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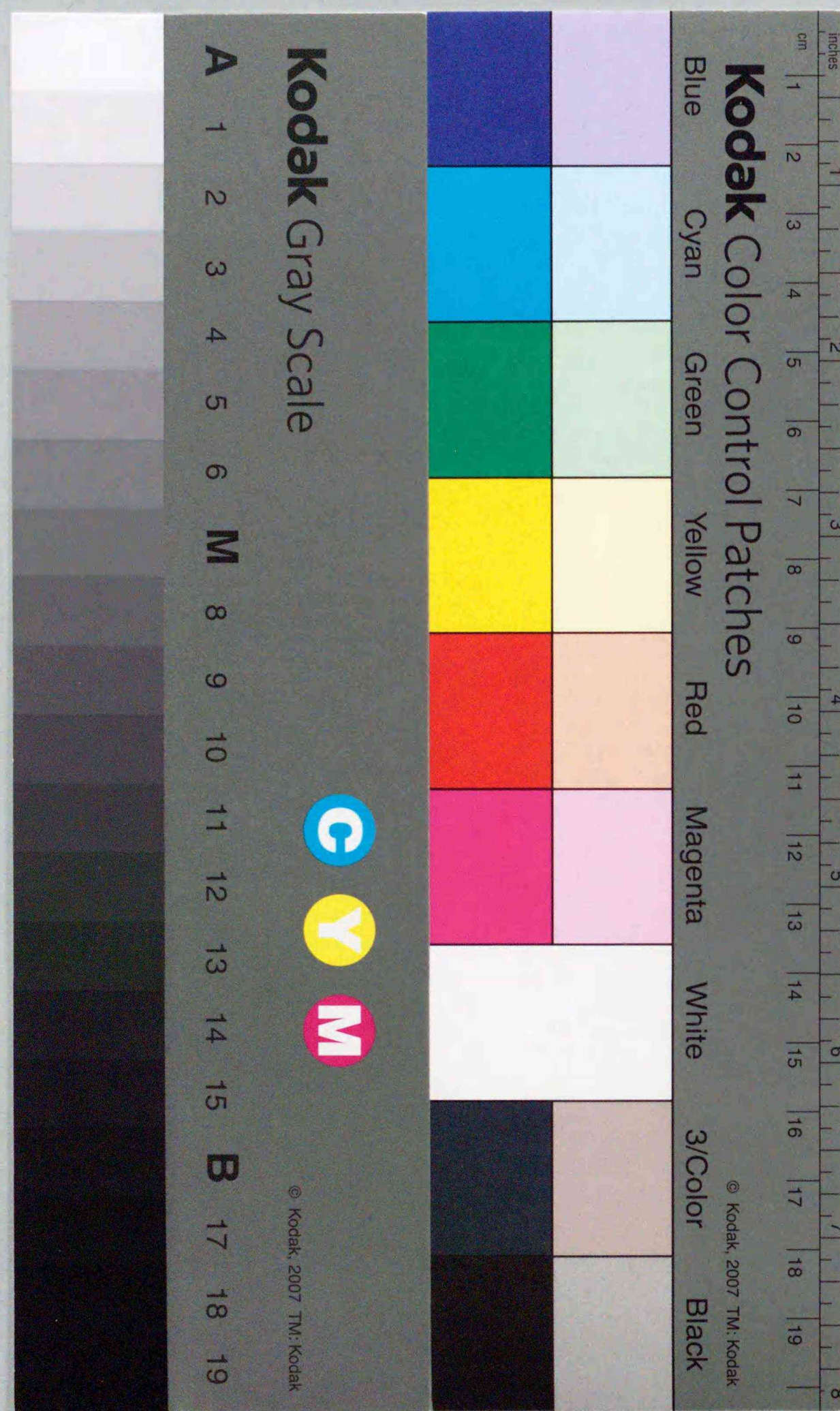
Studies on Two-Dimensionally Ordered Organic Molecular
Layers by Scanning Probe Microscopy

(走査プローブ顕微鏡による二次元規則配列をもつ
有機単分子層に関する研究)

Ryo Yamada

Physical Chemistry Laboratory
Division of Chemistry
Graduate School of Science
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Sapporo

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Chapter 1

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Introduction

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Introduction

1-1 General Introduction

Solid/liquid interfaces play important roles in many phenomena such as corrosion, lubrication, heterogeneous catalysis and electrochemical reactions. It is essential to investigate the structure of the solid/liquid interface at the molecular level to understand the nature of these phenomena as the property of the solid/liquid interface is dominated by the property of the region in several nm thick at the interface. However, the understanding of the solid/liquid interface on an atomic/molecular level is much less advanced than that of the solid surface in UHV due to a lack of experimental techniques and the difficulty of the theoretical analysis.

The development of the ultrahigh vacuum (UHV) system in the 1970s enabled the experimental study of clean surfaces.¹ Many surface analytical methods, including low energy electron diffraction (LEED), reflection high energy electron diffraction (RHEED), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and scanning electron microscopy (SEM) were subsequently developed. In contrast to the significant progress in the surface science of UHV, the understanding of the solid/liquid interface, i.e., the surface science in solution, was at a standstill since the analytical method based on an electron beam, which led to progress in the surface science under UHV conditions, can not be applied to the solid/liquid interface due to the presence of the solution. In addition, many scientists engaged in UHV work did not focus on the solid/liquid interface as it was considered to be a complicated and dirty system.

Although the structure of the solid/liquid interface has been one of the most important issues in electrochemistry for a long time, most of the studies involve the mercury electrode since it was difficult until recently to obtain and maintain a clean solid surface in solution. Along with the development of the surface analytical tool in UHV, the electrode

subjected to the electrochemical reactions was often transferred to and analyzed in UHV system. This ex-situ analysis provided a novel knowledge and understanding of the solid/liquid interface, i.e., the surface science in solution, progressed.

The desire of electrochemists for *in situ* analysis of the solid/liquid interface was realized by the development of spectroscopic methods² such as reflectance measurement, Raman^{2a} and infrared spectroscopy.^{2b} The application of the scanning tunneling microscopy (STM) to the solid/liquid interface opened a new stage of study of the solid/liquid interface.³ The STM enabled *in situ* structural observation of the solid surface in solution with a resolution of several Å. In addition, Clavilier *et al.* developed a simple method to prepare a single crystal electrode.⁴ As a result, the electrochemistry on the single crystal electrode is widely studied by STM. The recent development of synchrotron orbital radiation light and LASER system enables one to use a surface sensitive X-ray method,^{2d,2g} e.g., surface X-ray scattering and X-ray standing waves measurement, and non-linear optical methods,⁵ respectively, in solution. Nowadays, it is well established that a clean and ordered surface is obtained in solution and it is possible to discuss and control the structure of the solid/liquid interface on molecular and atomic level.⁶ The solid/liquid interface is now considered as a new field which has quality comparable to the UHV system.

The modification of the solid surface is an important process from a technological point of view. Recently, the creation of a well-defined material phase on a well-defined surface is available in the UHV system by methods such as vapor deposition and molecular beam epitaxy.⁷ The solid/liquid interface is also used as a stage for the construction of ordered material phases.^{6b} The well-ordered phase is obtained at a lower cost and under milder conditions than those in the UHV system by electrochemical deposition since the electrochemical deposition requires fairly simple instruments. Nowadays, the strategy of using an organic thin layer to functionalize the surface is of great interest.⁸ It is important to construct a well-ordered and highly-oriented molecular layer on the surface for this purpose. While the Langmuir-Brodgett method has been used for the construction of the

monolayer, the new method called the self-assembly method has been developed.^{8,9} The molecules used in this method consist of two functional groups which are connected by long alkyl-chain. One of the functional groups possesses a strong attractive interaction with the substrate and act as an anchor for the molecule, and the other functional group possesses the desired functionality to be attached on the surface. When the substrate is immersed in the solution containing the molecules, the ordered and highly-oriented monolayer is spontaneously formed on the surface. The monolayer formed by this method is called the self-assembled monolayer (SAM) and many studies on the practical applications of the SAM have been carried out.⁹

The solid/liquid interface is also useful for the observation of the molecular shape by STM. After the imaging of the liquid crystal molecules adsorbed on graphite with STM, the graphite surface in an organic solvent is used as a stage for molecular imaging.¹⁰ This system is also useful for the study of low dimensional physics. Recently, some groups have succeeded in imaging the internal atomic structure of a molecule, and the direct determination of the molecular structure with STM is becoming possible.

As mentioned above, the study of the solid/liquid interface has shown rapid progress over the past 20 years. However, the structure of the interface between an organic solution and metal surface, which should play important roles in heterogeneous catalytic reaction and lubrication, has not been investigated. The objective of this thesis is to investigate it with molecular resolution. In the following sections, the principle of STM, results of the STM investigation of organic molecules at the solid/liquid interface and the structure of the gold surfaces are briefly reviewed. Finally, the objectives of the present work are stated.

1-2 Principle of Scanning Tunneling Microscopy

Scanning tunneling microscopy (STM) was invented by Binnig *et al.* in 1980s.¹¹ When the metallic tip and the conductive substrate are only separated by a few Å with a bias voltage, a tunneling current flows between them. Surface morphology is obtained by

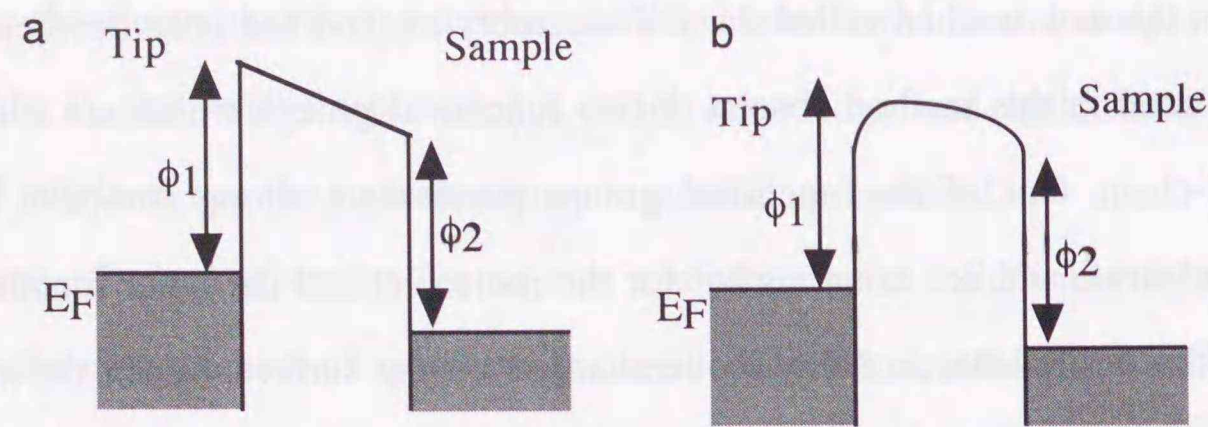


Figure 1-1. Energy diagram of tunneling junction between tip and sample (a) without and (b) with image potential.

scanning the tip in x-y direction while correcting the vertical position of the tip in order to keep the tunneling current constant (constant current mode).

The tunneling between the tip and the metallic sample is approximated to the model of one-dimensional tunneling through the potential barrier.¹² The two metal electrodes (tip and sample) are modeled as well for the electron, and the vacuum is a potential barrier as shown in Fig. 1-1a (actually, the edge of the potential is curved due to the image potential as shown in Fig. 1-1b¹³). The following equation for the current density of the tunneling current is deduced from this model.¹⁴

$$J_T = 2\pi e^2 \cdot \frac{k_0}{4\pi d} \cdot V \cdot \exp(-2k_0 d) \quad (1)$$

where d is the effective tunneling distance, V is the applied bias voltage and k_0 is the inverse decay length of the wave function which is described by

$$k_0 = \frac{2\pi\sqrt{2m\phi}}{h} \quad (2)$$

where ϕ is the effective barrier height, $\phi = (\phi_1 + \phi_2) / 2$ (ϕ_1 and ϕ_2 are the work functions of the tip and the sample respectively).

The relation of the electronic structure of the surface and STM image is deduced by the Tersoff-Hamann theory where the electronic structure of the tip is modeled by an s wave.^{13,15} The result is

$$J_T \propto V \rho_s(0, E_F) \exp(-1.025\sqrt{\phi} d) \quad (3)$$

where $\rho(0, E_F)$ is the local density of state (LDOS) at the surface around the Fermi level. Following this equation, the STM image reflects the surface electronic structure. The tunneling current exponentially varies with d and the decay constant is related to the work function of the substrate.

The T-H theory do not consider the electronic structure of the tip. A more detailed analysis is carried out based on the perturbation theory. According to the modified Bardeen's method,^{13,16} the tunneling current is

$$I = \frac{4\pi e}{\hbar} \int_0^{eV} \rho_s(E_F - eV + \varepsilon) \rho_t(E_F + \varepsilon) |M|^2 d\varepsilon \quad (4)$$

where $\rho_s(x)$ and $\rho_t(x)$ are the LDOS of the surface and the tip, respectively. The term M is called the tunneling matrix element defined by

$$M = \frac{\hbar}{2m} \int_{z=z_0} \left(\chi^* \frac{\partial \psi}{\partial z} - \psi^* \frac{\partial \chi}{\partial z} \right) dS \quad (5)$$

where ψ and χ represent the wave function of the surface and the tip. If M does not change within the range of interest, the tunneling current is determined by the convolution of the LDOS of the surface and the tip.

The shape of the tip has a serious effect on the actual STM imaging. When two sharp points on the tip contribute to the tunneling current, a ghost will appear on the STM image, which is called the double tip effect.⁶ In addition, the different shape of the tip leading to a different wave function of the tip causes a different image for the same sample. The theoretical calculation considering the shape of the tip has been carried out by Tukada *et al.*¹⁷

The mixing of the molecular orbital with the surface wave function, the resonant and

the inelastic tunneling play roles in tunneling through an adsorbed layer.^{18,19} The resonant tunneling is an enhancement of the tunneling probability due to the energy level located between the energy gap formed by the Fermi level of the tip and the sample, i.e., the gap formed by the bias voltage. The energy of the electron before and after tunneling is kept constant (Fig. 1-2a) in this process.

The inelastic tunneling is a tunneling in which the energy of the electron is not kept constant before and after the tunneling process (Fig. 1-2b). In the case of the adlayer of molecules, the lowest unoccupied molecular orbital (LUMO) or the highest occupied molecular orbital (HOMO) is expected to have an effect on the tunneling process. If the molecules are weakly adsorbed (physisorption), the wave function of the surface is not affected by the molecular orbital. In this case, the molecular orbitals are located between the tunneling gap (Fig. 1-3). Although the location of the HOMO and LUMO relative to the tip and the sample is not apparent, the vacuum level of the molecule is assumed be the same as that of the sample.¹⁹ When the molecular orbital is within the energy gap formed by the bias voltage, the tunneling process is influenced by resonant tunneling and the molecular orbital concerning this process is expected to be imaged as higher regions. When the molecular orbital is far from the energy level defined by the bias voltage, the resonant effect is not expected. The molecule, however, has a chance to be imaged if it sticks out from the surface as it acts like an antenna for the tunneling current.^{19,20,21} The tunneling current from the molecules due to the very weak interaction between the energy of molecule and the surface can overcome the one which directly flows from the

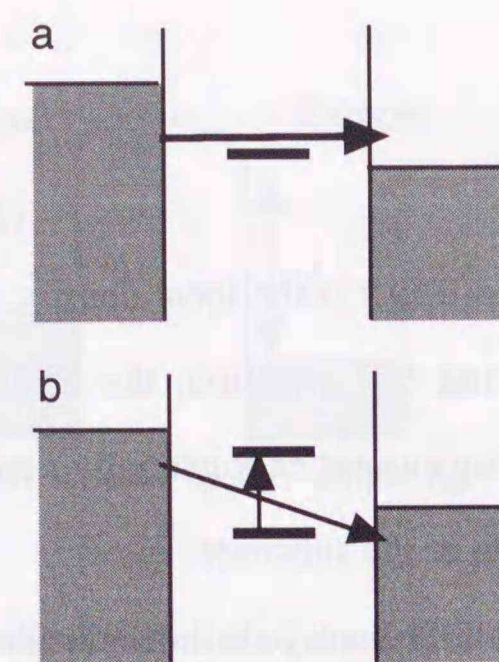


Figure 1-2. Schematic diagram for (a) resonant and (b) inelastic tunneling.

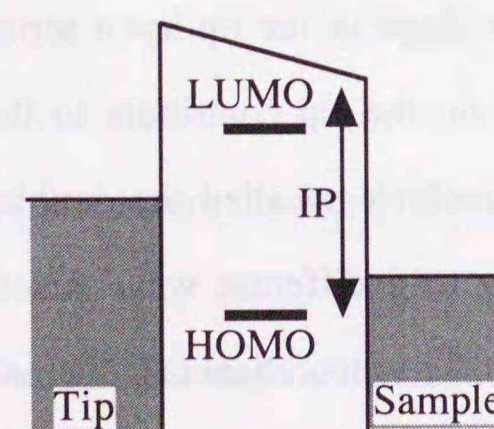


Figure 1-3. Energy diagram of tunneling junction with weakly adsorbed molecule.

surface as the tunneling current is significantly dependent on the distance. The role of the solvent in the tunneling process at the liquid/solid interface has not been studied well, although the solvent is expected to play an important role in it.

1-3 Formation of Physisorbed Two-dimensional Ordered Organic Molecular Layers at the Solid/Liquid Interface

1-3-1 Preparation

Although the Langmuir-Brodget method, which uses the liquid/air interface to make the ordered single molecular layer, is the most popular way to form a physisorbed ordered organic molecular layer, we restrict the subject to the ordered organic molecular layer formed at the solid/liquid interface. Graphite is the most popular substrate for the formation of an organic molecular layer. When the graphite is immersed in a dilute solution of the molecule, an ordered molecular 2D layer is spontaneously formed. In many cases, the solvent is phenyloctane and the molecule contains long alkyl chains, which may produce the appropriate van der Waals interaction with the graphite and between the molecules to form ordered phases. There are also some reports that succeeded in forming the organic molecular layer at the electrolyte/metal interface. In the following sections, a brief review of the results of STM investigations of physisorbed ordered organic molecular layers at the solid/liquid interface is given.

1-3-2 Structure of Two-dimensional Ordered Organic Molecular Layers in Organic Solvent

a. Liquid Crystal

The STM imaging of the liquid crystal (4'-n-alkyl-4-cyanobiphenyl : nCB) on graphite with molecular resolution was first reported by Foster *et al.* and Smith *et al.*²²⁻²⁵ The substrate was heated to a temperature at which a smetic phase is formed in the bulk phase. The STM measurement was carried out after the substrate was cooled to room temperature. Figures 1-4a and b show an STM image of 8CB and the corresponding

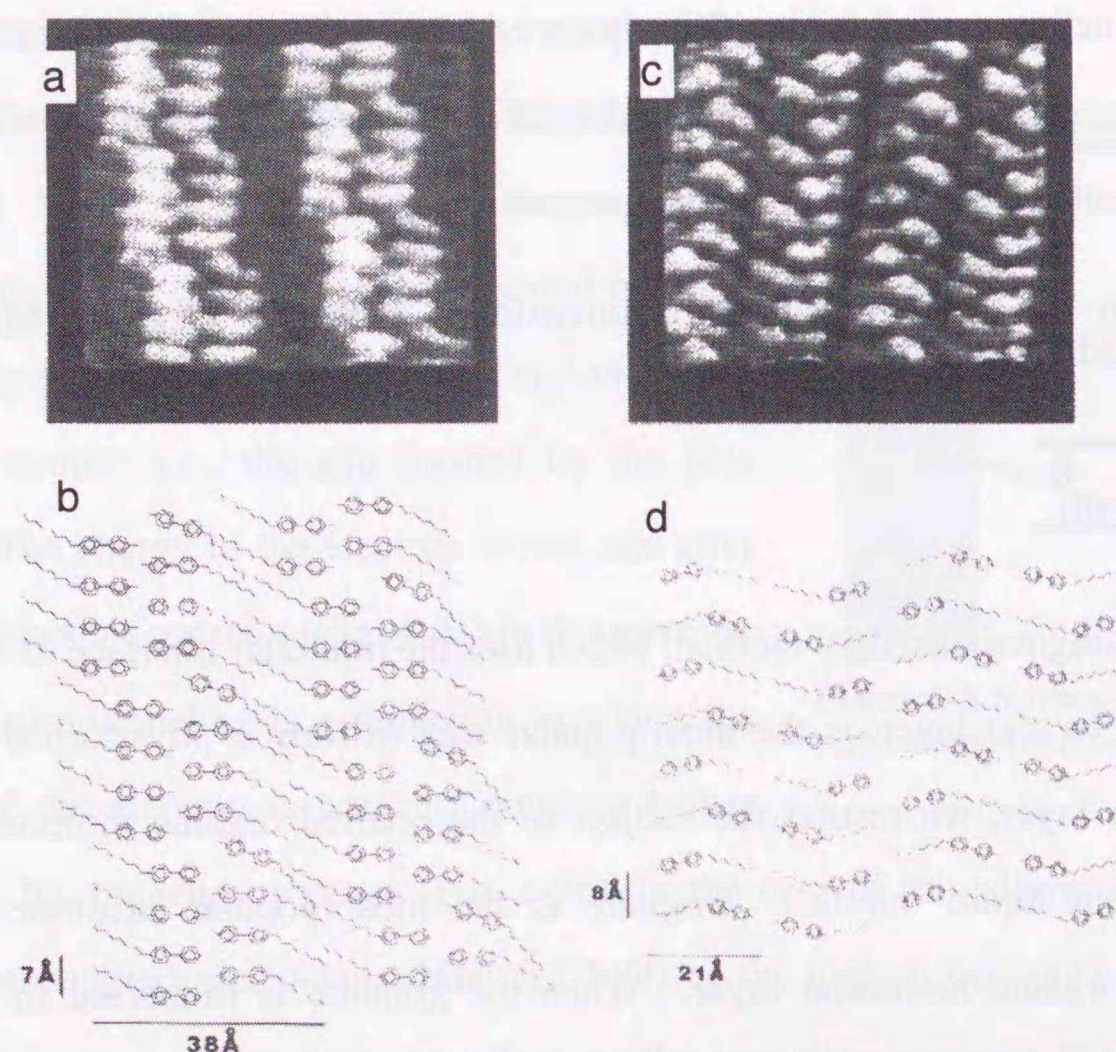


Figure 1-4. (a) STM image of graphite covered with 8CB and (b) the model. (c) STM image of MoS₂ surface covered with 8CB and (d) the models.²⁶

model, respectively. The brighter region of the image was assigned to the aromatic group of the molecules. The similarity in the molecular orbital and STM image was pointed out and, therefore, the molecular orbital is expected to affect the tunneling process. All the molecules are in a head-to-head arrangement, i.e., the aromatic groups of the molecules face each other and one molecular row is formed by a pair of the molecules. Hara *et al.* reported that the different molecular arrangement of 8CB was formed on MoS₂ (Fig. 1-4c, d).²⁶ In this case, molecular arrangement is commensurate with the substrate, and the aromatic groups of the molecules are alternately arranged. The molecular row is formed by a single molecule. The formation of the different molecular arrangement is explained by considering the structure of the substrates and registry of the molecule. The registry of the alkylchain on the graphite is restricted to the center of the benzene ring of graphite, resulting in the 3 fold rotational freedom while that on MoS₂ is both in an atomic row direction and the direction tilted by 30° from the atomic row of the MoS₂. The 6 fold rotational freedom in the orientation of the alkyl chain enables the formation of the

commensurate lattice. The strong interaction between the molecule and substrate may also be one of the origins of the commensurate lattice formation on MoS₂. This study showed that the structure of the substrate has a significant influence on the structure of the adlayer.

