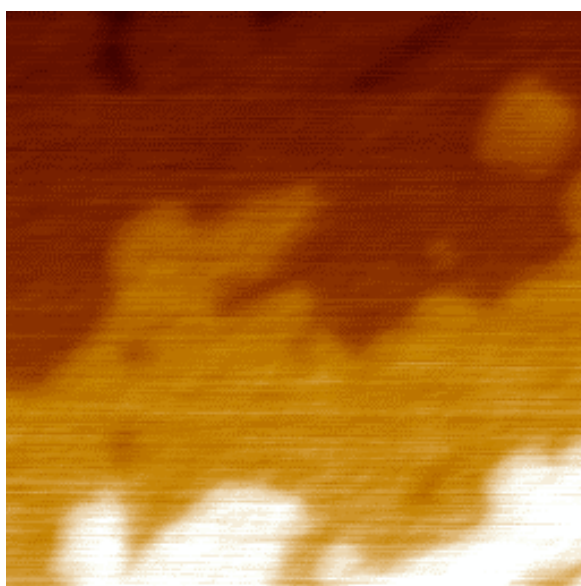


Fig. 9. LEED pattern of the $\text{TiO}_2(110)-(1 \times 1)$ surface observed with a primary electron energy of 100 eV. The arrows shown are for the crystals in real space (see Fig. 12).

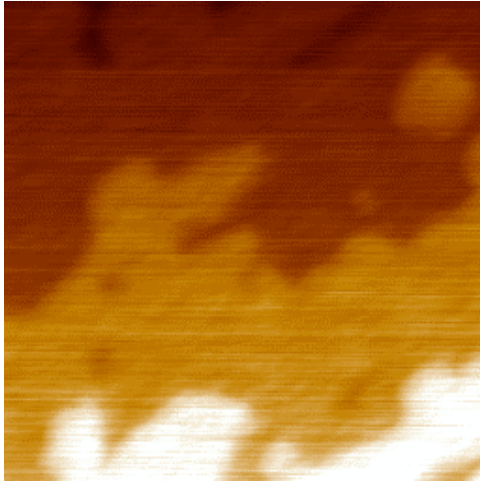


(a)

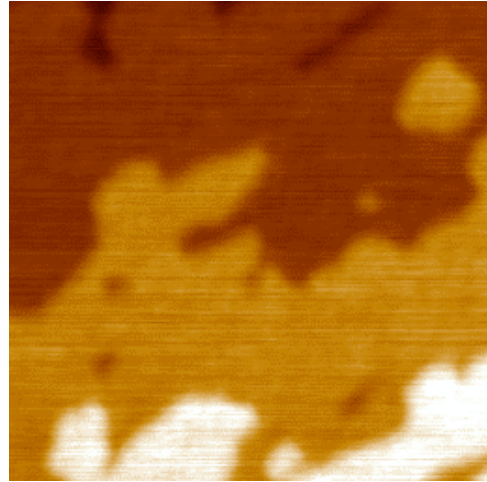


(b)

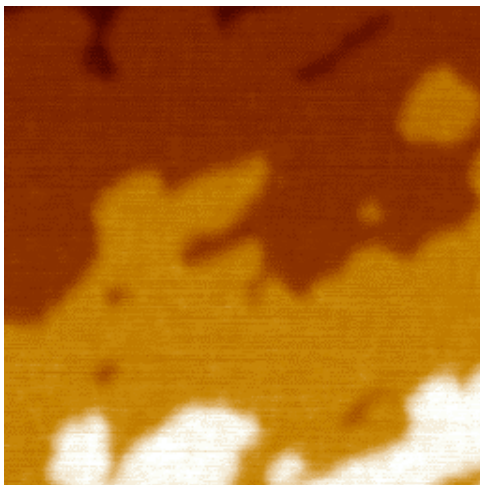
Fig. 10. NC-AFM images (300 nm x 300 nm) of TiO_2 (110)-(1x1) using the cantilever covered with dodecyl monolayers prepared as is (a) and after annealing treatment at 423K for 15h (b). The Sample bias voltage was set at 0 V.



(a)



(b)



(c)

Fig. 11. NC-AFM images of TiO₂ (110)-(1x1) using the covered cantilever at sample bias voltages of 0 V (a), 1 V (b), and 2 V (c). Frequency shift was set at -16 Hz.