In contrast to the above studies, Stabel *et al.* showed that a subtle difference in a big head group leads to a different two-dimensional (2D) crystalline structure on graphite.²⁷ They observed the 2D crystal of the alkylated anthrone derivatives, 2-hexadecyl-anthrone (Fig. 1-5, 1), 2-hexadecyl-diazoanthrone (Fig. 1-5, 2) and 2-hexadecyl-anthraquinone (Fig. 1-5, 3) in phenyloctane on graphite. The STM image of the 2D crystal of hexadecylanthrone (1) and the model is shown in Figs. 1-6a and b, respectively. The brighter regions should correspond to the aromatic group in the molecules as was the case for the 8CB imaging. The alkyl chains of the molecules are aligned along the main axis of the graphite and molecules are in a head-to-tail arrangement, i.e., the aromatic groups are positioned at the end of the alkyl chain of neighboring molecules. The direction of the molecular row is rotated by 15° with respect to the graphite's main axis. The STM image showed a Moiré pattern, indicating that the molecular arrangement is incommensurate with the graphite lattice. A detailed analysis of the structure revealed that the plane formed by the aromatic group is not parallel to the surface plane, but slightly, within 20°, tilted. This configuration allows the molecules to form a close-packed structure with the alkyl chains in the extended all-trans configuration. The structure of the 2D crystal of hexadecyldiazoanthrone (2) is

strikingly different from the one of hexadecylanthrone (1) as shown in Fig. 1-6c. In this case, the molecules are in a head-to-head arrangement, i.e., the aromatic groups face one of the neighboring molecules and the direction of the molecules in a molecular row are

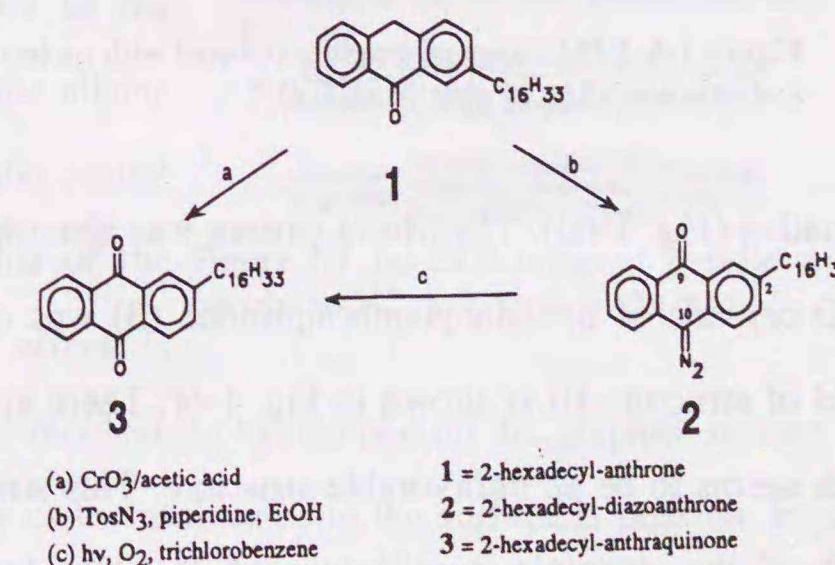


Figure 1-5. Structure and synthetic scheme for alkylated anthrone derivatives.²⁷

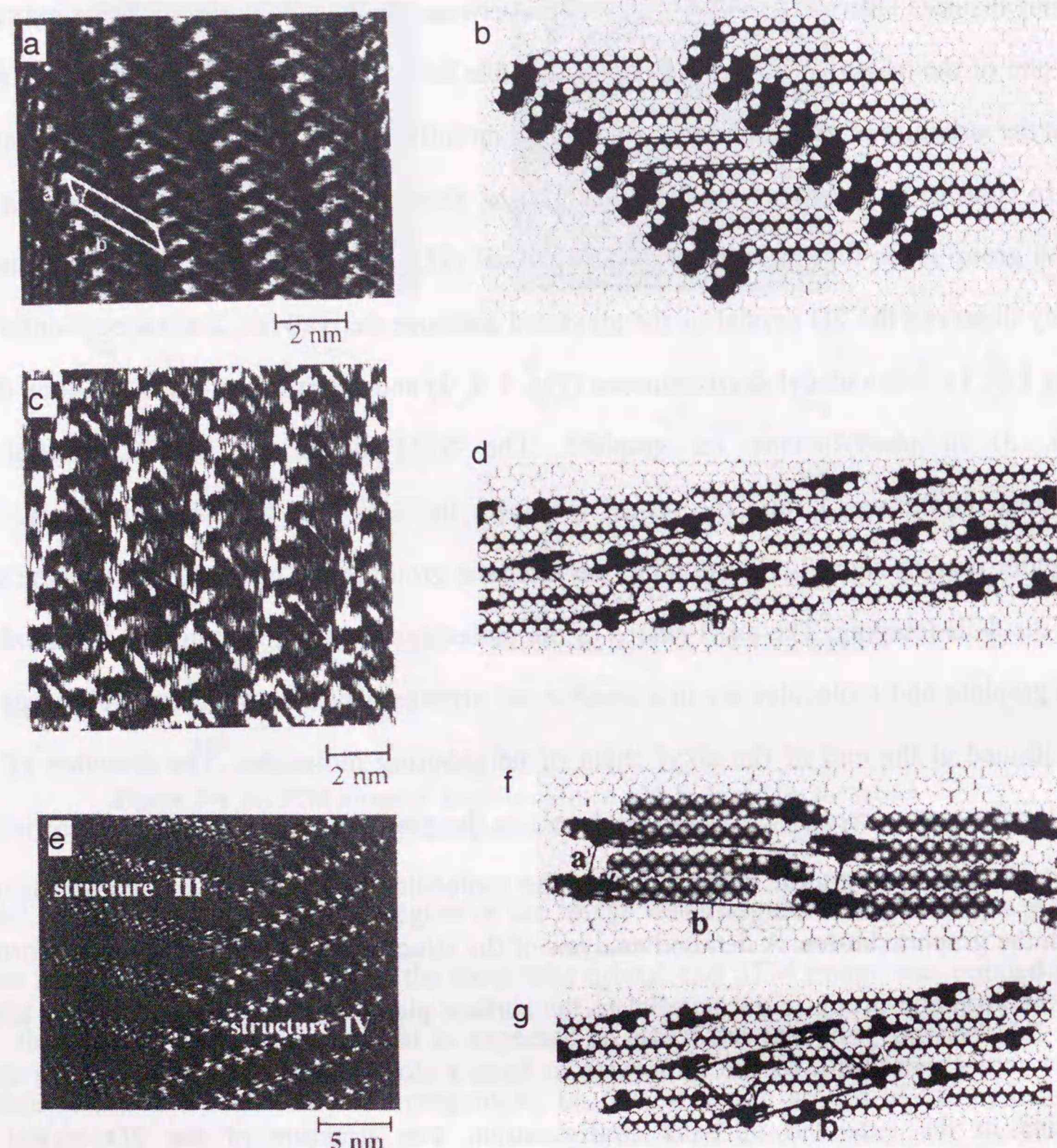


Figure 1-6. STM image of graphite covered with molecule (a)1, (c)2 and (d)3 of Fig. 1-2 and corresponding models (b, d, f, g).²⁷

alternative (Fig. 1-6d). The Moiré pattern was also observed. The coexistence of two kinds of 2D crystals of hexadecylanthraquinone (3) was observed as shown in Fig. 1-6e. The model of structure III is shown in Fig. 1-6f. There are free volume between the molecules which seems to be an unfavorable structure. This structure is believed to be observed as a result of the dynamic equilibrium of the two forms. The one structure consists of molecules with aromatic groups perpendicular to the surface plane and the other is parallel. Structure IV (Fig. 1-6g) is identical to the structure observed in the 2D crystal of

hexadecyldiazoanthrone (2). The stability of the structure is dependent on the solvent. Structure III is stable in hexadecane while structure II is stable in diphenylether. The above results are interesting as they showed that the subtle difference in the molecular structure affects the structure of the 2D crystal and solvent. Furthermore, it plays a role in determining the structure of the 2D crystal.

b. Alkanes

Although the imaging of alkanes with STM was considered to be difficult since alkanes are insulators, it is actually possible. For example, alkyl chain of the liquid crystals are observed as seen above. McGonigal *et al.* reported the structure of the 2D crystal of n-alkanes ($C_{32}H_{66}$) in iso-octane and n-decane on graphite (Fig. 1-7a).²⁸ The STM image clearly showed that the rods are arranged in rows and these rods were assigned to be n- $C_{32}H_{66}$. The molecular axis is perpendicular to the molecular row. The STM image also shows the *apparent* atomic structure, i.e., small spots are overlapped in the rod structure. These spots do not correspond to the atomic structure of $C_{32}H_{66}$ but correspond to the lattice of the graphite surface. This result indicates that the electronic structure of the graphite surface is imaged through the alkane 2D crystal and, therefore, the molecular orbital

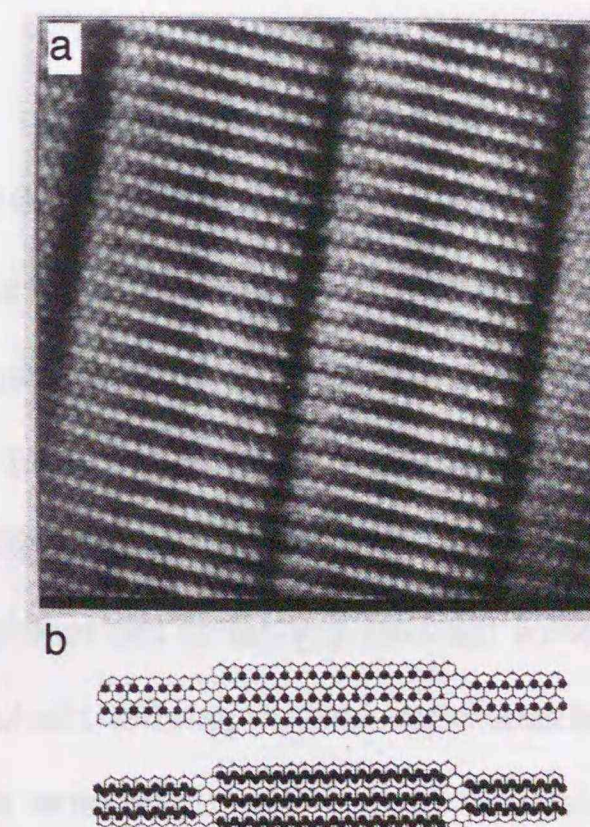


Figure 1-7. (a) STM image of graphite surface covered with $C_{32}H_{66}$ and (b) the model.²⁸

of the alkanes is not mixed with that of the graphite surface. This seethrough effect is reported in the STM imaging of other molecules physisorbed on the graphite surface. The accurate determination of the registry of the molecules to the surface is possible by using this effect and it is clear that alkanes are commensurate with the graphite lattice and the molecular axes are parallel to the main axis of the graphite lattice as shown in Fig. 1-7b.

There are, however, some reports which describe that the alkanes formed an incommensurate lattice on the graphite.²⁹

The observation of the real internal atomic structure of alkanes was reported by Claypool *et al.*²⁹ They observed the $C_{35}H_{72}$ adlayer in phenyloctane on graphite with high gap impedance (bias voltage was 1.2 V and tunneling current was 650 pA). The STM image shown in Figure 1-8. STM image of graphite covered with $C_{35}H_{72}$, showing the position of hydrogens.²⁹ Fig. 1-8 shows 35 bright spots, which closely correspond to the positions of the 35 upward-facing hydrogen atoms in the alkane chains, in each alkane rod.

Watel *et al.* reported the formation of the second layer of alkanes in saturated decane solution of $C_{36}H_{74}$ on graphite (Fig. 1-9).³⁰ The center region of Fig. 1-6a is assigned to the first layer of $C_{36}H_{74}$ surrounded by a second layer of $C_{36}H_{74}$. The molecular row of the second layer is rotated by 60° with respect to the one of the first layer (Fig. 1-9b). It is apparent that the first layer of alkanes is not a precursor of the bulk crystal as the bulk crystal of the alkanes consists of parallel stacking of the molecular layers. The formation of the rotated second layer is explained as follows. Although the parallel overlayer should be favorable when considering the total adsorption energy, the highest adsorption energy for a single molecule is achieved when the molecule adsorbs on the molecular row with a rotation of

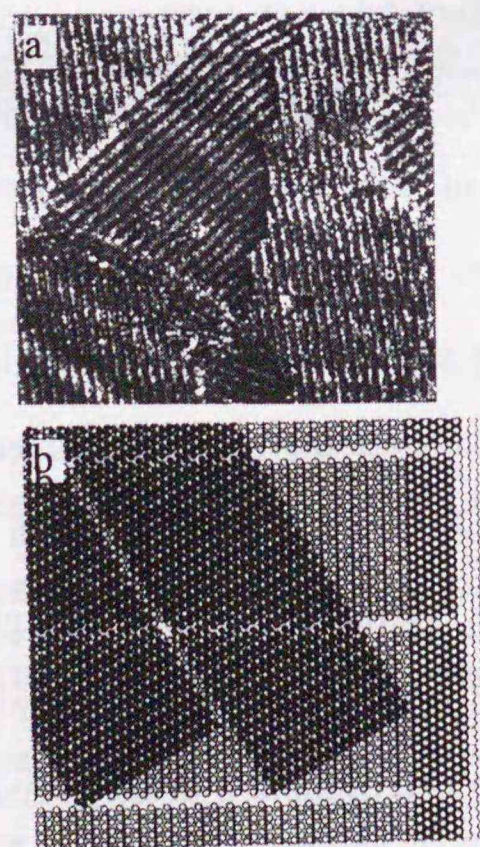
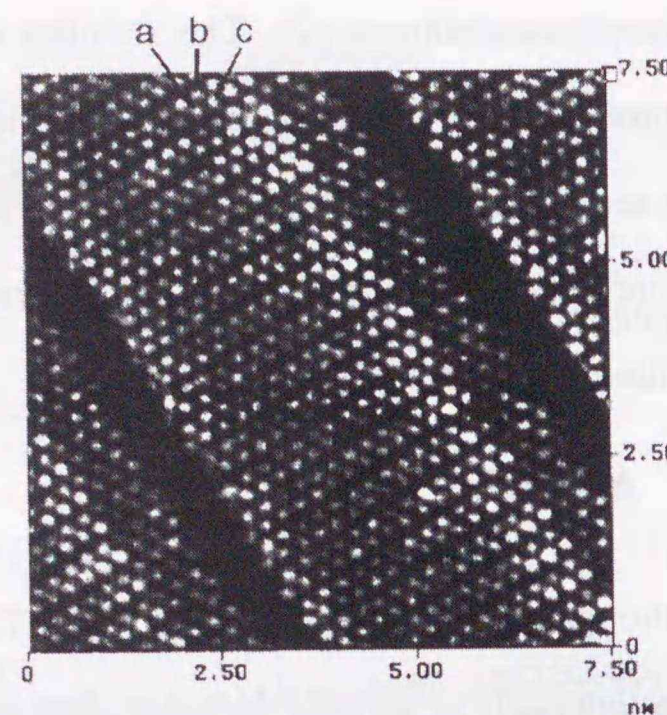


Figure 1-9. (a) STM image of graphite covered with $C_{36}H_{74}$. (b) The model of (a).³⁰

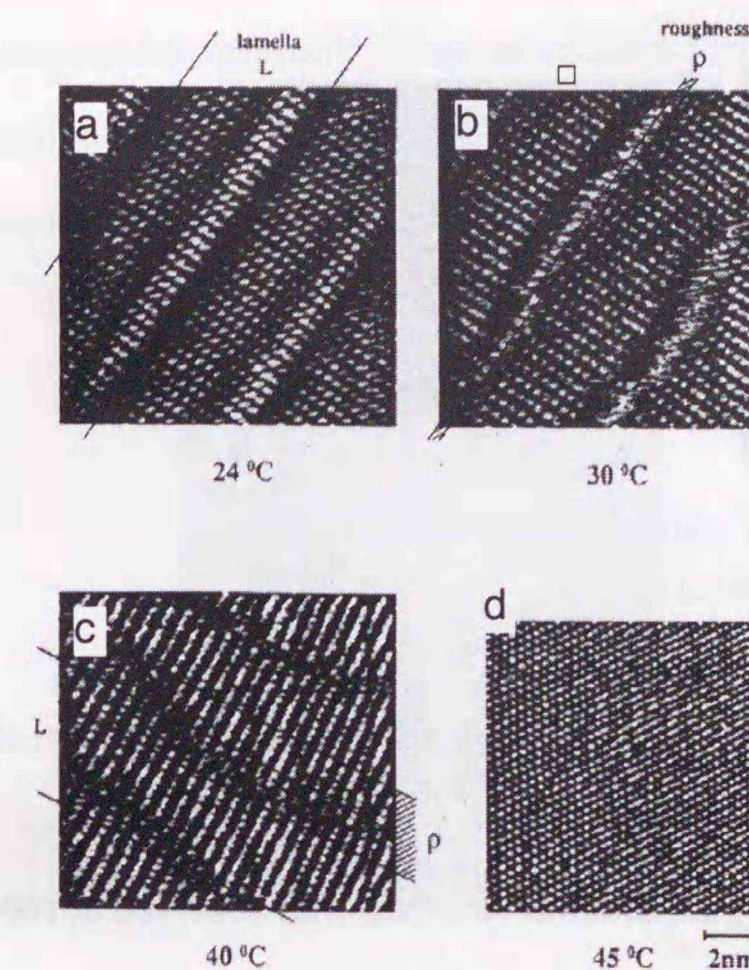


Figure 1-10. STM image of graphite covered with $C_{24}H_{30}$ in phenyloctane.³¹

60° as molecules do not cross the trough of the first layer and all of the hydrogens of the molecule are able to interact with the ones of the first layer. As a result, the rotated overlayer is formed probably because the molecule, which does not cross the trough of the first layer, acts as a nucleation center. Askadskaya and Rabe observed the phase transitions of the 2D crystal of $C_{24}H_{50}$ in phenyloctane on a graphite surface.³¹ An STM image obtained at room temperature showed highly ordered molecular arrangement (Fig. 1-10a). A small dynamic roughening of the lattice of the alkane was observed upon heating to 30°C (Fig. 1-10b). Further heating to 40°C caused a continuous increment in roughness (Fig. 1-10c). The elongated molecular feature is due to the high mobility of the molecules compared to the scan speed of the tip. At 45°C , no molecular structure was observed (Fig. 1-10d). The other type of phase transition is observed in neat $C_{24}H_{50}$. The STM image (Fig. 1-11a) shows the graphite lattice and superimposed straight lines with a separation equal to the width of the alkane. The orientation of the lines was the same as one of the molecular rows in the ordered alkane lattice such as seen in Fig. 1-10a. Therefore, the line structure is attributed to the edge of the molecular row and the molecules are supposed to diffuse along the molecular rows. The molecules are not imaged as the mobility of the molecules within the molecular row is too high compared to the scanning speed of the STM. The different mechanism of the phase transition in phenyloctane and neat liquid is explained as follows. In phenyloctane, creation of the short-lived free space due to the conformational defects of alkanes may frequently occur and, as a result, molecular

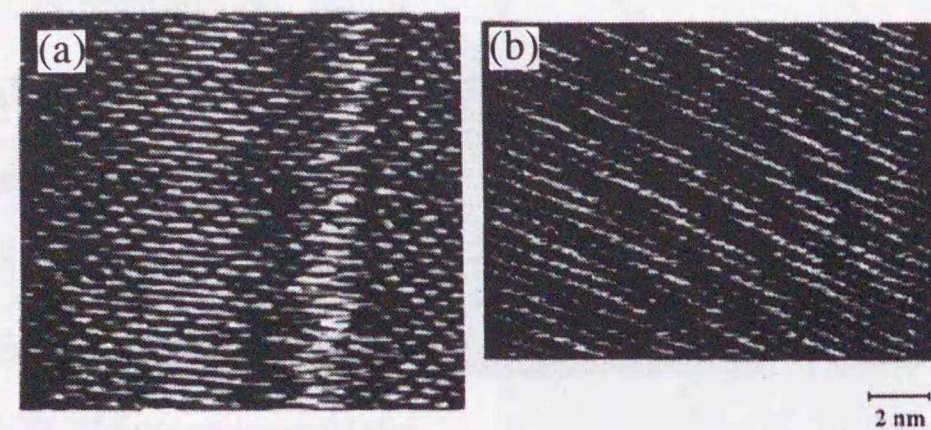


Figure 1-11. STM image of graphite covered with (a) neat $C_{24}H_{30}$ at $56^\circ C$ and $C_{192}H_{384}$ at $65^\circ C$.³¹

disorder along the molecular axis is dominant while the free space is not formed in the neat liquid.

When the alkyl chain is longer, $C_{192}H_{386}$, no ordered structure was observed at room temperature. However, a partially ordered monolayer was observed (Fig. 1-11b) at $65^\circ C$. This phase is named columnar, since it exhibits good ordering between the molecules, while the end of the molecules could not be identified.

c. Alkane derivatives

Claypool and Cyr *et al.* observed a series of alkane derivatives.^{29,32,33} Functional groups imaged by them include halides (F, Cl, Br, I), amines, alcohols, nitriles, alkenes, alkynes, ethers, thioethers, disulfides and thiols and representative results are shown in Fig. 1-12. I, SH and NH groups are imaged as spots brighter than the alkanes while Br, Cl and OH are darker. Functional groups are distinguishable from each other except for Cl and OH. The relationship between the imaging contrast and ionization potential is observed.²⁹ It is qualitatively explained as follows. If the energy level of the molecular orbital is pinned relative to the Fermi level of the graphite substrate, the location of the MOs will be closer to the Fermi level of the graphite when the ionization potential is lower. As a result, the contribution of the MOs in the tunneling process becomes large and it was imaged as the brighter spot in the STM images. Faglioni *et al.* carried out a computer simulation based on this idea and it showed qualitative agreement with the

experimental results.³⁴ They concluded that the origin of the imaging contrast of the functional groups are electronic coupling while the one for the alkyl chain is the so called "antenna effect".

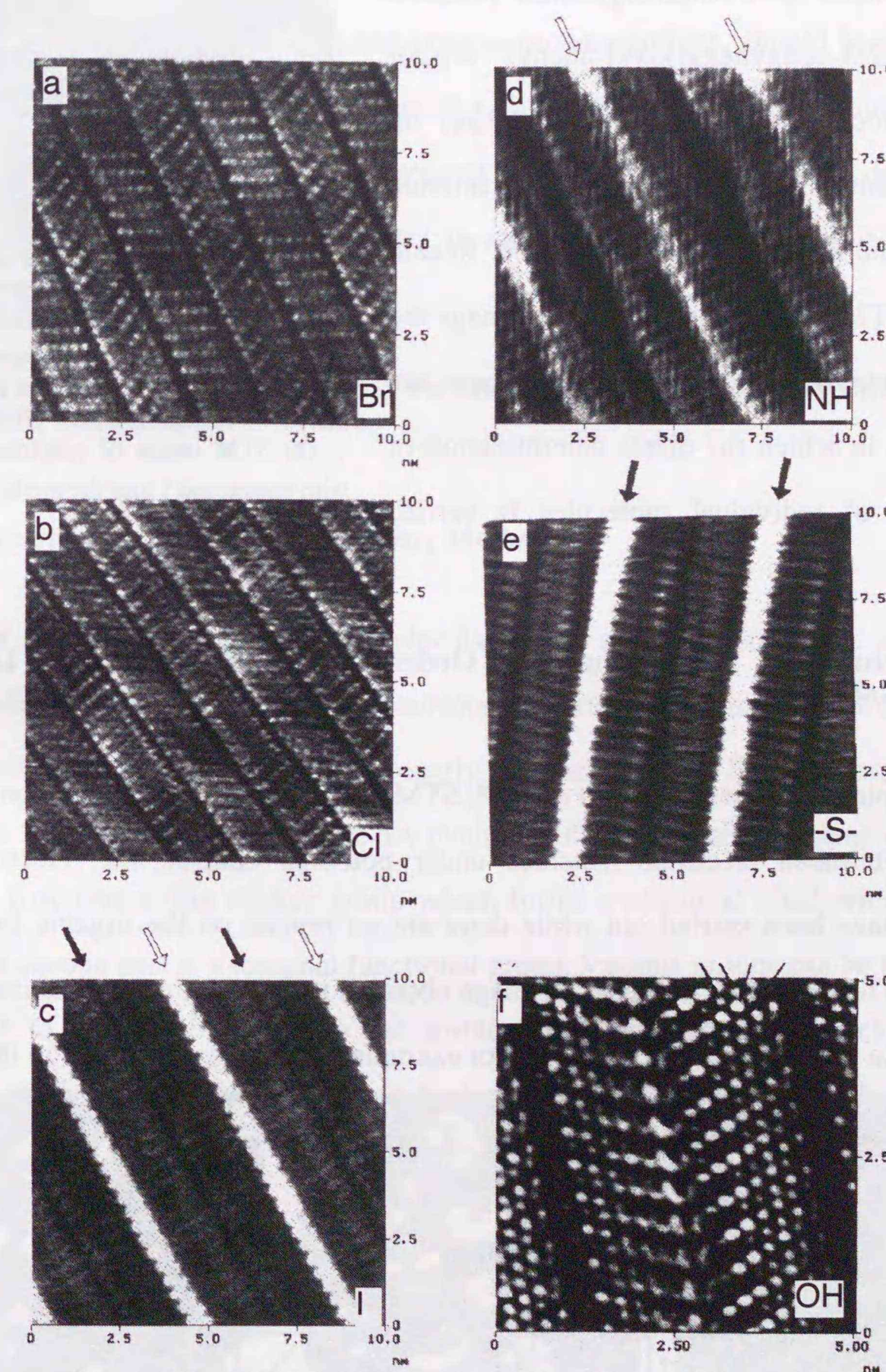


Figure 1-12. STM image of graphite covered with (a) $BrC_{12}H_{24}OH$, (b) $ClC_{12}H_{24}OH$, (c) $IC_{12}H_{24}OH$, (d) $(C_{18}H_{37})_2NH$, (e) $C_{16}H_{33})_2S$ in phenyloctane and (f) $C_{16}H_{33}OH$.²⁹

d. Chiral molecules

The observation of the 2D crystal of the liquid crystal with a chiral center was reported by Walba *et al.*³⁵ They observed a chiral crystalline structure of 4[(R,R)-(2,3-epoxyhexyl)oxy]-phenyl 4-[(S)-(3,7-dimethyloctyl)oxy]benzoate (Fig. 1-13a) on graphite as shown in Fig. 1-13b while the internal structure of the molecules was not visible. Recent progress in STM imaging enables one to image the atomic structure of the molecules and there are some reports in which the direct determination of the chirality of individual molecules is carried out.³⁶⁻³⁸

1-3-3 Structure of Two-dimensional Ordered Organic Molecular Layers in Electrolyte Solutions

After the pioneering work of Tao *et al.*³⁹, STM investigations of organic compounds at the electrolyte/metal electrode interface under potential control, i.e., electrochemical conditions, have been carried out while there are no reports on the organic liquid/metal interface.^{3b} The resolution of the STM image obtained under electrochemical conditions is comparable to the one obtained in UHV. For example, Yau *et al.* succeeded in imaging the

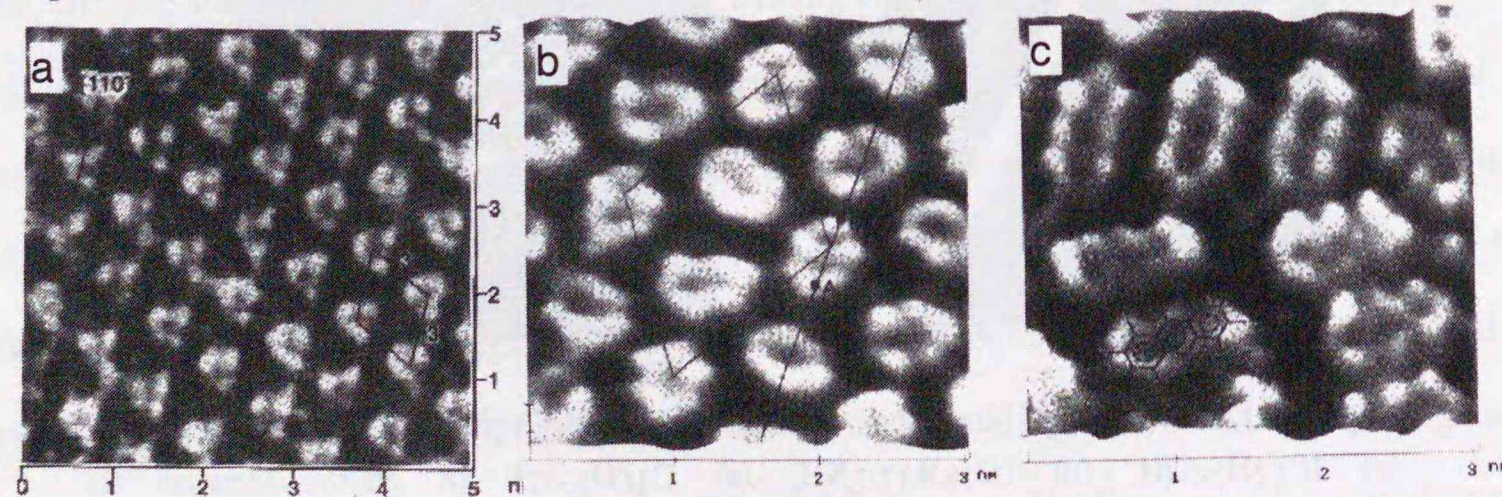


Figure 1-14 STM image of Ru(111) surface in 10 mM HF solution covered with (a) benzene²¹, (b) naphthalene and (c) anthracene.⁴¹

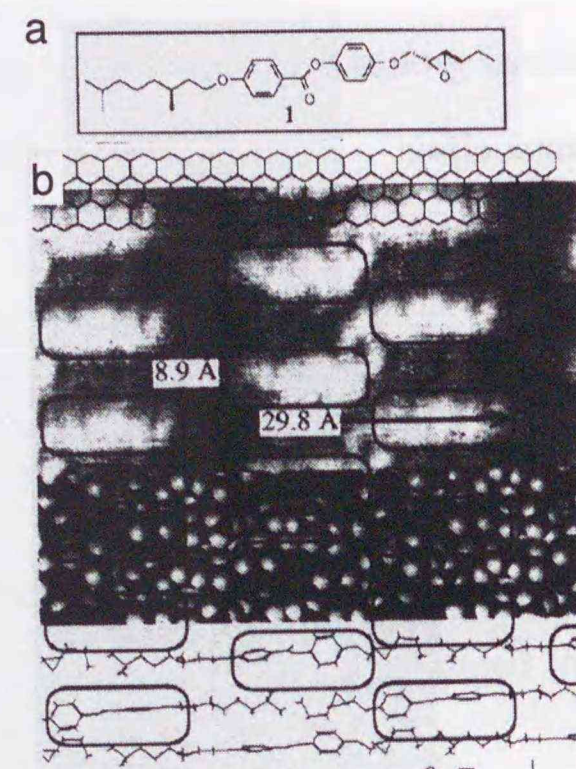


Figure 1-13. (a) Structure of compound 1. (b) STM image of graphite covered with compound 1 and the model.³⁵

internal structure of benzene,⁴⁰ naphthalene⁴¹ and anthracene⁴¹ as shown in Fig. 1-14a, b and c, respectively, on Ru(111) in HF solution. It is also reported that iodine-modified Au or Pt surfaces are excellent substrates for preparing highly-ordered adlayers of organic molecules while the disordered phase is often formed on bare surfaces.^{3b} The strong interaction, which prohibits the ordering process on bare surface, should be weakened by the iodine layer, resulting in the formation of a highly ordered layer of organic molecules. It is also reported that the iodine arrangement is directly imaged without destroying the organic layer when the tunneling current is increased,^{42,43} which enables an accurate determination of the adsorption site.

11-4 Formation of Chemisorbed Two-dimensional Ordered Organic Molecular Layers at the Solid/Liquid Interface

1-4-1 Preparation - the Self-Assembling Method

Most of the ordered chemisorbed molecular layers are prepared by the self-assembly (SA) method.^{8,9,44-46} The SAM is spontaneously formed by the immersion of a substrate into a solution of a molecule which is properly designed to cause SA in an organic solvent (Fig. 1-15). The molecule used for the SA method generally consists of three parts (Fig. 1-16a). The first part is the anchor group which forms a chemical bond with the surface atoms. The second part is a terminal functional group. Various groups can be introduced in this region to provide functions to the surface. The last part is the backbone of the molecule which connects the anchor and the functional groups. The alkyl chain is used as

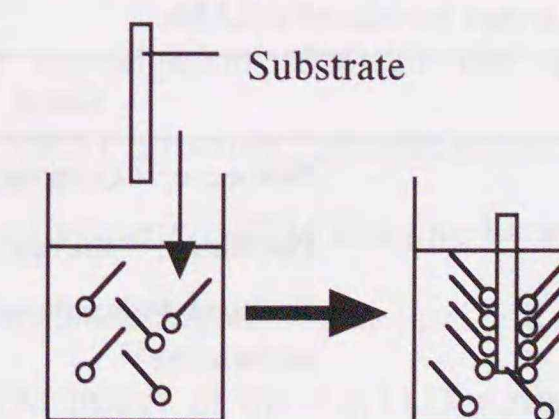


Fig. 1-15. A method to form the SAMs.

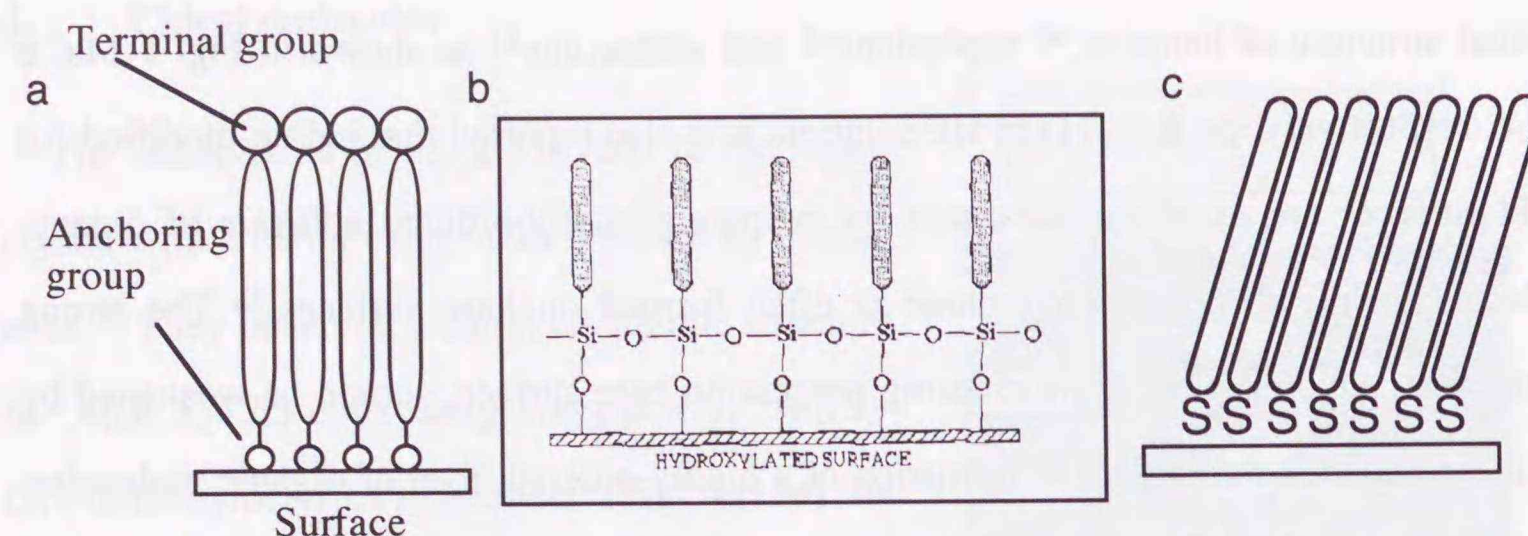


Fig. 1-16 Schematic view of the structure of the SAMs (a) in general, (b) of organosilicon and (c) of alkanethiols.

the backbone of the molecule in many cases and the van der Waals interaction between the alkyl chain is one of the origins of the two dimensional order and rigidity of the SAM. The backbone group is also important for achieving an ordered arrangement of the functional groups in the vertical direction from the surface. The SAM is widely studied since it is stable, flexible in the design and easy to form. The proper design of the surface group enables one to control the surface wetting, electron transfer process and chemical activity, and the application field of the SAM includes the construction of sensors, biocompatible surfaces and molecular devices. There are two representative practical SAM systems. One system is organosilicon on hydroxylated surfaces (SiO_2 on Si, Al_2O_3 on Al, glass etc., Fig. 1-16b) and the other is organo-thiols on metals (gold, silver and copper, Fig. 1-16c).^{8,9,44}

The SAMs of alkanethiols and their derivatives on a Au(111) surface are the most extensively studied systems and we focus on this system in the following sections. The

Table 1-1. Functions and chemical groups introduced to SAMs.

Function	Group
Electrochemical Activity	Ferrocene, ⁴⁷ Quinone, ⁴⁸ $\text{Ru}(\text{HN}_3)_6^{2+}$ ⁴⁹
Photoelectrochemical Activity	Porphyrine, ⁵⁰ $\text{Ru}(\text{bpy})_3^{2+}$ ⁵¹
Optical Activity	Ferrocenyl-nitrophenyl-ethylene, ⁵² azobenzene ⁵³
Wettability Control	COOH , ⁵⁴ OH , ⁵⁴ CH_3 , ⁵⁵ NH_3 ⁵⁶

representative functions introduced on the Au(111) surface by the SAMs are listed in Table 1-1. The SAMs of alkanethiols are prepared by the immersion of the gold substrate into a $\sim\text{mM}$ solution of alkanethiols in a solvent for minutes to hours. The growth process of the SAM of alkanethiols and their derivatives in solution was investigated *in situ* using a quartz crystal microbalance,⁵⁷ surface plasmon resonance spectroscopy⁵⁸ and second harmonic generation measurement.⁵⁹ The results of these investigations showed that the growth process of the SAM of an alkanethiol is divided into two processes, the initially faster and the following slower one. The *ex situ* IR study showed that the SAM of the alkanethiols becomes more slid-like as the immersion time is increased and, therefore, the second slower process is assigned to the rearrangement of the SAM.⁶⁰

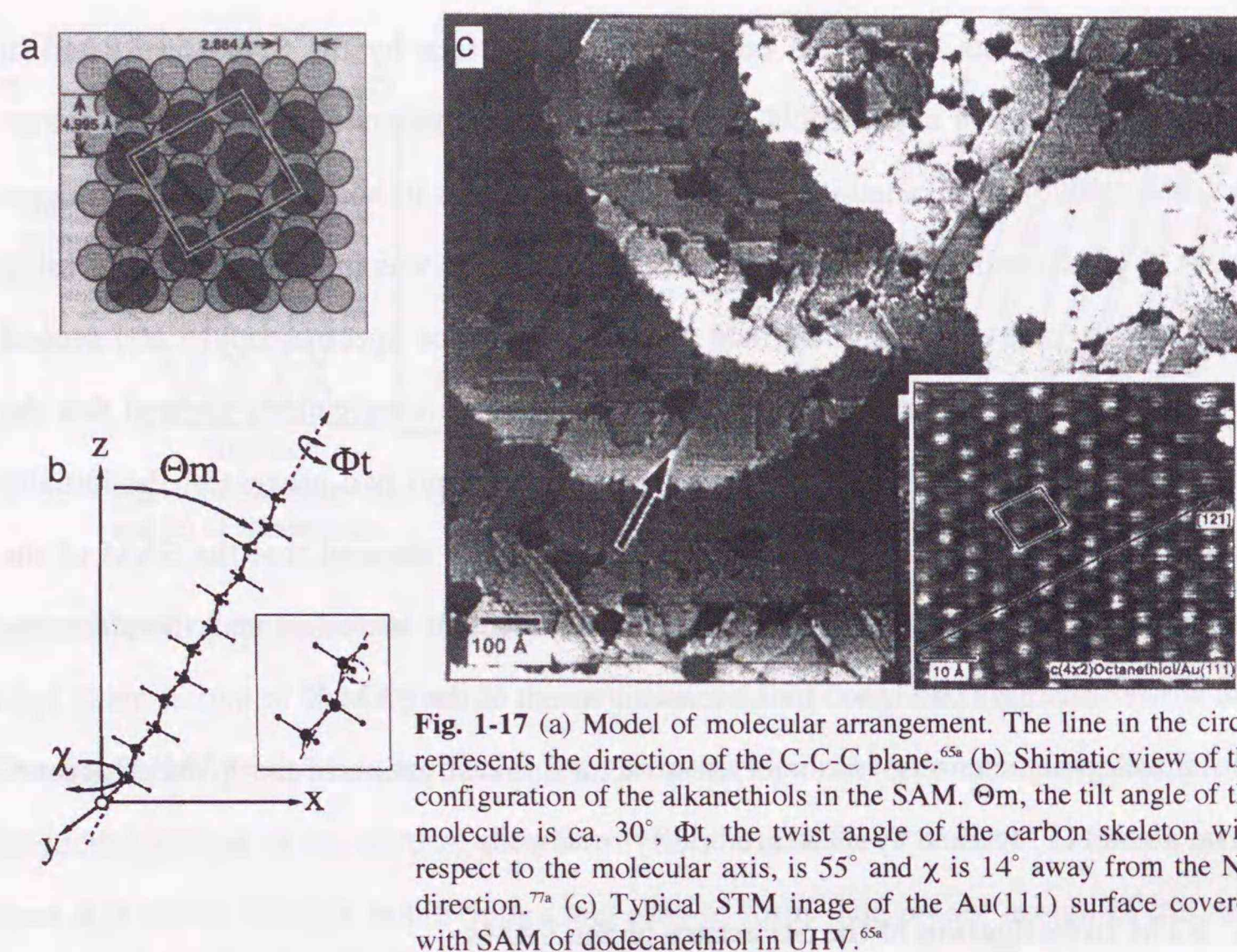
In the following sections, results of the structural investigation of the SAM of organo-thiols on a Au(111) surface by STM are briefly reviewed.