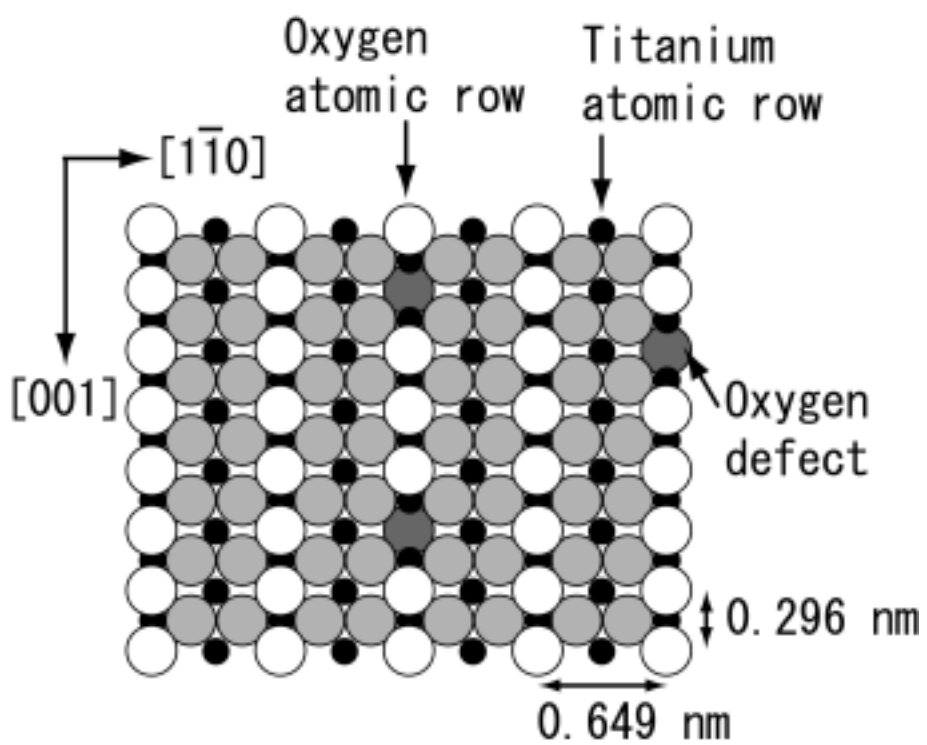


Fig. 12. Model of the TiO_2 (110)-(1x1) surface.

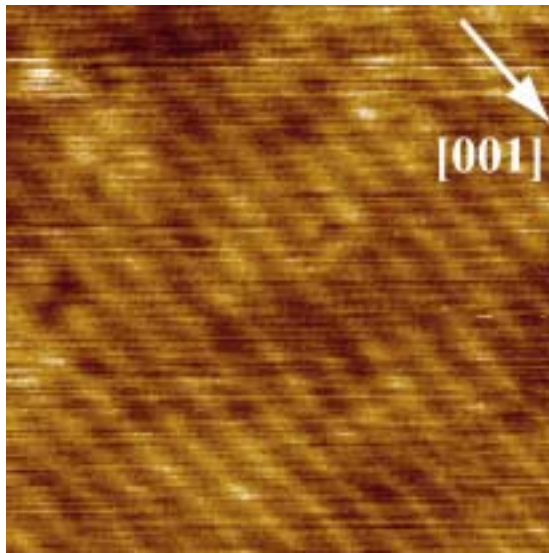


Fig. 13. High-resolution NC-AFM image of the TiO₂ (110)-(1x1) surface (10x10 nm). Frequency shift and sample bias voltage were set at -186 Hz and 2V, respectively.

Chapter

Conclusion

In this work, I prepared organic monolayers anchored covalently to Si(111) by wet process, and characterized morphology, conformation, stability, and surface properties using AFM, IR and contact angle measurement (Chapter). I also demonstrated the possibility of 2-dimensional patterning in nanometer scale (Chapter) and 3-dimensional molecular assemblies (Chapter). In addition, I proposed novel method to prepare chemically modified cantilevers for force microscopy (Chapter). The results are summarized as follows:

1. AFM images of alkyl monolayers on Si(111) exhibited flat and etch-pit free terraces with monoatomic steps, indicating the formation of highly ordered densely packed films. It was found that surface properties such as wettability were able to be modified by immobilizing functional molecules. SFG spectroscopy revealed that an alkyl chain in the film consisted of an all-trans head part with a twisted stem. It was found that the films became solid-like with increasing reaction temperature. The films were thermally stable up to 440K in vacuum but irreversible conformational disorder in the chain was introduced by heating the film above 440K. The monolayers were also chemically stable. The exchange reaction did not occur at ordinal reaction condition and the films exhibited high resistivity against NH_4F .
2. Local oxidation of dodecyl monolayers anchored to Si (111) was performed with a contact-mode AFM by applying positive bias voltage to the surface with respect to a conducting cantilever in air. The minimum width of the lines oxidized was 40 nm in the present work. Oxidized areas were selectively removed by etching with NH_4F . The grooves formed by the etching were modified by different alkyl molecules. These modifications of alkyl monolayers will become of greatly useful for the nanofabrication of organic/inorganic interfaces based on Si-C covalent bond.
3. It is essential to use anchor molecules for construct three dimensional molecular assemblies. I have synthesized 1 - (3 - propenyl) - 2, 2, 5, 5 - tetramethyl - 2, 5 - disilazole (protected aminopropene) and examined the films growth. Fluorescein - 4 - isothiocyanate (FITC) molecules were then immobilized to monolayers. The fluorescence intensity was found to depend on the dopant concentration of silicon substrates. Although further studies to optimize growth conditions are required, the method proposed in this study will become of useful for three dimensional molecular assemblies in nanometer scale.

4. Cantilevers covered with organic monolayers anchored via Si-C bonds were prepared by an UV induced reaction and used for chemical force microscopy. Hydrocarbon (CH) and fluorocarbon (CF) areas were distinguished by adhesion force measurement and friction force microscopy.

Cantilevers covered with organic monolayers were also used for non-contact atomic force microscopy (NC-AFM) of TiO_2 (110)-(1x1) surfaces. Clear images of atomic rows on atomically flat terraces were observed with the dodecyl-coated cantilevers. The cantilevers covered with organic monolayers via covalent bonds are useful for CFM with contact and non-contact mode AFM in various conditions since the interface between molecules and cantilevers is thermally and chemically stable.

The Si-C systems have recently received much attention and become of importance as a useful method to prepare functional surfaces. I hope that my works facilitate the progress of this research field.

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Original Papers:

1. Masato Ara, Harald Graaf and Hirokazu Tada,
Nanopatterning of Alkyl Monolayers Covalently Bound to Si(111) with an Atomic Force Microscope,
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(2003.06.13) シリコン製被加工物への微細パターンの形成方法。

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4. Hirokazu Tada, Masato Ara and Shoji Tanaka,
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