1-4-2 STM Investigation of the Structure of the SAMs

a. Alkanethiols

It is known from diffraction studies that the alkanethiols are closely packed and basically arranged in the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ structure on a Au(111) surface⁶¹ while the existence of a superstructure called $n\sqrt{3}\times\sqrt{3}$ was also reported (Fig. 1-17a).⁶² In addition, IR measurements showed that the molecular axis is tilted from the surface normal by ca. 30° and the plane formed by the carbon skeleton forms a herringbone structure (Fig. 1-17b).⁶³

Although early STM investigations showed the spots which correspond to the arrangement of the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ structure, the destruction of the SAM frequently occurred during the imaging.⁶⁴ Non-destructive STM imaging became possible by the measurement with a high gap impedance (tunneling current is $\sim\text{pA}$ and bias voltage is ca. 1 V).⁶⁵ Figure 1-17c shows a typical STM image of the Au(111) surface covered with the SAM of an alkanethiol (dodecanethiol).^{65a} Pits and missing rows running between the pits are visible.



The pit is attributed to a depression in the gold substrate since the molecular arrangement is also visible in the pit and the depth of the pit is the same as one of the monoatomic steps of the gold surface.⁶⁶ These pits are, therefore, called vacancy islands (VIs) of the gold surface. The missing row is attributed to the domain boundary of the SAM.⁶⁷ The magnified image of a flat region shows spots which are arranged in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure and, thus, the arrangement of the alkanethiols is imaged (Fig. 1-17c, inset). There are subtle and ordered height differences among the molecules. The structure of the molecular arrangement considering this height difference is denoted as $4\sqrt{3} \times 2\sqrt{3}$ or $c(4 \times 2)$ of the $(\sqrt{3} \times \sqrt{3})R30^\circ$, which is consistent with the structure reported in the early diffraction studies.⁶² There were cases when different structures but in the same notation, $4\sqrt{3} \times 2\sqrt{3}$, were imaged in the STM although it is possible to attribute it to a tip artifact.^{65c}

It is known that VIs of the gold surface undergo Ostwald ripening,⁶⁸ and appropriate annealing results in reducing the number of VIs since VIs are merged with the steps of the gold substrate.⁶⁹ The mechanism of the construction of VIs of the gold surface is still not clear while three mechanisms, the chemical etching of the gold due to alkanethiols,⁷⁰ the

compression of the surface lattice^{66b} and ejection of the excess amount of gold atoms than that expected during the lifting of the reconstruction of the gold surface⁷¹ during the adsorption of the alkanethiols, are proposed.

Camillone *et al.* reported that the SAM of alkanethiols shows a stripe phase when the coverage is low.⁷² In addition, Poirier and Pylant investigated the growth process of the SAM of alkanethiols on Au(111) in UHV.⁷³ Although their report was not directly related with the molecular layer at the solid/liquid interface, their result is reviewed here. Figure 1-18 sequentially shows the STM images obtained during the exposure of hexanethiol in UHV. The herringbone structure of the Au(111)

surface is visible before the exposure of the hexanethiol (Fig. 1-18a and see section 1-5). The deformation of the herringbone structure occurred with the short time duration after the exposure of the hexanethiol was started. The ordered structure due to the molecules were not visible in this stage. The deformation of the reconstruction shows a surface pressure due to the molecules. The stripe structure was constructed in the hcp region of the gold surface after further exposure of the molecules and VIs of the gold surface were also formed (Fig. 1-18b). The stripe phase is assigned to the structure formed by the molecules whose molecular axis is parallel to the surface plane. As the time passed, the stripe phase spread and deformation of the reconstruction of the gold surface proceeded. After the surface was fully covered with the stripe phase, islands, which consist of molecules in stand up form showing the

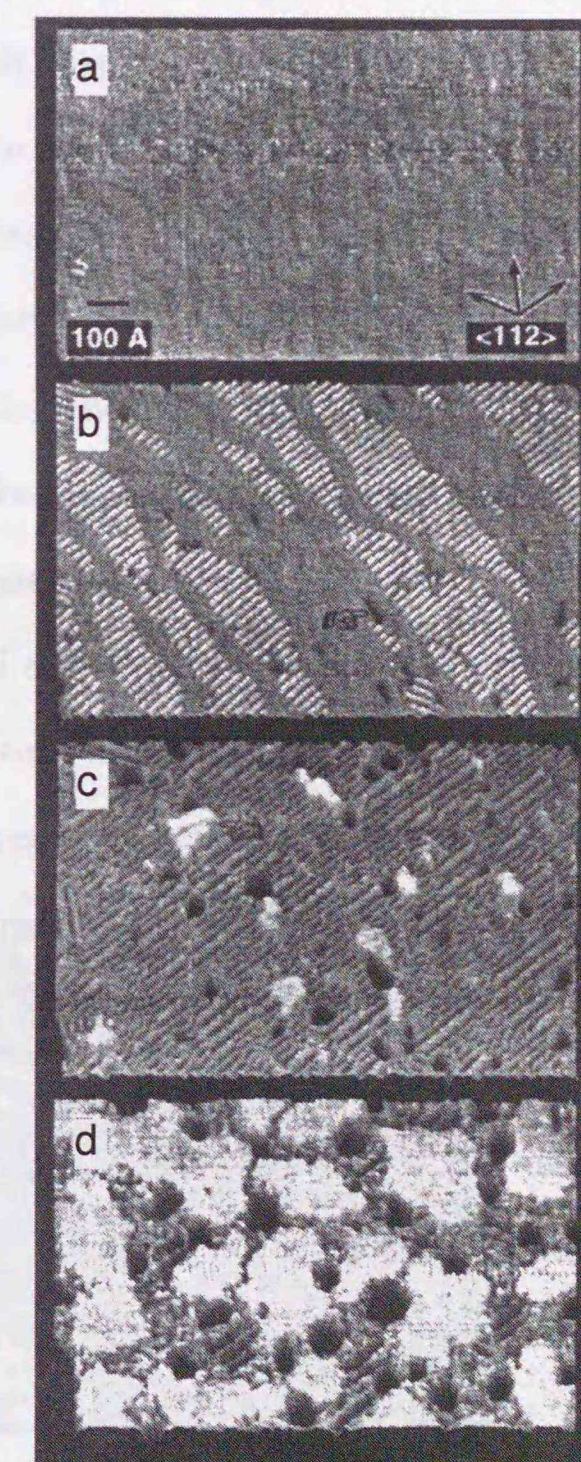


Fig. 1-18 STM image of Au(111) exposed to the vapor of hexanethiol in UHV. (a) Bare Au(111) surface. After 600 (b) 1000 (c and d) Langmuire exposure.⁷³

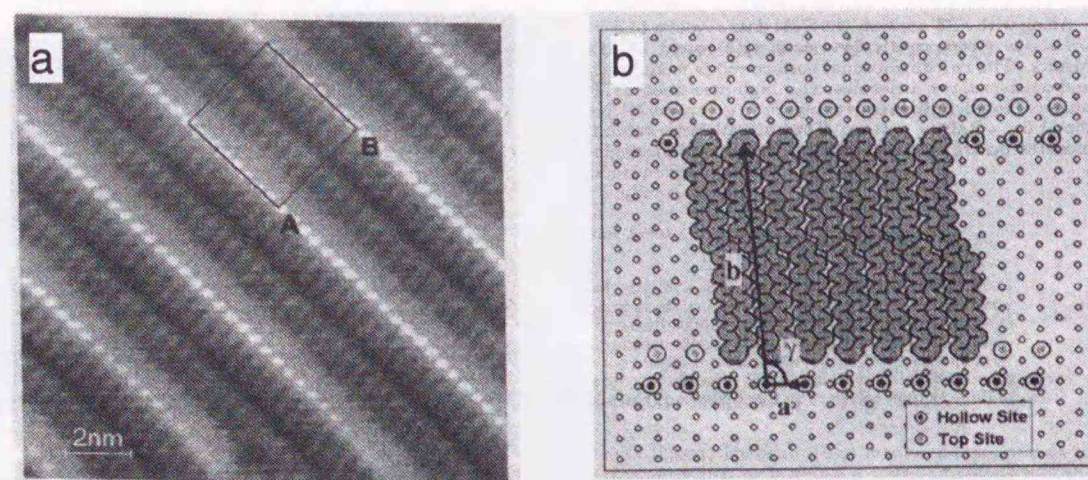


Fig. 1-19 (a) STM image of Au(111) covered with the stripe phase of decanethiol obtained in UHV. (b) the model for the STM image.⁷⁴

($\sqrt{3} \times \sqrt{3}$)R30° structure, were formed (Fig. 1-18c). The islands grew with time (Fig. 1-18d) and finally, the surface was covered with the islands, i.e., the monolayer formation was completed. This study showed that the surface lateral pressure plays an important role in the formation of the SAM. It is also reported that the stripe phase is formed after the modification in very dilute ($\sim \mu\text{M}$) solution in a short time. The structure of the stripe structure was not distinctly determined since only bright lines or spots, which should correspond to the thiol group, were imaged. Staub et al. succeeded in STM imaging of the alkyl chains between the bright stripe line as shown in Figs. 1-19a and b⁷⁴ and it is now obvious that the stripe structure consists of the alkanethiols whose molecular axis is parallel to the surface. However, several different stripe structures are reported⁷⁵ and the structure of the stripe phases is not completely understood.

b. Alkanethiol derivatives

While the most characteristic point of the SAM is that functional groups can be arranged in an ordered manner on the surface, the STM imaging of the SAM of functionalized alkanethiols is still difficult probably because the surface with functional groups is easy to be contaminated and the molecular order is not very good. The molecularly resolved image is obtained on the SAM with azobenzene⁷⁶ and hydroxy groups.⁷⁷

c. Other thiol derivatives

An STM image of the Au(111) surface covered with the SAM of pyridinethiol (Fig. 1-20a), which is known to promote the electrochemical reaction of metalloproteins such as cytochrome c, is shown in Fig. 1-20b.⁷⁹ It was obtained in 50mM HClO₄ solution under potential control. The ladder-like structure is attributed to the arrangement of the dimerized PySH (PySSPy). The SAM formed by PySSPy showed the same structure.

The structure of SAMs of aromatic thiols, which are expected to possess an electric conduction ability, is also observed by STM.⁸⁰ The STM image of the Au(111) surface covered with the SAM of the aromatic thiol (Fig. 1-21a) is shown in Fig. 1-21b. The molecules are arranged in the ($\sqrt{3} \times \sqrt{3}$)R30° structure.

Mesoscopic patterns are also constructed by the SAM of the thiol derivatives. Nakamura et al. reported that a honeycomb structure is formed by the SA of 1,8-Bis(5-mercaptopomethyl-2-thienyl)octane (Fig. 1-22a) as shown in Fig. 1-22b while the molecular arrangement is not clear.⁸¹ Ohtani et al. reported that the 2D chiral molecular arrangement is constructed by the SA of 1,1'-binaphthalene-2,2'-dithiol (Fig. 1-23a; BNSH).⁸² Figures 1-23b and c show the STM image of the SAM of (R)- and (L)- BNSH,

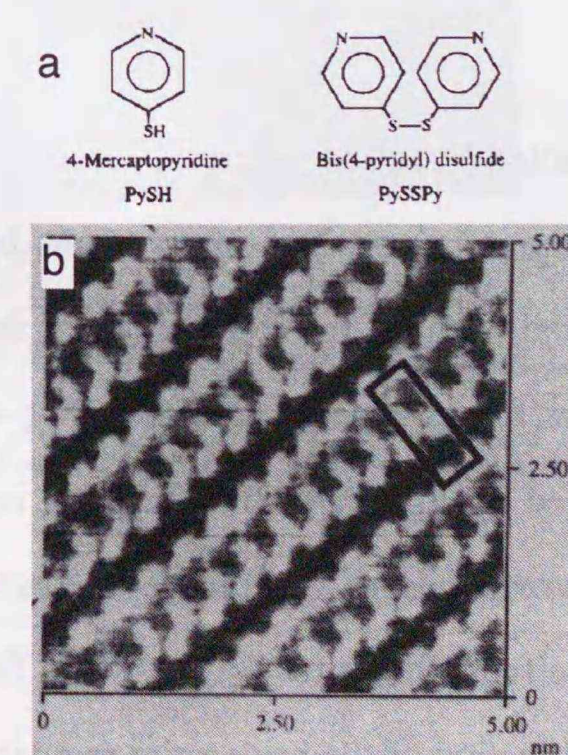


Fig. 1-20 (a) Structure of pyridinethiol and its dimer form. (b) STM image of the SAM of PySH or PySSPy on Au(111) obtained in 0.05M HClO₄ solution at 0.8 V vs RHE.⁷⁹

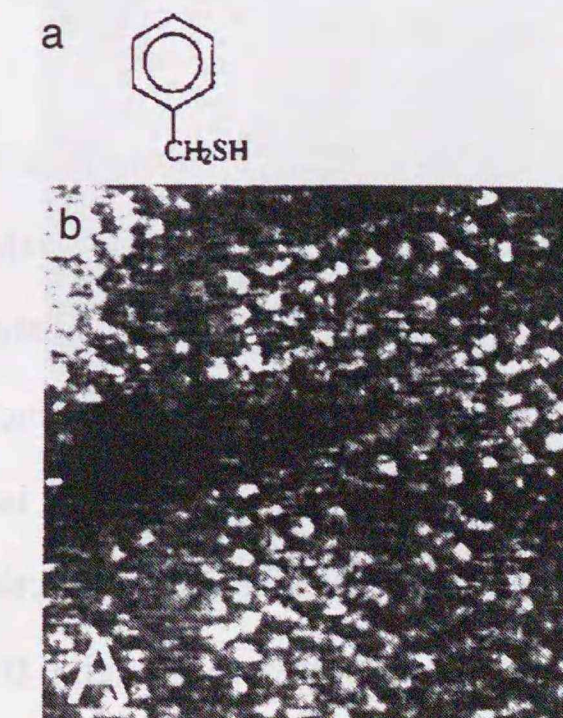


Fig. 1-21 (a) Structure of aromatic thiol. (b) STM image of the SAM of Compound 1 in 8x8 nm square. The molecules are arranged hexagonally with 4.9Å apart.⁸⁰

respectively. The rotation of the three triangular units consists of 6 spots in the image and is opposite of that in Fig. 1-23b and c, indicating that this arrangement is a reflection of each image and, thus, the structure possesses a 2D chirality. The formation of the chiral surface by a chemisorbed organic layer is expected to open the way to design a stereoselective catalysis and sensors.

1-5 Structure of the bare Au(111) and Au(100) surface

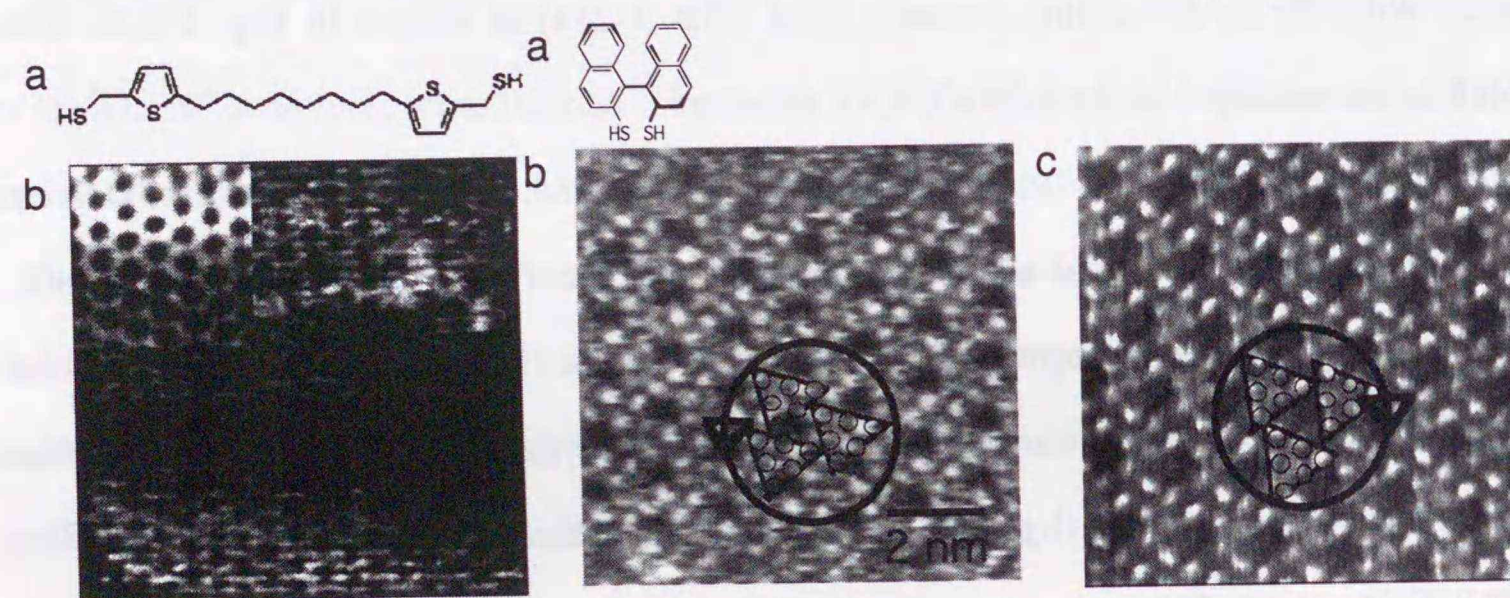


Fig. 1-22 (a) Structure of 1,8-Bis(5-mercaptomethyl-2-thienyl)octane. (b) STM image of the SAM of the molecule (6.7x6.7 nm).⁸¹

Fig. 1-23 (a) Structure of 1,1'-binaphthalene-2,2'-dithiol (BNSH). STM image of the SAM of (b) (R)- and (c) (S)-BNSH.⁸²

The clean Au(111) surface shows a reconstructed structure which is described as a $22\times\sqrt{3}$ structure.⁸³⁻⁸⁶ It consists of a uniaxial compression of the surface atoms by about 4% in the [110] directions and 23 atoms are located in the 22 atomic spaces of the (1x1) structure. The STM image of the reconstructed Au(111) surface is shown in Fig. 1-24.⁸⁴ A paired stripe structure with gold atoms is imaged in Fig. 1-24a. The brighter region of the image which runs in the [121] direction corresponds to the bridge site where the registry of the surface atoms are changing from the fcc to hcp sites (Fig. 1-24b). The STM image of a large area (Fig. 1-24c) shows that the direction of the bridge site regularly turns and it forms a herringbone structure. The formation of the herringbone structure is a result of the formation of stress domains.^{87,88} The stress domains will be formed when a reconstructed surface possess an orientational degeneracy and has an anisotropic stress

tensor. The Au(111) surface satisfies these conditions since the $(22\times\sqrt{3})$ cell has three possible orientations and the stress is applied anisotropically along the $\langle 110 \rangle$ direction. The herringbone structure of the reconstructed Au(111) surface is well reproduced by the numerical calculations done by Narasimhan and Vanderbilt.⁸⁹

The surface stress at the gold surface is determined by the balance between a repulsive interaction of the filled d-shells and compressive stress of the s-p electrons.⁹⁰ It is expected that the compressive stress due to the s-p electrons would be reduced when the surface is positively charged. Actually, the phase transition from the $22\times\sqrt{3}$ structure to the (1x1) structure takes place when the potential is swept positive relative to the point of zero charge under electrochemical control.⁸⁵ The lifting of the surface reconstruction is also induced by the modification of electronic structure and change in the surface stress due to the chemical or physical adsorption of the molecules.⁹¹

The Au(100) surface shows a reconstructed structure which is described as

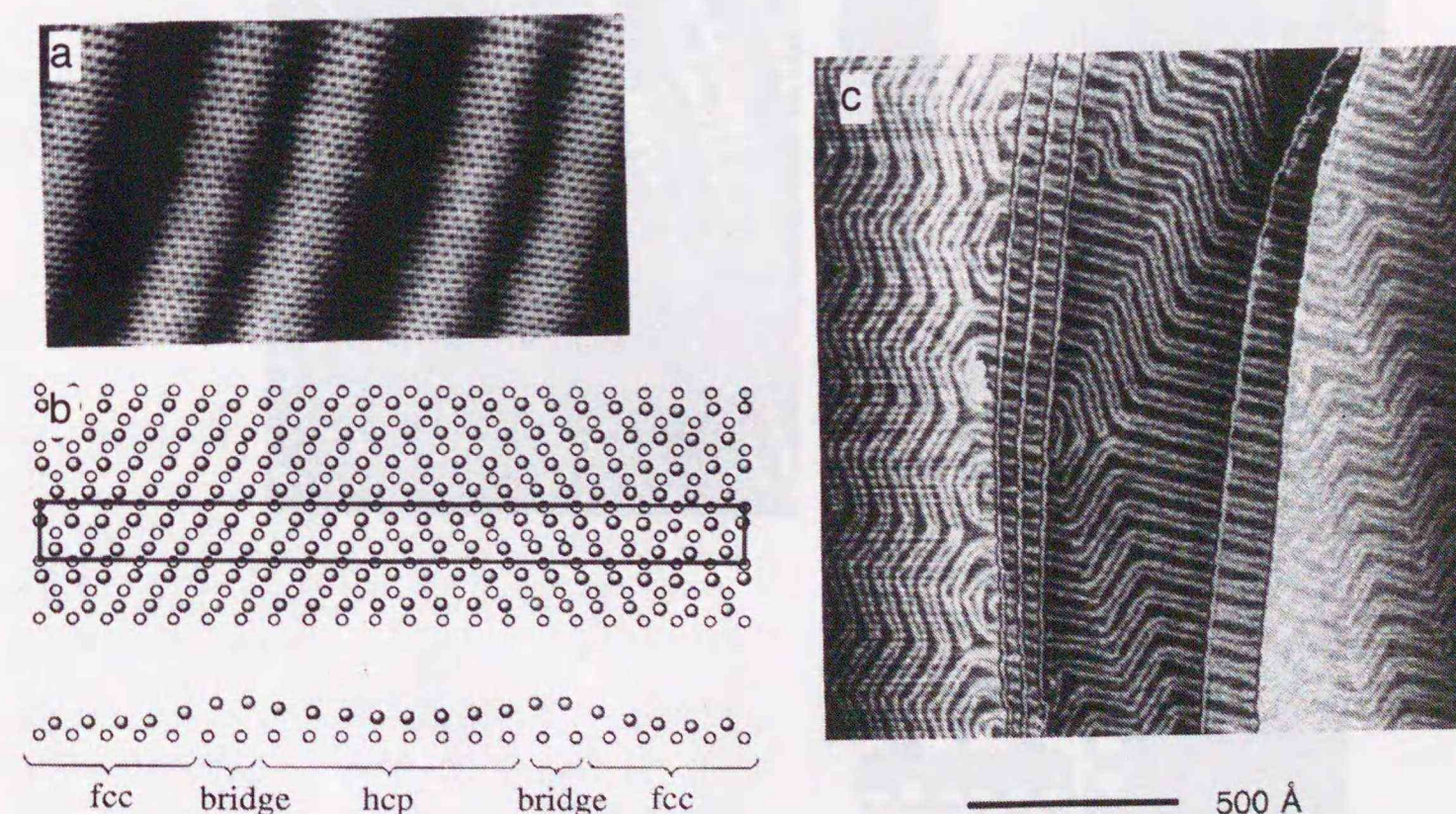


Figure 1-24 (a) STM image of reconstructed Au(111) surface.⁸⁴ (b) Model of $22\times\sqrt{3}$ structure.⁹² (c) STM image of reconstructed Au(111) surface in large scale.⁸⁴

(5x20).^{85,86,93,94} As the surface atoms form quasi-hexagonal arrangement, this structure is also called the hex-Au(100) phase. Figure 1-25a and b show STM images of the hex-Au(100) phase obtained in UHV.⁹⁵ The image of large area (Fig. 1-25a) shows a stripe structure parallel to the step. The magnified image (Fig. 1-25b) shows that the stripes are attributed to the corrugation of the gold surface. The subtle height corrugation parallel to the stripe is also observed in Fig. 1-25b. As shown in the model in Fig. 1-25c, these features are due to the difference in the registry of the gold atoms of the top layer to the second layer. The reconstruction of the Au(100) surface is lifted by the adsorption of the molecules and the positive potential sweep under electrochemical control.⁸⁵

1-5 Objectives and Outline of This Thesis

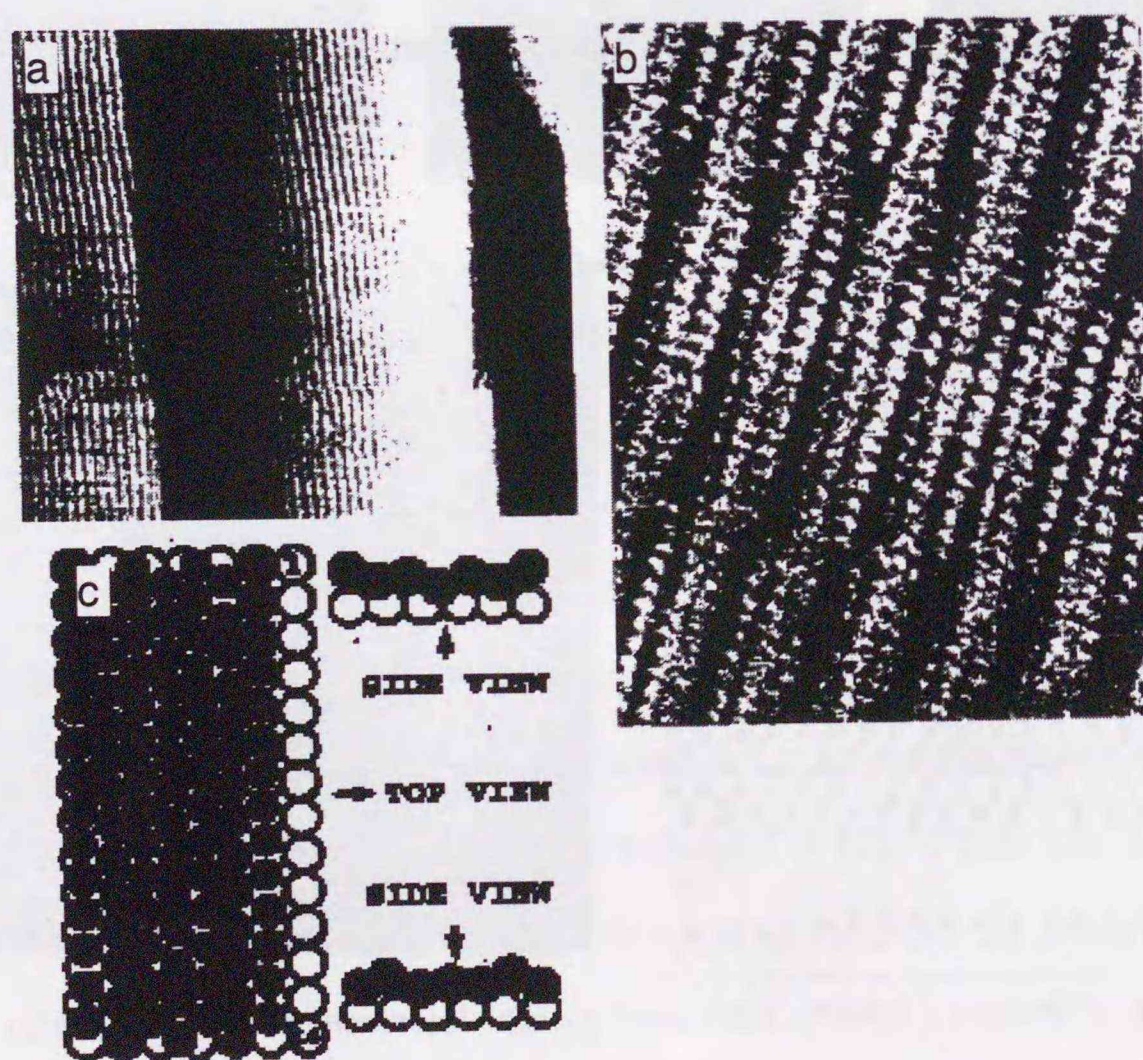


Figure 1-25 (a) STM image of reconstructed Au(100) surface. (b) Atomic resolution image. (c) Model of the hexagonal structure.⁹⁵

The objectives of this thesis is to reveal the origins which promote the formation and determine the structure of the 2D ordered physisorbed and chemisorbed organic molecular layers on a metal surface. This thesis consists of the following chapters.

Chapter 2 describes the formation of the alkane 2D crystals on Au(111) and (100) surfaces in neat liquids investigated by STM.

Chapter 3 treats the formation of the SAM of alkanethiols on a Au(111) surface. The growth process and the effect of the temperature and the solvent on the structure of the SAM is discussed.

Chapter 4 summarizes the present results.

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Chapter 2

Formation of Physisorbed Two-dimensional Crystals of Alkanes on Au Surfaces

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2-1 Introduction

Organic thin films of single molecular thickness at the solid/liquid interface play important roles in many phenomena such as crystal growth, lubrication, wetting and chemical reactions. In addition, formation of a well-ordered molecular layer on the surface is a key step in the construction of molecular devices and self-assembly (SA) and the Langmuir-Blodgett (LB) technique have been developed for this purpose.¹ It is essential to understand the nature of the interaction between molecules and surfaces for the advanced design of the molecular layer. n-Alkanes are the simplest but very important molecules because they form the basis of lipids, surfactants, liquid crystals and polymers. The interaction between the alkylchain and the substrate as well as alkylchains is also known to play important roles in the SA^{2,3} mechanism, and it is important to investigate the interaction between alkanes and metal surfaces.

The adsorption of the alkane on a metal surface was studied under UHV conditions. Firment and Somorjai showed that the alkanes formed ordered monolayers on Pt(111)⁴ and Ag(111)⁵ under UHV conditions by low energy electron diffraction (LEED). In addition, the physisorption of alkanes has been studied on Au(111),⁶ Pt(111),^{7,8} Pt(110),⁹ Ir(110),¹⁰ Cu(100),¹¹ Ru(001),¹² and Cu(111)¹³ under UHV conditions. However, the local arrangement of the alkanes on a metal surface has not been investigated in contrast to numerous reports of alkane adlayers on graphite at the solid/liquid interface,¹⁴⁻²¹ although studies using molecular dynamics^{12,22-27} and infrared spectroscopy²⁸⁻³² under UHV conditions have been carried out after the reports by Firment and Somorjai. Furthermore, the structure of the alkane/metal interface in solution was not investigated. The formation of an ordered layer of the alkanes at the solid/liquid interface was expected

from the solvation force measurement³³ which showed an oscillational feature when two surfaces were close to the short separation distance ($\sim$ nm). A molecular dynamics study of the confined organic films showed the periodic density profile of alkanes in a direction normal to the surface plane,³⁴ supporting the results of the force measurement. The density profile in the direction normal to the surface plane may be influenced by the two-dimensional order of the alkanes on the surface. There is, however, no direct structural information on the two-dimensional order of the alkane layer on the surface.

In this chapter, the formation and the structure of the ordered alkane adlayer, i. e., the 2D crystals of alkanes on a Au(111) surface in neat liquids were investigated by *in situ* STM measurement.

2-2 Experimental

All chemicals (C_nH_{2n+2} : $n = 12 - 17$) were purchased from Tokyo Chemical Industry (purity : $> 98\%$) and were used without further purification. The Au(111) facet of a single crystalline bead, which was prepared by the Clavilier's method,³⁶ was used as a substrate. The Au single crystalline bead was fixed on a Pt sheet and placed in an STM cell after a flame-annealing treatment. The iodine modification was carried out by immersing the gold substrate in a 5 mM aqueous solution of KI for several minutes. The STM measurements were carried out using a PicoSPM (Molecular Imaging) controlled by a Nanoscope E (Digital Instrument) controller in a home-made cell in Ar atmosphere. The STM tip was made of a Pt/Ir (8:2) wire sharpened by mechanical cutting. A small amount of alkane liquid was put in the cell, and STM measurements were carried out in a thin layer of neat alkanes at room temperature ($\sim 25^\circ\text{C}$).

2-3 Results and Discussions

2-3-1 Formation of the Two-dimensional Crystals of Alkanes on Au(111) Surface

a. Bare Au(111) Surface

Figures 2-1 show the STM images of a Au(111) surface obtained in dodecane ($C_{12}H_{26}$

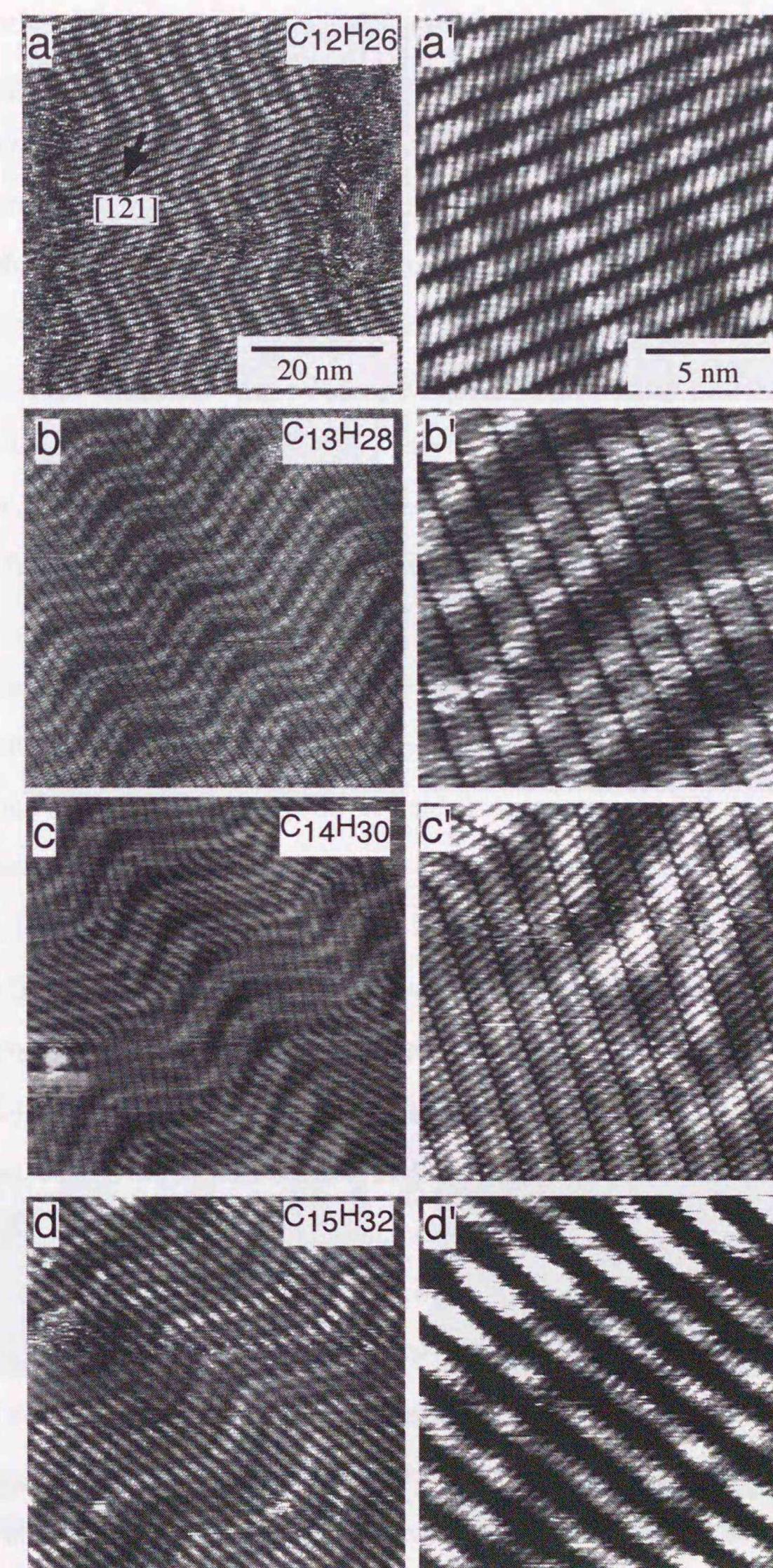
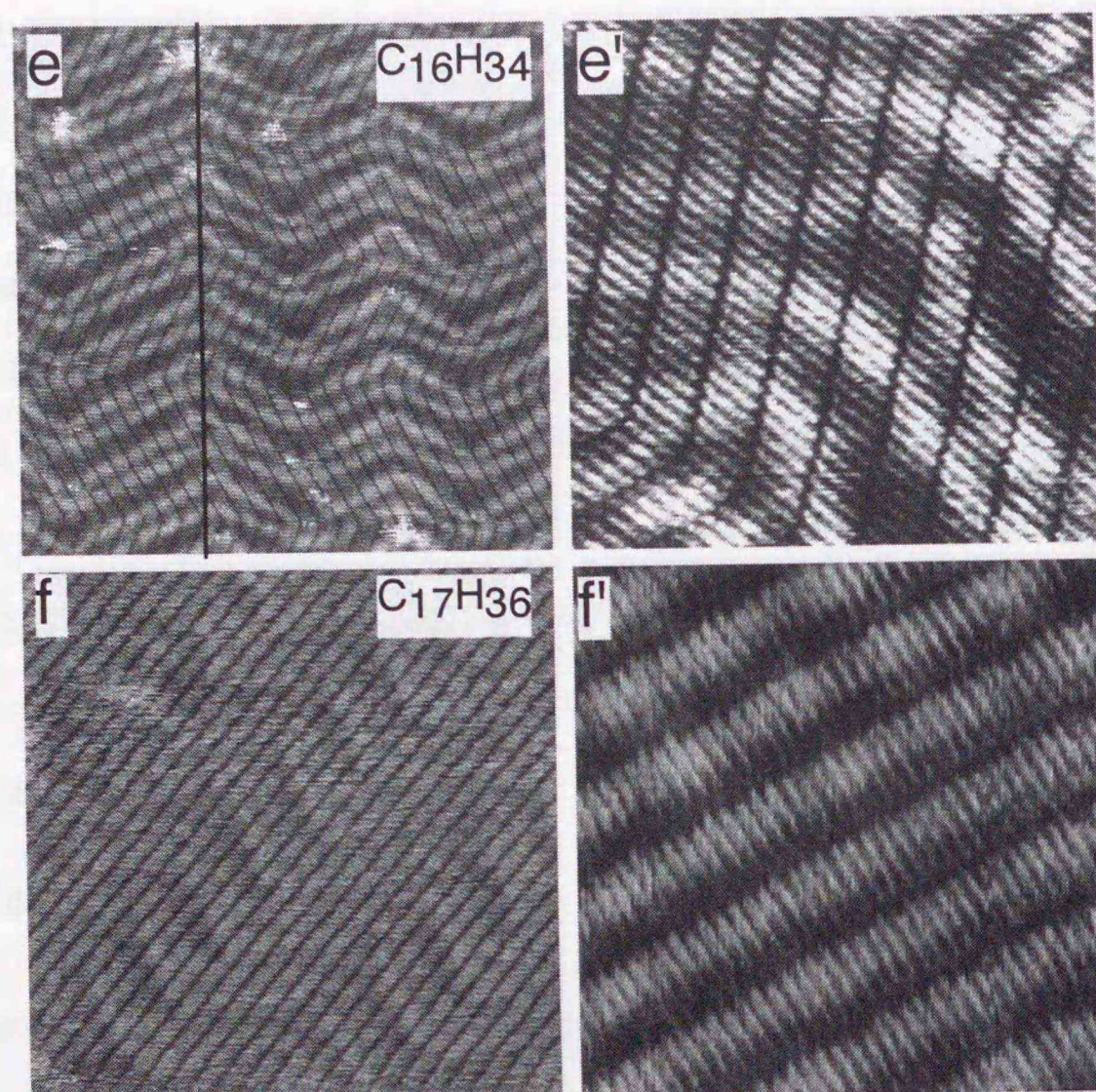


Fig. 2-1 STM images of Au(111) surface obtained in C_{12} (a and a'), C_{13} (b and b'), C_{14} (c and c'), C_{15} (d and d'), C_{16} (e and e') and C_{17} (f and f'). Continued to the next page.



(Fig. 2-1 continued)

: C₁₂, a and a'), tridecane (C₁₃H₂₈ : C₁₃, b and b'), tetradecane (C₁₄H₃₀ : C₁₄, c and c'), pentadecane (C₁₅H₃₂ : C₁₅, d and d'), hexadecane (C₁₆H₃₄ : C₁₆, e and e') and heptadecane (C₁₇H₃₆ : C₁₇, f and f'). The paired bright rows forming the herringbone structure indicated by an arrow in Fig. 2-1a were observed in all the images. They correspond to the bridging sites between the fcc and hcp stacking regions of the reconstructed gold surface and are known to run along the $[1\bar{2}1]$ direction.³⁷ The orientational registry of the gold surface was determined from this structure. The large scale images (50 x 50 nm²) of the gold surface in the even-numbered alkanes (Fig. 2-1a, c and e) showed a zigzag row structure except for the image obtained in C₁₂ in addition to the herringbone structure. First, let us discuss the structure observed in C₁₆ in detail (Figs. 2-1e and e'). The magnified image (15 x 15 nm²) shown in Fig. 2-1e' revealed that the row structure consisted of the rods of 2.2 nm long which were separated by ca. 0.43 nm

from each other. These values were comparable to the length and width of a C₁₆ molecule, respectively, in the all-trans conformation. Thus, one can conclude that the C₁₆ molecules lay on the Au(111) surface with their molecular axis parallel to the surface plane and formed a two-dimensional (2D) crystal. The molecular row ran close to the $[0\bar{1}1]$, i.e., the nearest neighbor (NN) atomic direction of the Au(111) surface. The molecular axis was also oriented close to the NN direction of the gold atoms because the angle formed by the molecular axis and the molecular row was ca. 60~65°. The magnified image (15 x 15 nm²) of the gold surface in other even-numbered alkanes, C₁₂ and C₁₄, (Figs. 2-1a, a', c and c') showed the identical molecular arrangement as to that observed in C₁₆, except for that the lengths of the rods were 1.6 nm, and 2.0 nm for C₁₂ and C₁₄, respectively.

The structure of the reconstructed Au(111) surface also affected the orientation of the alkanes. In all the cases, the molecular axis was preferentially oriented close to the NN direction which crossed the bridging row of gold reconstruction by 30°, i.e., the $[1\bar{1}0]$ and $[0\bar{1}1]$ directions, although there is another NN direction which crosses the bridging row by 90°, i.e., the $[\bar{1}01]$ direction (Figs. 2-2a and b; we refer to the former and the latter as NN(30) and NN(90), respectively). The influence of the surface corrugation due to the reconstruction of the gold surface was apparent in the image shown in Figs. 2-3 which was obtained in C₁₆. The domain boundary of the molecular rows was formed following to the

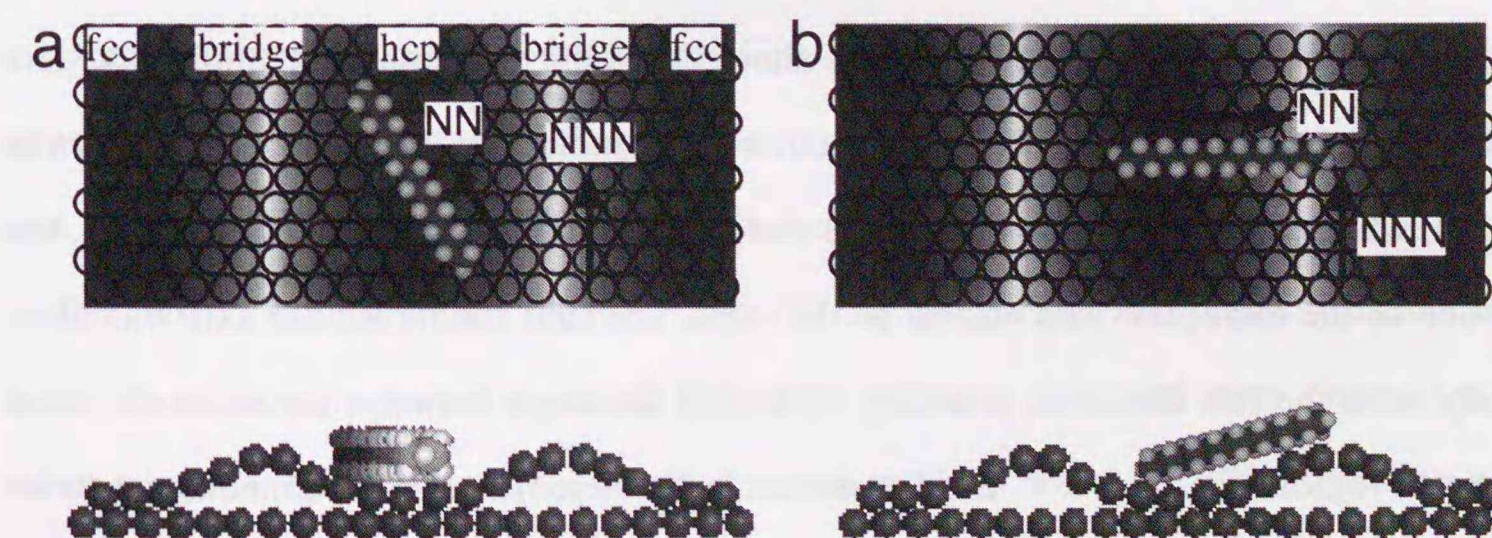


Fig. 2-2 Schematic model of the reconstructed gold surface and relative arrangement of alkanes. (a) NN(30) and (b) NN(90).

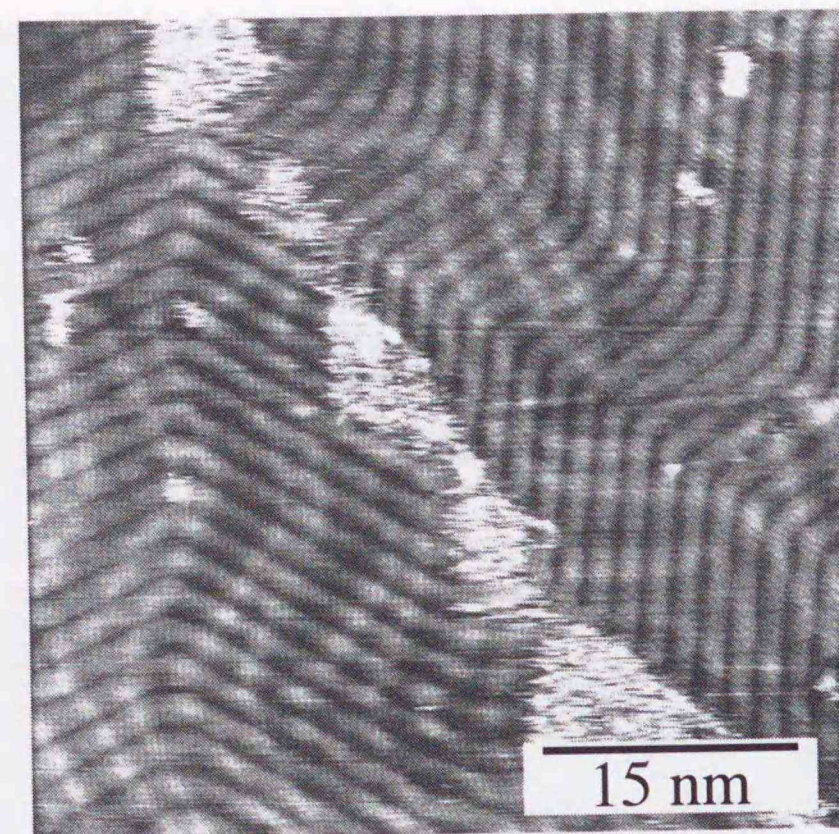


Fig. 2-3 An STM image of Au(111) surface in C₁₆ which shows the domain boundary of the alkane structure and the herringbone of the gold surface.

domain structure of the herringbone structure of the gold surface (see the center of the figure). On the contrary, the domain of the molecular row continued over the step on the gold substrate when the domain of the herringbone structure also continued beyond the step. The preferential orientation of the molecular axis to NN(30) can be explained by considering the corrugation of the gold surface. The winding of the gold surface is less in NN(30) (Fig. 2-2a) than that in NN(90) (Fig. 2-2b), and it should be unfavorable to adapt the molecular skeleton to the NN(90) direction.

The detailed analyses of the STM image showed that the direction of the molecular axis slightly changed by $12 \sim 15^\circ$ when the direction of the molecular row changed as shown in Fig. 2-4, which was obtained in C₁₄. If the molecular axis is along the $[1\bar{1}0]$ direction, the direction of the molecular axis should be the same, and thus the molecular axis was tilted slightly from the NN direction, probably by half of the angle between the molecular axes in the two regions, i.e., $6 \sim 7.5^\circ$, and the molecular arrangement is not commensurate with the gold surface.

The 2D crystals but with a different molecular row structure were observed when the STM measurement was carried out in the odd-numbered alkanes, C₁₃, C₁₅ and C₁₇, as

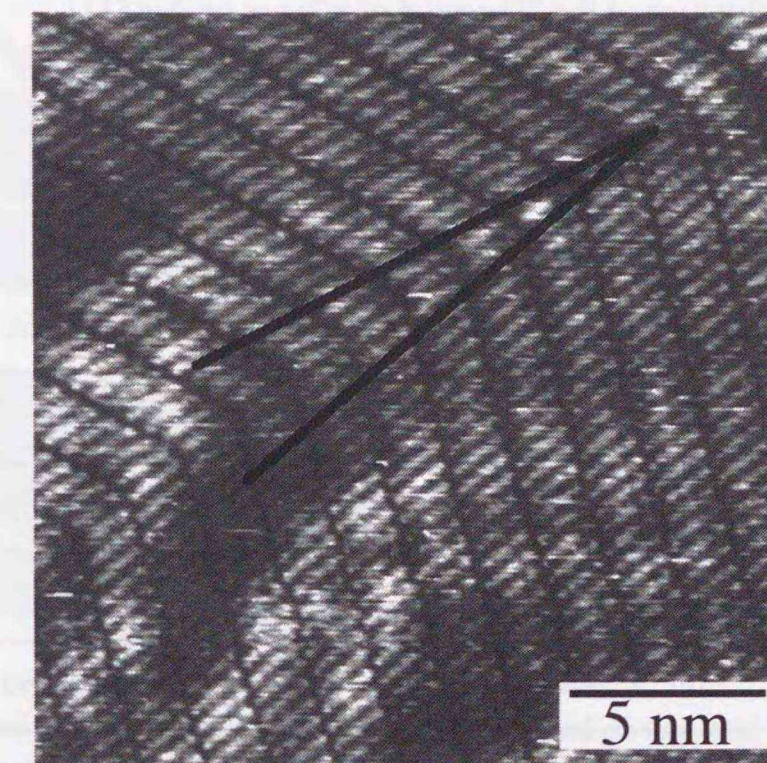


Fig. 2-4 An STM image of the Au(111) surface in C₁₄.

shown in Fig. 2-1b, b', d, d', f, and f', respectively. Let us discuss the structure observed in C₁₇ in detail (Figs. 2-1f and f'). In contrast to the case of the even-numbered alkanes, the straight rows ran in the $[\bar{1}\bar{1}2]$, i.e., the next-nearest neighbor (NNN), direction of the gold surface (Fig. 2-1f). The magnified image shown in Fig. 2-1f' showed that the row structure again consisted of rods of 2.3 nm length and the angle formed by the molecular row and molecular axis was ca. 90° , indicating that the molecular axis was oriented in the $[1\bar{1}0]$ direction, i.e., the NN direction of the gold surface. The magnified image of the gold surface in other odd-numbered alkanes, C₁₃ and C₁₅, showed an identical molecular arrangement to that observed in C₁₇ except for the molecular lengths, which were 1.8 nm and 2.4 nm in C₁₃ and C₁₅, respectively, as shown in Figs. 2-1b' and d'.

The above results clearly showed that 2D crystals of alkanes were formed on the Au(111) surface in neat liquid and that their structure was odd-even dependent. As summarized in Table 2-1, the molecular row ran in the NN and the NNN direction when the carbon number was even and odd, respectively, while the molecular axis was close to the NN direction regardless of the carbon number. Figures 2-5a, b show the proposed model structures of the 2D crystals of even- and odd-numbered alkanes, respectively.

Table 2-1 Summary of the structure of the 2D crystal of alkanes on Au(111).

n: (C _n H _{2n+2})	Direction of the molecular row	Angle formed by molecular axis and molecular row (direction of the molecular axis)
12	NN	about 60 (NN)
13	NNN	90 (NN)
14	NN	about 60 (NN)
15	NNN	90 (NN)
16	NN	about 60 (NN)
17	NNN	90 (NN)

These models were constructed based on the STM images and considering the structures of 2D crystals of alkanes on other metal surface previously reported under UHV conditions. The difference in the structure of the 2D crystal between the odd- and even-numbered alkanes may arise from the difference in the symmetry of the molecule which is determined by the direction of the terminal methyl group as shown by arrows in Fig. 2-5 (discussed later in detail). Considering the close packing structure of the even-numbered alkanes, the two models can be constructed as shown in Figs. 2-5a and a'. Apparently, the observed structure was similar to the model shown in Fig. 2-5a. The molecular lattice shown in Fig. 2-5a was formed probably because it was favorable for the molecular terminal to be arranged in the NN direction of the gold surface. A very similar structure was also observed in the 2D crystal of hexane on a Ag(111) surface in UHV.⁵ The two models were proposed for the 2D crystal of the odd-numbered alkanes shown Figs. 2-5b and b'. The molecular arrangement shown in Fig. 2-5b was constructed by the translation of the molecular row while the neighbor row was inverted in the model shown in Fig. 2-5b'. It was impossible to decide which model was correct from the STM images. The models shown in Figs. 2-5b and b' are identical to the structures of the 2D crystals of heptane on Ag(111) and Pt(111), respectively. Because the structure of the 2D crystals of

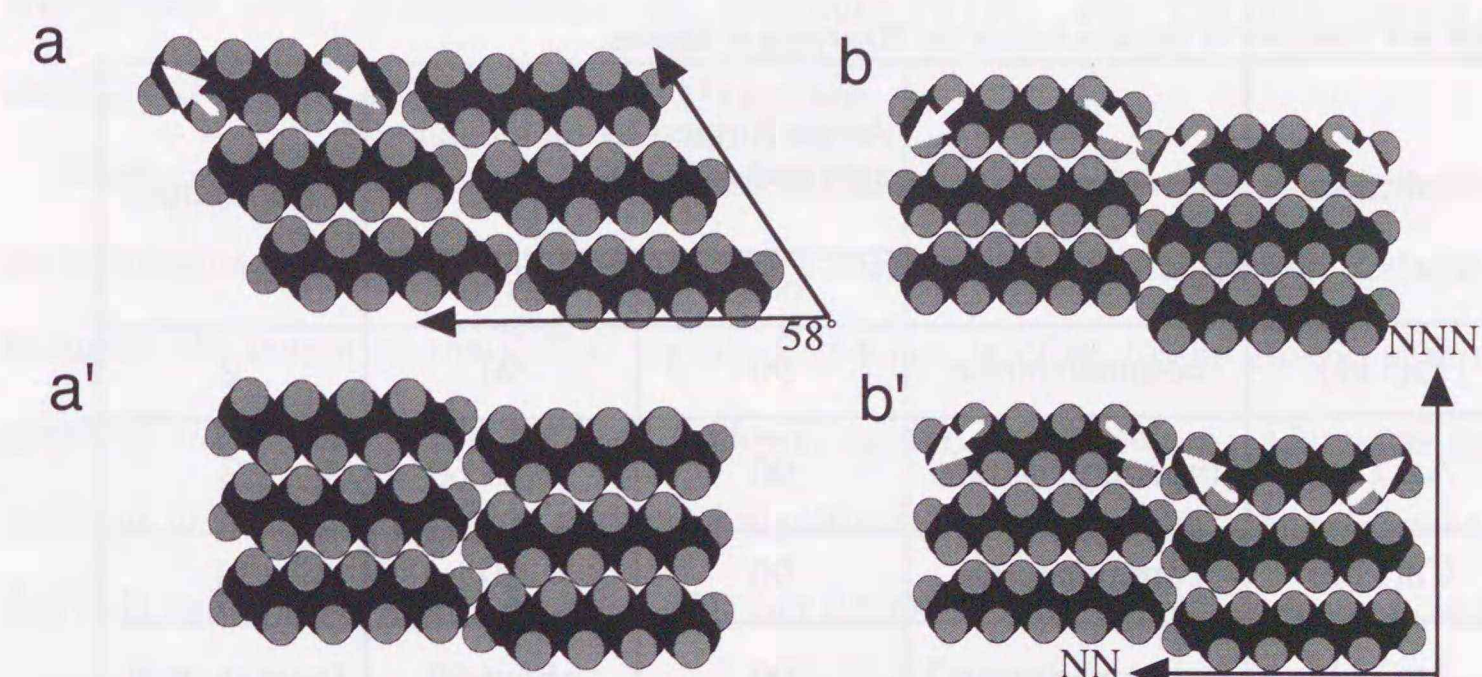


Fig. 2-5 Proposed model of the 2D crystal of even (a and a') and odd (b and b') alkanes.

the even-numbered alkanes on Au(111) was similar to that on Ag(111) and the atomic distance of the Au (0.288 nm) is almost identical to that of Ag, the model shown in Fig. 2-5b seems to be more appropriate.

As mentioned before, the zigzag molecular rows were formed in the 2D crystals of the even-numbered alkanes (e.g., see Fig. 2-1e). The formation of the zigzag molecular row is explained as follows. The well-ordered herringbone structure of the reconstructed gold surface is considered to possess mirror symmetry with respect to the plane parallel to the line formed by connecting the elbows of the herringbone structure in the $[\bar{1}\bar{1}2]$ direction (see Fig. 2-1e) and perpendicular to the gold surface. The direction of the molecular axis is restricted to that close to the NN(30) direction and the directions of the molecular row available for the even-numbered alkanes are those crossing the $[\bar{1}\bar{1}2]$ direction by $\pm 30^\circ$. If the 2D crystal of alkanes consisted of the molecular row with only one direction, the 2D crystal has an anisotropic strain when it is adapted to the reconstructed Au(111) surface. The molecular row in the two directions should equivalently appear to cancel the strain in a macroscopic view. The regular turn of the molecular row may indicate the formation of the stress domain which is formed when anisotropic stress with a long range interaction exists.^{38,39,40} The molecular row of the odd-numbered alkanes was formed in $[\bar{1}\bar{1}2]$ direction, and the structure of the 2D crystal possesses a common symmetric axis with the

Table 2-2 Summary of the structure of the 2D crystal of alkanes.

Substrate	Lattice	Angle formed by molecular axis and row		Reference
		odd	even	
Pt(111)	commensurate	90	90	2
Ag(111)	incommensurate	90	about 60	3
Cu(111)	commensurate	90	60	11
Au(111)	incommensurate?	90	about 60	Present study
hex-Au(100)	incommensurate	90	90	Present study (Section 2-3-2)

gold substrate. As a result, a straight molecular row was formed.

The structure of the alkane adlayer was investigated by low energy electron diffraction on Pt(111),⁴ Ag(111)⁵ and Cu(111)¹³ as summarized in Table 2-2. The odd-even effect on the alkane adlayer was observed on all substrates although the structure was different. Although the angle formed by the molecular axis and the molecular row was 90° regardless of the number of carbons on Pt(111), the number of molecules in a unit cell was higher than that of even numbered alkanes. On the other hand, the angle formed by the molecular axis and the molecular row on Ag(111) was about 60° and 90° for the even- and odd-numbered alkanes, respectively. The herringbone structure of octane ($n = 8$) was observed on Cu(111), while the molecular axis of nonane ($n = 9$) was perpendicular to the molecular row. The molecular axis was in the NN direction in all cases. The preferential orientation of the molecular axis in the NN direction was consistent with the molecular dynamics simulation which showed that diffusion and adsorption along the NN direction was favorable on Pt(111).^{23,24} The local structure of the 2D crystals of alkanes was investigated by STM on graphite in solution; the molecular arrangement was commensurate and the angle between the molecular row and the molecular axis was 90° in both odd^{20,21} and even¹⁴⁻¹⁹ alkane 2D crystals on the graphite. The molecular

arrangement was commensurate on graphite, Pt(111) and Cu(111) but it was incommensurate on Ag(111) and Au(111) surface.

Whether the lattice of alkanes is commensurate or incommensurate should depend on the adsorption energy and matching of surface corrugations with the carbon skeleton. For example, the length of the C-C-C zigzag, 0.254 nm, is close to the atomic spacing of graphite, 0.246 nm (space between hollows), and it is possible to adapt the carbon skeleton to the surface lattice without a significant mismatch. The atomic distances at Ag(111) and Au(111) surfaces are 0.288 and 0.289 nm, respectively, which show large mismatching with the C-C-C zigzag structure. The atomic distance on Pt(111) and Cu(111) is 0.277 nm and 0.256 nm, respectively, resulting in less mismatch with the C-C-C zigzag structure than with the Ag and Au surface.

The adsorption energy of the alkanes on a metal surface has been measured on various metals under UHV conditions.⁶⁻¹² The desorption energy was proportional to numbers of the methylene, ca. 6.5 kJ/mol per methylene unit. The larger adsorption energy on the Pt(111) is expected due to the higher electronic density around the Fermi level of Pt because the van der Waals interaction between the metal surface and a helium atom was shown to be roughly proportional to the electronic density.⁴⁴ Actually, the desorption energy of the alkanes on Pt(111) surface is larger by ca. 5 kJ/mol than that on Au(111).^{6,7,8} Thus, the origin of the commensurate 2D crystal formation on Pt(111) may be due to both strong adsorption energy and lattice matching. Although the desorption energy of alkanes on Cu(111) was not investigated, that on Cu(100) was lower than that on Au(111). Thus, the origin of the commensurate 2D crystal formation on Cu(111) may be mainly attributed to the better lattice matching.

The odd-even effect has also been found in the structure of single crystals of alkanes. The molecular axis is normal and tilted to the layer plane formed by the alkanes when the number of carbons is odd⁴⁵ and even,⁴⁶ respectively. The odd-even effect on the single crystals of alkanes was explained by the rules shown by Kitagorodskii.⁴⁷ The odd-numbered alkanes have an inversion center while the even-numbered alkanes have a

mirror plane at the center of the molecule. The inversion center and the mirror plane, which coincides with the layer plane in a single crystal, should be retained in the crystal lattice to achieve a close packing structure. In addition to the symmetrical requirement, there are two different factors in the packing of alkanes.⁴⁸ The first factor is the interaction between molecules in the same layer which is proportional to the carbon number, and the second one is interlayer interaction, i. e., the packing of methylene terminals. The second factor prefers the tilting of the molecular axis to the layer plane while the first factor prefers for the molecular axis to be normal to the layer plane when the carbon number is even. It is known that when the carbon number in the alkane is over 26, the crystalline structure become monoclinic, i.e., the molecular axis is perpendicular to the molecular layer regardless of the carbon number. This is because the interaction between the molecules within the layer exceeds that between the layer. The same consideration should be applied to the two-dimensional crystals of alkanes. The angle between the molecular row and the molecular axis is restricted to be 90° when the carbon number is odd (Fig. 2-5b), while that could be both tilted and 90° when the carbon number is even. In the present case, the structure of the substrate should be one of the factors in determining the structure.

b. Effect of Iodine Modification on the Formation of 2D Crystals on Au(111) Surface

The STM investigation of the iodine-modified Au(111) surface (I-Au(111)) in C₁₆ was carried out to clarify the effect of the substrate. Figure 2-6 shows an STM image which shows the spots in a hexagonal arrangement 0.46 nm apart with a long-range hexagonal height variation. These features were similar to the rotated hexagonal structure of iodine on Au(111).^{41,42} There were no structures which corresponded to alkane adlayers. The absence of the alkane adlayer is explained in two ways. One reason is that the alkanes were not adsorbed on the surface, and the other is that the alkanes were actually adsorbed on the surface but the STM investigation itself swept them away. Although these two cases are indistinguishable from the STM measurement, it is obvious that the adsorption

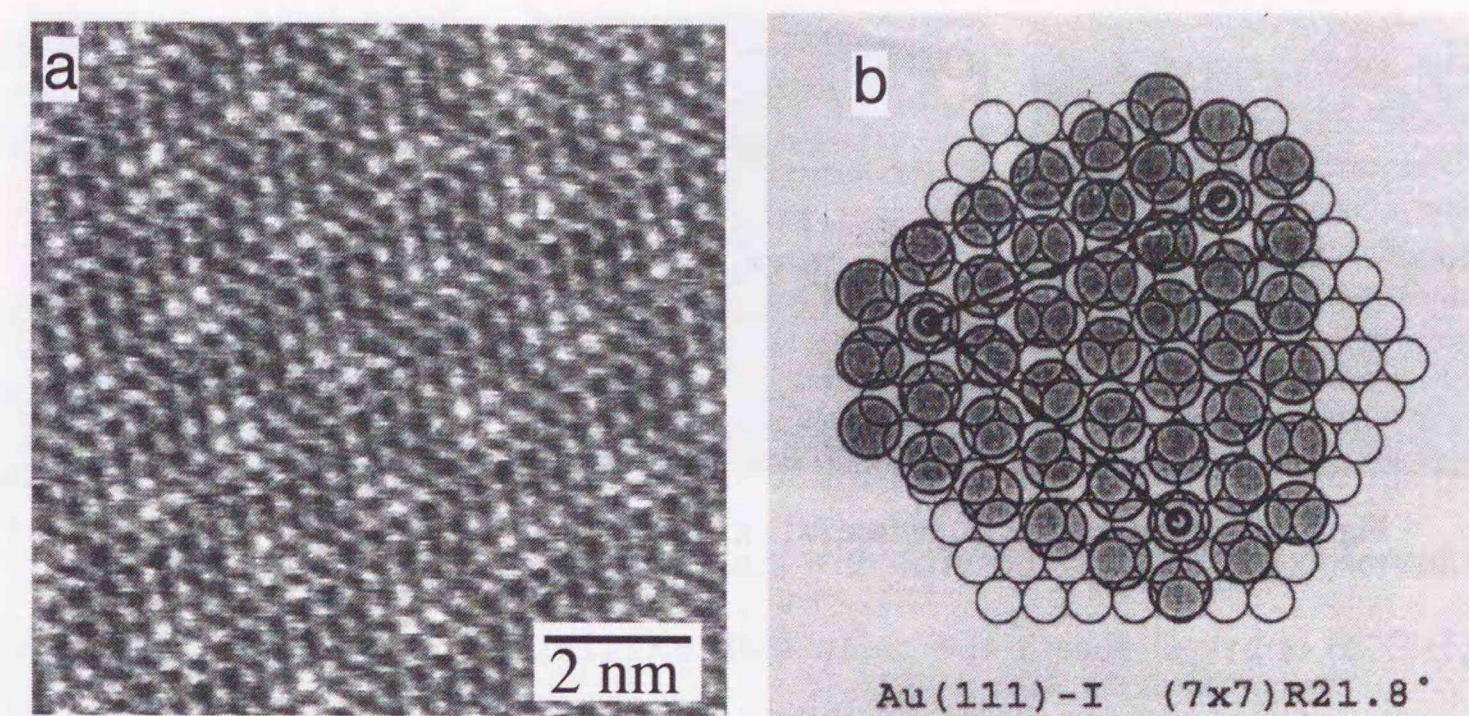


Fig. 2-6 (a) An STM image of I-Au(111) surface in C₁₆. (b) Model structure of (a).⁴²

of the alkanes on the surface was weaker on the I-Au(111) surface than that on a bare-Au(111) surface. It is interesting to compare the present results with the reports of Ogaki *et al.*⁴³ in which ordered layers of organic molecules such as porphyrin and crystal violet were easily formed on iodine-covered Au, Ag and Pt surfaces, although these molecules formed disordered structures on the bare metal surfaces. The formation of the disordered structure on the bare surface should indicate that the surface diffusion and reorientation of the molecules, which were essential for the self-ordering process of the molecules, were prohibited due to the strong attractive interactions between the molecules and the substrates. Ogaki *et al.* suggested that interaction between the molecules and the surface was weakened and became a physical nature on the iodine layer, resulting in the formation of ordered molecular structures. In the present case, the interaction between the alkanes and the substrate was weak even on the bare gold and became too weak to fix the alkanes on the iodine-modified surface.

c. Effect of Temperature on Structure of 2D Crystal of Hexadecane on Au(111) Surface

The effect of the temperature on the structure of the 2D crystal of C₁₆ was investigated by STM with temperature tunable stage. When the temperature of the substrate was increased from room temperature, ca. 25°C, the ordered structure was observed up to

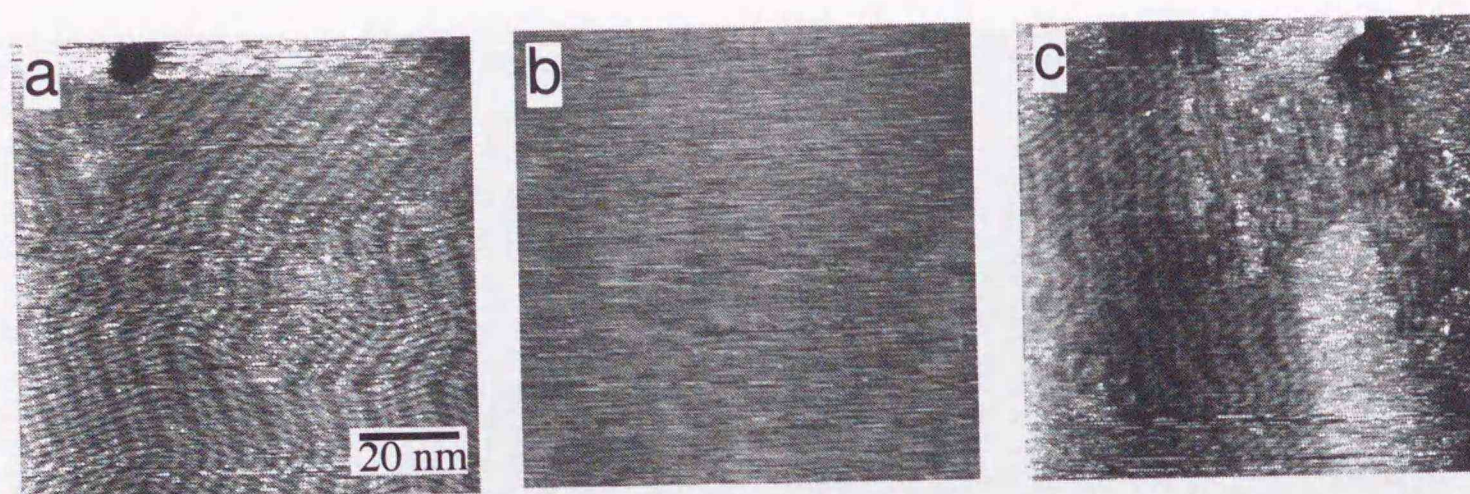


Fig. 2-7 STM images Au(111) surface in C₁₆ at (a) 52°C, (b) 60°C and (c) 68°C.

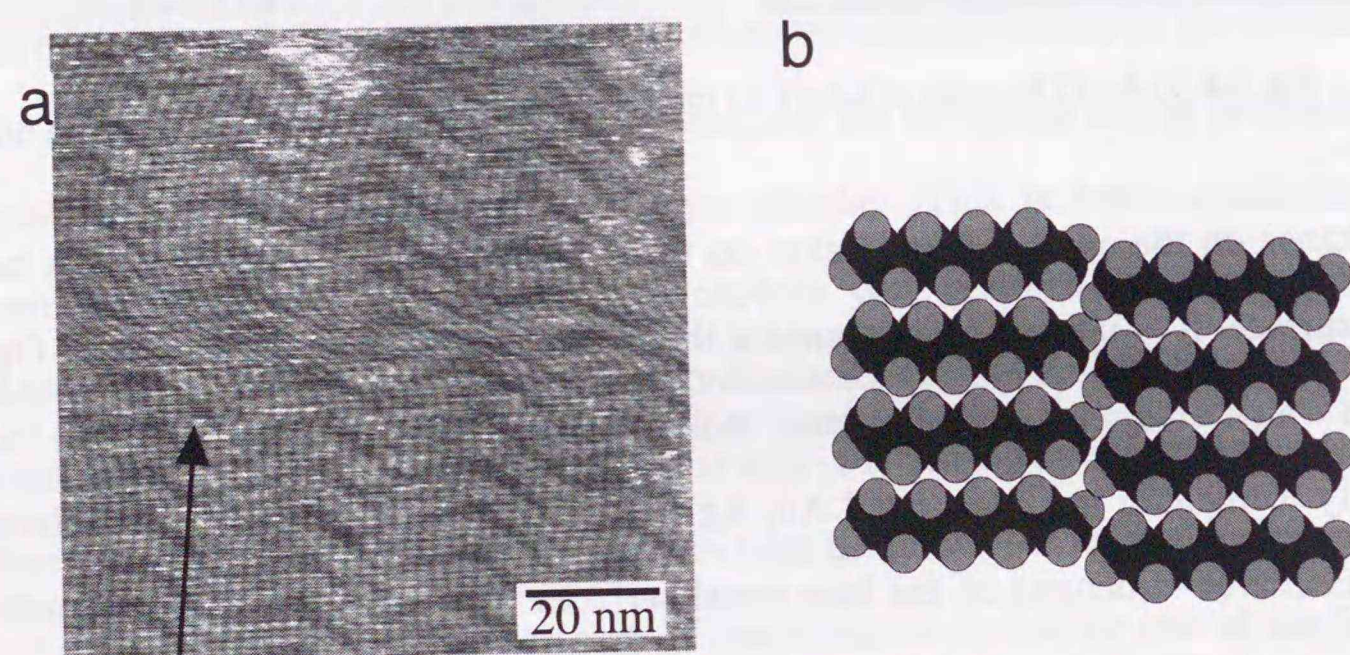


Fig. 2-8 (a) STM images of the Au(111) surface in C₁₆ at 65°C. (b) A proposed model for (a).

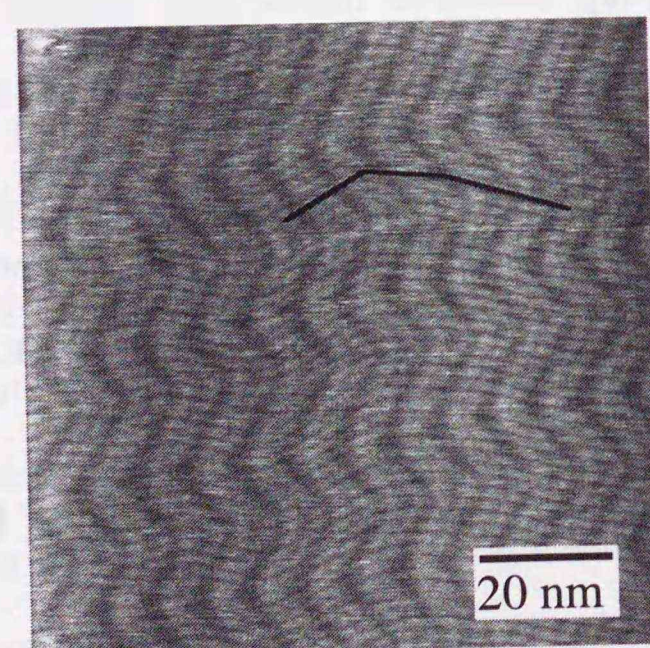


Fig. 2-9 An STM image of the Au(111) surface in C₁₆ cooled from 65°C to 55°C.

around 50°C (Fig. 2-7a). Usually, no ordered regions were observed after the further increment of the temperature up to 65°C (Fig. 2-7b). However, there were cases when the ordered structure was partially observed even at 68°C (Fig. 2-7c). The temperature of order-disorder transition was, therefore, not reproducible. This should be because the order-disorder transition observed here was not a pure-thermal phase transition but was caused by the adsorption of contaminants or destruction of the structure by the tip.

Interestingly, the ordered phase of alkanes with different structure was observed when the neat C₁₆ was put on the Au(111) surface which was already heated to 65°C (Fig. 2-8a). Unfortunately, the structure was easily destroyed during the imaging probably due to the tip and it was difficult to obtain molecularly resolved images. In addition, the image shown in Fig. 2-8a were distorted due to the severe thermal drift. In spite of the distortion, however, the direction of the molecular row was still able to be estimated by comparing to the structure of the gold reconstruction. A line formed by connecting the elbow (indicated in the figure) ran in $\langle 121 \rangle$ direction when the very ordered reconstructed surface was obtained and the molecular row was parallel to this direction. The structure of the 2D crystal of C₁₆ formed at 65°C was similar to the one of the 2D crystal of *odd* alkanes rather than the one of the 2D crystal of even alkanes formed at room temperature since the direction of the molecular row was $\langle 121 \rangle$ and $\langle 110 \rangle$ in the 2D crystal of odd and even alkanes, respectively, as shown previously. The proposed model for the 2D crystal of C₁₆ at 65°C is shown in Fig. 2-8b. When the substrate was cooled to 55°C, the molecular row was slightly curved as shown in Fig. 2-9 although it was not the *zigzag* molecular row observed at the room temperature. When the substrate was heated to 65°C again, the similar structure to the one shown in Fig. 2-8a was observed, indicating that the phase transition between these two structures was reversible, although it is not apparent that the structure at 55°C was stable or meta-stable. Further cooling to 25°C resulted in the formation of the *zigzag* molecular row and re-heating up to 65°C did not showed reproducible result which was the case obtained in the phase transition of the 2D crystal formed at room temperature.

The formation of the crystalline structure of C_{16} formed at 65°C may be explained as follows. When the substrate was heat up, the thermal motion or torsion along the molecular axis were induced and symmetry of the molecules was considered to quasi-cylindrical. As a result, the interaction between the molecular layers were weakened and the interaction between the molecules in molecular row became

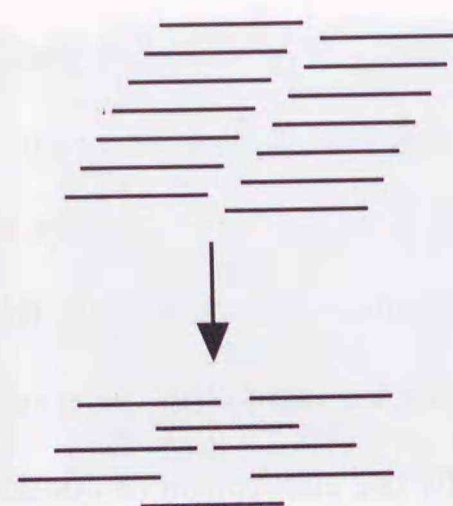


Fig. 2-10 A schematic model for the transition to the hexatic phase.

dominant. The similar phases, which are called rotator phases (R-phases), are known to exist in bulk crystal of alkanes.⁴⁹ One of the phase transitions to R-phases in bulk crystal undergoes the change of the molecular tilt angle with respect to the plane of molecular layer from leaned to perpendicular. Thus, we can conclude that the present result is the first report that showed the existence of the R-phase in two dimensional alkane crystals. In the following, the 2D crystal phase of C_{16} at room temperature and at 65°C is denoted as a normal-phase and R-phase of C_{16} , respectively.

The irreversible behavior of the phase transition between heating up and cooling down is explained as follows. When the 2D crystal of alkanes were heated up from the normal-phase, the induced molecular motion would cause a desorption of the molecule. As a result, molecules on the surface were able to move along the direction parallel to the molecular axis, and molecular row was destructed, resulting in forming the partial-ordered phase in which only the order in short range or one dimension was kept (Fig. 2-10).^{4,5,30,31}

2-3-2 Formation of the Two-dimensional Crystals of Alkanes on Au(100) Surface

To clarify the effect of the atomic arrangement of the substrate on the 2D crystal structure of alkanes, the STM measurement was carried out on the Au(100) surface. Figure 2-11 shows an STM image ($150 \times 150 \text{ nm}^2$) of the Au(100) surface in $C_{16}H_{34}$. The orientation of the gold surface can be determined from the well defined straight

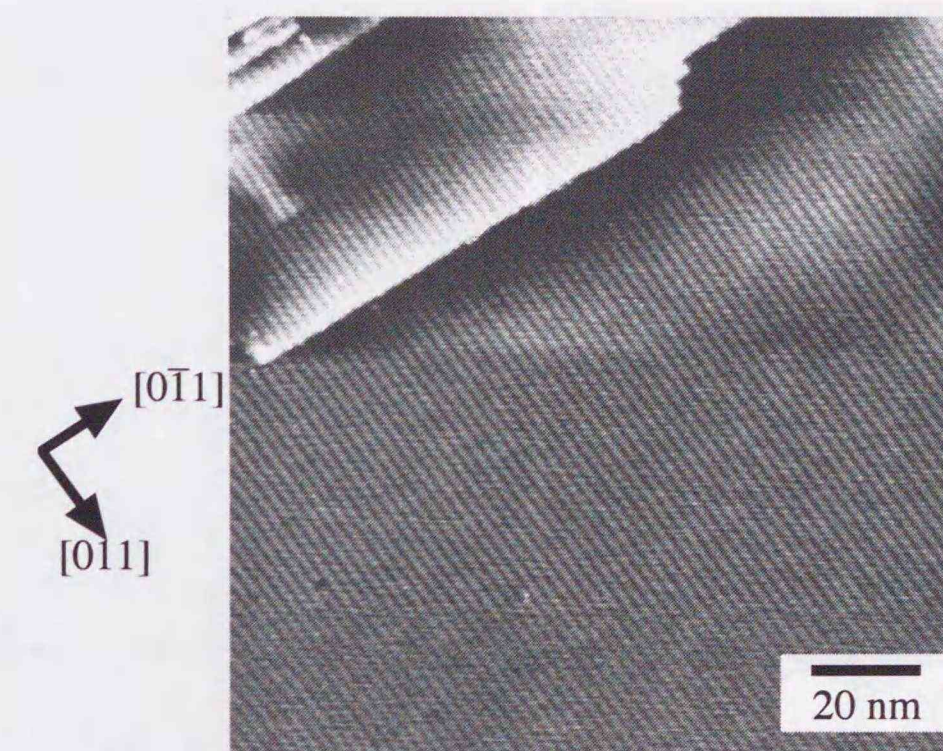


Fig. 2-11 An STM image of the Au(100) surface in C_{16} .

mono-atomic step of the substrate. The stripe structure running perpendicular to the step of the gold substrate, i.e., the $[011]$ direction, is visible in the image. Similar structures were also imaged on the Au(100) surface in $C_{17}H_{36}$. The stripe structure showed a very large domain, e.g., over 300 nm square and continued over the step. Figures 2-12a and b show the magnified STM images ($16 \times 16 \text{ nm}^2$) of the Au(100) surface in $C_{16}H_{34}$ and $C_{17}H_{36}$, respectively. These images clearly show that the stripe structure shown in Fig. 2-11 consisted of rows of rods. The direction of the rows was $[011]$ as defined above and the lengths of the rods were 2.4 nm and 2.6 nm in $C_{16}H_{34}$ and $C_{17}H_{36}$, respectively. The distances between the rods were 0.48 and 0.49 nm in $C_{16}H_{34}$ and $C_{17}H_{36}$, respectively. These values are slightly larger than but close to those of the molecular lengths of $C_{16}H_{34}$ (2.2 nm) and $C_{17}H_{36}$ (2.4 nm) and the widths (0.43 nm). Thus, we can conclude that $C_{16}H_{34}$ and $C_{17}H_{36}$ also formed 2D crystals on the Au(100) surface. The direction of the molecular axes of $C_{16}H_{34}$ and $C_{17}H_{36}$ was perpendicular to the molecular row, i.e., in the $[0\bar{1}1]$ direction. The molecular arrangements of both $C_{16}H_{34}$ and $C_{17}H_{36}$ were identical except for the rod, i.e., molecular length. This is in contrast to the result obtained for the structures of the 2D crystal of alkanes formed on the Au(111) surface

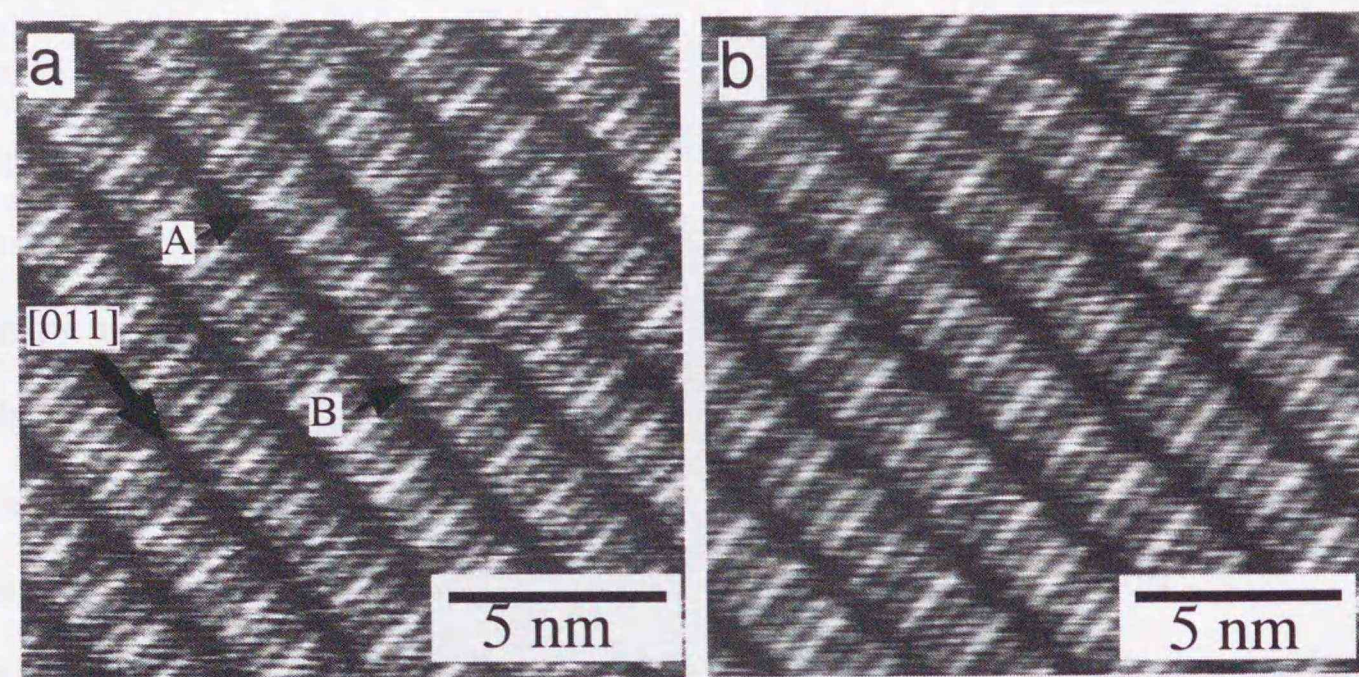


Fig. 2-12 STM images of the Au(100) surface in (a) C₁₆ and (b) C₁₇.

where a clear odd-even effect was observed as shown in the previous sections. Figure 2-12 also shows that there is a regular height variation among the molecules. The elevated molecules appeared nearly every three molecules and the distance between the elevated molecules is ca. 1.4 nm. The existence of elevated molecules can be explained by considering the surface structure of the reconstructed Au(100) surface. It is well known that the annealed Au(100) surface shows the (5x20) or "hex" reconstruction, which shows height variations due to the dislocation of the first surface atomic layer with respect to the second atomic layer as shown in Figs. 2-13a and b.⁵⁰⁻⁵³ The elevated gold atoms form stripe lines directed in the $[0\bar{1}1]$ direction. The observed period and direction of the height variation of the alkane molecules observed in the present study were consistent with those of the surface corrugation due to the hex-Au(100) surface. Thus, we can conclude that the alkane molecules existed on the hex-Au(100) surface with their molecular axes parallel to the elevated atom-rows of the underlying Au(100) surface (Figs. 2-14a and b). This direction also corresponded to the nearest neighbor (NN) atomic direction of the hexagonal gold lattice on the hex-Au(100) surface and is consistent with the molecular orientation observed on the Au(111) surface as shown in the previous sections.

It seems that the lattice of the 2D crystal of alkanes was not commensurate with the one

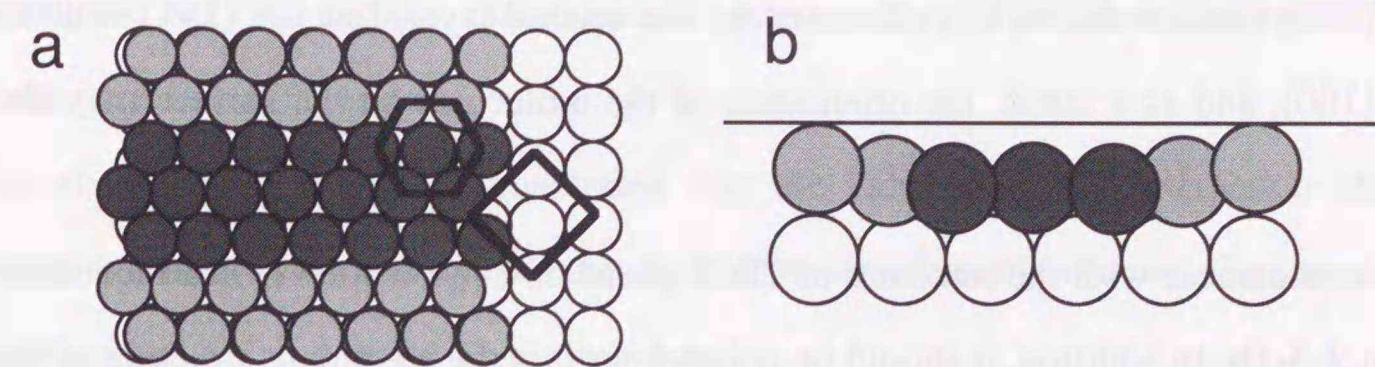


Fig. 2-13 A model of the hex-Au(100) surface.

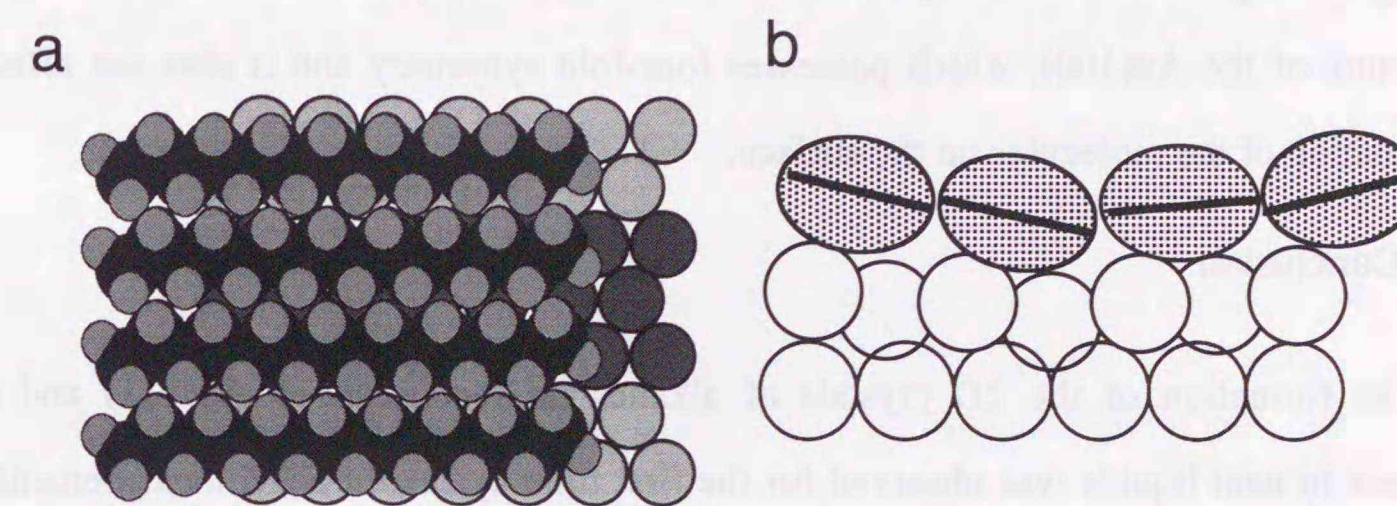


Fig. 2-14 (a) Proposed model of the 2D crystal of C₁₆ and C₁₇ on the hex-Au(100) surface. (b) Sectional view.

of the gold surface as a shift in the molecular location with respect to the substrate was observed. For example, the single molecule indicated by "A" was elevated while a couple of molecules indicated by "B" were elevated in Fig. 2-12a.

As shown above, the structure of the 2D crystal of alkanes did not show odd-even effects on the hex-Au(100) surface, although the microscopic atomic arrangement of the hex-Au(100) surface is similar to the one of Au(111) surface on which a clear odd-even effect was observed. The reason for this difference can be explained as follows. The direction of the molecular axis should be restricted to the one along the surface corrugation in order to fit with the substrate. The distance between the elevated region of the hex-reconstructed Au(100) surface affords three molecules to be arranged (Fig. 2-14a) and the plane formed by the carbon skeleton is not identical among the molecules (Fig. 2-14b) when the plane of the carbon skeleton is fitted to the surface. As a result, the packing of the molecules becomes loose and the interaction between the molecular row is weak. In addition, it should be pointed out that the electronic structure of the top hexagonal layer of

the Au(100) surface should be influenced by the second layer, i.e., the (1x1) structure of the Au(100), and as a result, the orientation of the molecules on the surface may also be affected.

It is comparable with the structure of 2D R-phase of C₁₆ on Au(111) surface shown in **Section 2-3-1b**. In addition, it should be pointed out that the electronic structure of the top hexagonal layer of the Au(100) surface could be affected by the second layer, i.e., (1x1) structure of the Au(100), which possesses four-fold symmetry and it also can affect the orientation of the molecules on the surface.

2-4 Conclusion

The formation of the 2D crystals of alkanes on reconstructed Au(111) and (100) surface in neat liquids was observed for the first time by *in situ* STM measurement. The structure of the 2D crystal of alkanes on Au(111) surface showed clear odd-even effect. The odd alkanes formed molecular rows in which the molecular axis was perpendicular to the molecular row while the molecular axis of the even alkanes was tilted by ca. 65° with respect to the molecular row. The direction of the molecular row of odd and even alkanes with respect to the gold substrate was in the NNN and the NN directions, respectively while the molecular axis of both odd and even alkanes was aligned in the NN direction (the direction molecular row of even alkane was apparently slightly different (~5°) from the NN direction). The observed structures were similar to those of the 2D crystal of alkanes on Ag(111) formed in UHV. The subtle corrugation due to the surface reconstruction of the Au(111) surface affected the molecular orientation. The R-phase of the 2D crystal was observed when the alkane was put on the Au(111) surface at 65°C.

The 2D crystalline structure of alkanes on the Au(100) surface did not clearly show an odd-even effect in contrast to the results obtained on the Au(111) surface. The molecular axis and molecular row were directed in the [0 $\bar{1}$ 1] and [011] directions, respectively, i.e., perpendicular to each other, in both C₁₆H₃₄ and C₁₇H₃₆. A height variation in the molecules was observed and it was assigned to the corrugation of the underlying

reconstructed Au(100) surface. The molecular axis was parallel to the stripe formed by the reconstructed Au(100) surface.

The above result clearly demonstrated that the balance of the interaction between substrate and molecules and among the molecules significantly affected the structure of the physisorbed ordered layers on the surface.

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Chapter 3

Formation of Chemisorbed Two-dimensional Ordered Layers of Alkanethiols on Au(111) Surface - The Self-Assembled Monolayer -

The formation of a self-assembled monolayer (SAM) of alkanethiols on a gold surface is a well-known phenomenon. The process involves the chemisorption of thiol groups onto the gold surface, followed by the self-assembly of the alkyl chains into a highly ordered two-dimensional lattice. This process is typically carried out in a solution of the thiol in an appropriate solvent, with the gold surface being exposed to the solution for a certain period of time. The resulting SAM is characterized by its high degree of order and its stability against desorption. The SAMs formed on gold surfaces have a wide range of applications, including in the field of catalysis, where they can be used to modify the surface properties of the gold particles. They are also used in the field of electronics, where they can be used to create molecular wires and other nanoscale devices. The study of SAMs is an active area of research, and many new techniques have been developed to study their structure and properties. One of the most common techniques used to study SAMs is X-ray photoelectron spectroscopy (XPS), which can be used to determine the chemical composition and the binding energy of the atoms in the SAM. Another technique that is commonly used is atomic force microscopy (AFM), which can be used to image the surface of the SAM and to measure its mechanical properties. The study of SAMs is also important for understanding the fundamental principles of self-assembly and for developing new materials and devices.

Chapter 3

Formation of Chemisorbed Two-dimensional Ordered Layers of Alkanethiols on Au(111) Surface

-The Self-Assembled Monolayer -

3-1. Introduction

One of the most useful ways to form the chemisorbed two-dimensionally (2D) ordered molecular layers is the self-assembly (SA) method as mentioned in Section 1-4. Self-assembled monolayers (SAMs) of alkanethiols on gold have been the subjects of numerous studies¹⁻¹¹ because they have wide varieties of potential applications such as sensors, corrosion inhibition, wetting control, and biomolecular and molecular electronic devices. Although it is generally believed that the SAMs of alkanethiols are formed as a result of the chemical bond formation between substrate atoms and sulfur atoms of thiols and the hydrophobic interaction between alkylchains, their growth process is not clear yet. To construct well designed SAMs, it is essential to understand their fine structure and growth process. The molecular arrangements of the SAMs of alkanethiols on gold at the saturation coverage have been investigated by scanning probe microscopy,¹²⁻¹⁸ He atom diffraction¹⁹ and other methods.²⁰⁻²² These investigations showed that the SAMs of alkanethiol have a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure and a $c(4 \times 2)$ structure of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ basic lattice at the saturation coverage. We refer the latter structure as “ $c(4 \times 2)$ structure” in the following sections for simplicity.

STM investigations of the self-assembled monolayer (SAMs) shows that there are pit-like defects and many domain boundaries.¹³ The pit-like defect was revealed to be the pits of the gold substrate, which is called vacancy islands (VIs) of the gold surface as a depth of them, 2.4 Å, was consistent with a monoatomic step height of Au(111) and the STM image within the pits showed the structure consistent with the one of SAMs of alkanethiols, i. e., the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure.^{23,24} It is also known that the domain boundary runs between the VIs as though it is a crack connecting the VIs and, thus, the

number of the VIs is one of indicators of the defect density of the SAM. The formation mechanism of the VIs of gold surface is still not clear. Poirier and Pylant carried out *in situ* observations of the SA process by scanning tunneling microscopy (STM) in UHV conditions^{25,26} and observed that the VIs of the gold surface was formed at the very early stage of the SA process²⁶ and went through Ostwald ripening.²⁷ They suggested that the VIs of gold surface was formed by the ejection of excess amount of gold atoms than the amount expected for the lifting of the gold reconstruction when the reconstruction of the gold surface was relaxed although the driving force for extra atom ejection was unclear.²⁶ The other explanations proposed up to the present were shrinkage of the surface lattice²⁴ and chemical etching of the gold surface.^{28,29} The latter is important when the SAMs are prepared in solution.

It is essential to investigate the formation process of the SAM to the advanced design of the SAMs in solution and there have been many studies of the SA process of the SAM of alkanethiol by *in situ* and *ex situ* macroscopic techniques such as contact angle measurement,³ ellipsometry,³ infrared spectroscopy (IR),³⁰⁻³² thermal desorption spectroscopy,³³ soft X-ray spectroscopy,³⁴ X-ray photoelectron spectroscopy,³⁵ second harmonic generation measurement,³⁶ quartz crystal microbalance (QCM),³⁷⁻⁴² and surface plasmon resonance spectroscopy.^{43,44} Many of these observations have concluded that the self-assembly (SA) process of alkanethiols consists of two (or more) steps (faster initial and following slower steps),^{3,33,34,38,41,43,44} the former being the random adsorption and the latter being the rearrangement of the adsorbed molecules. While the structure of the SAMs of alkanethiol at the saturation coverage has been extensively studied as mentioned above, the structural change during the SA steps in molecular level has not been reported.

Poirier and Pylant carried out an STM investigation of the SA process of alkanethiols onto Au(111) in UHV condition by controlling the surface coverage using a gas-phase transportation technique.²⁵ In addition to the well known densely-packed upright phases, e. g., the $c(4 \times 2)$ structure and a stripe structure (denoted $p \times \sqrt{3}$)⁴⁵ was observed when

the surface coverage was low. They also mentioned briefly that such stripe structures appeared when gold substrates were dipped into a dilute alkanethiol solution for a short period.

As most of the SAMs are formed in liquid phase, it is very important to clarify the SA process of alkanethiols in solution and compare it with that in UHV. Tamada *et al.* carried out an *ex situ* observation of the SA process of alkanethiols in ethanol by atomic force microscopy.⁴⁶ Although they found the domain formation of the alkanethiols on the gold surface at the initial stage of the SA process, the molecularly resolved image has not been observed and the real SA process should not be clear by *ex situ* examinations.

The objective of the study shown in this chapter is to reveal the SA mechanism in solution in molecular level and to examine the effect of the solvent and temperature of the solution used for the SA on the structure of the SAM by STM.

3-2 *In situ* STM Observation of the Self-Assembly Process of Alkanethiols on Au(111) Surface in Solution

3-2-1 Experimental

Decanethiol ($\text{CH}_3(\text{CH}_2)_9\text{SH}$: C_{10}SH , Wako Pure Chemicals), pentanethiol ($\text{CH}_3(\text{CH}_2)_4\text{SH}$: C_5SH), octadecanethiol ($\text{CH}_3(\text{CH}_2)_{17}\text{SH}$: C_{18}SH , Tokyo Chemical) and heptane (Wako Pure Chemicals) were reagent grade chemicals and were used as received without further purification. Gold substrates were prepared by vacuum evaporation of gold onto a slide glass whose temperature was kept at 300 °C during evaporation. The rate of evaporation was kept 0.01 nm / s and STM investigation of the obtained gold surface shows that (111) terraces of ca. 200 nm diameter were existed on the gold surface. The gold substrates were flame-annealed to remove surface contaminants before they were put into an STM cell.

STM measurements were carried out with a Pico-SPM (Molecular Imaging) STM unit controlled by a Nanoscope E (Digital Instruments) at room temperature (ca. 25 °C). The dimension of the STM cell is 6 mm in diameter and 5 mm in depth. STM tips were

prepared from Pt-Ir (8:2) wire (Tanaka Precious Metal) by mechanical cutting method and used without any coating. STM images were taken in constant current mode with bias voltage of 0.7 ~ 1 V and tunneling current of 30 pA.

3-2-2 Results and Discussions

(a) Self-assembly of Decanethiol ($C_{10}SH$).

The gold surface was first investigated in pure heptane to make sure that terrace of Au(111) was atomically flat and there was no crucial surface contamination. An STM measurement was stopped and droplets of 0.5 μM $C_{10}SH$ solution in heptane were injected into the STM cell. The estimated concentration of $C_{10}SH$ in the STM cell was ca. 0.3 μM . The STM measurement was restarted within 5 min after the addition of the $C_{10}SH$ solution and the SA process of $C_{10}SH$ on Au(111) surface was continuously monitored for ca. 1 hour.

Figure 3-1 shows STM images of Au(111) surface obtained a. 3 min, b. 7 min, c. 12 min and d. 56 min after the addition of the $C_{10}SH$ solution. Note that the concentration of $C_{10}SH$ in the STM cell changed with the adsorption of $C_{10}SH$ onto the gold surface since the amount of the $C_{10}SH$ molecule in the solution was only ca. 40% of that required for the saturation coverage in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. Figure 3-1a shows that stripe structures as well as the triangular pits were existed on the gold terrace just after the addition of the $C_{10}SH$ solution. A typical magnified image (Fig. 3-2a) shows that the spacing of the row is about 2.3 nm (Fig. 3-2b, cross section). The triangular pits were observed from the first image after the addition of the $C_{10}SH$ solution and the shape of them were not significantly changed after the imaging was continued, indicating that their formation was not induced by the tip. The depth of these pits is close to the one of the gold monoatomic step, 0.24 nm and, therefore, these pits should be the VIs of gold surface. In Fig. 3-1b which was obtained 7 min after the addition of the $C_{10}SH$ solution, islands whose height is ca. 0.2 nm from the gold surface were observed. Furthermore, the size of the triangular pits became slightly large, suggesting that etching of the gold surface or

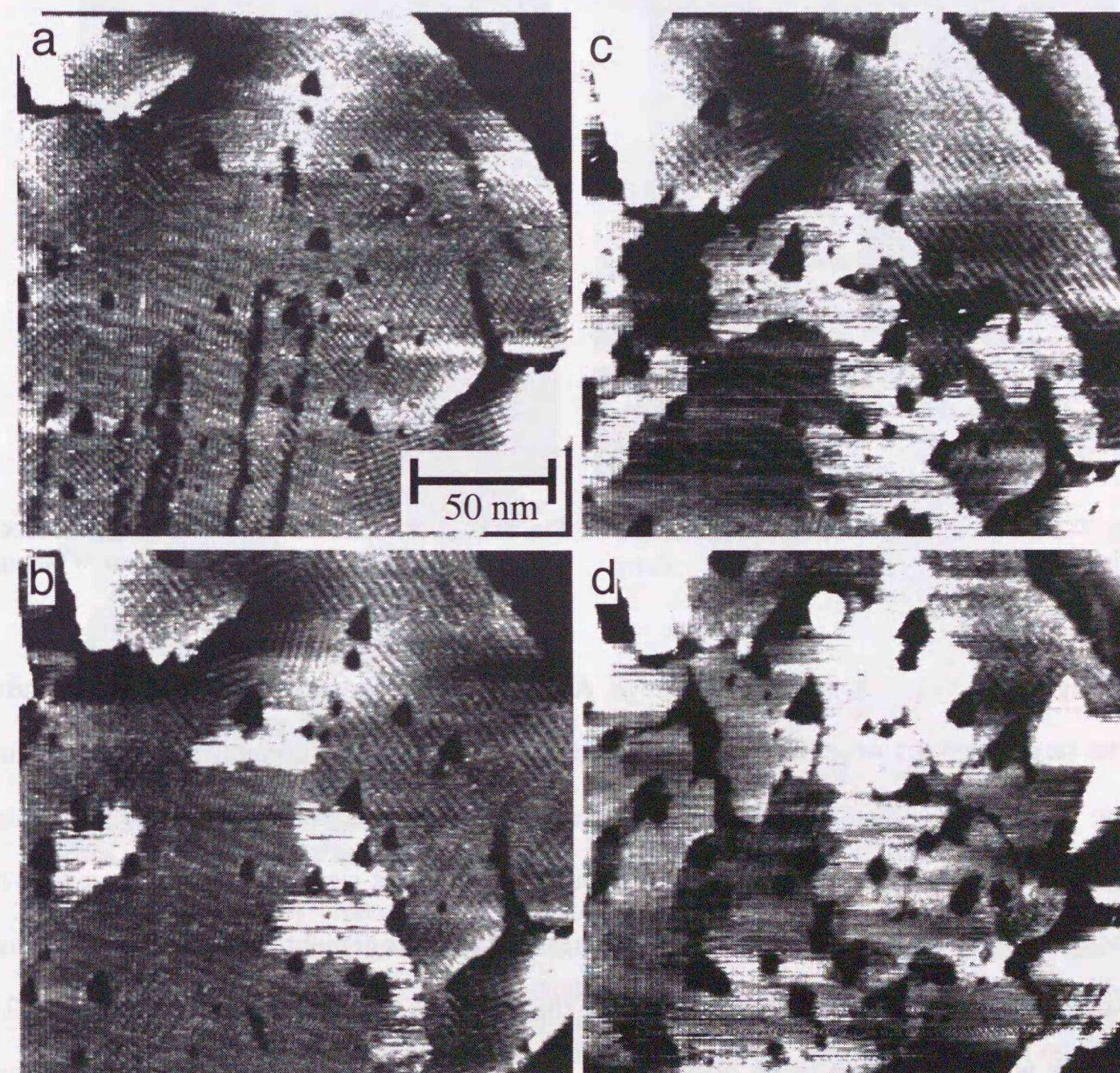


Fig. 3-1. STM images of a gold surface in a heptane solution containing ca. 0.3 μM $C_{10}SH$, captured (a) 3 min, (b) 7 min, (c) 12 min and (d) 56 min after the addition of the modifying solution.

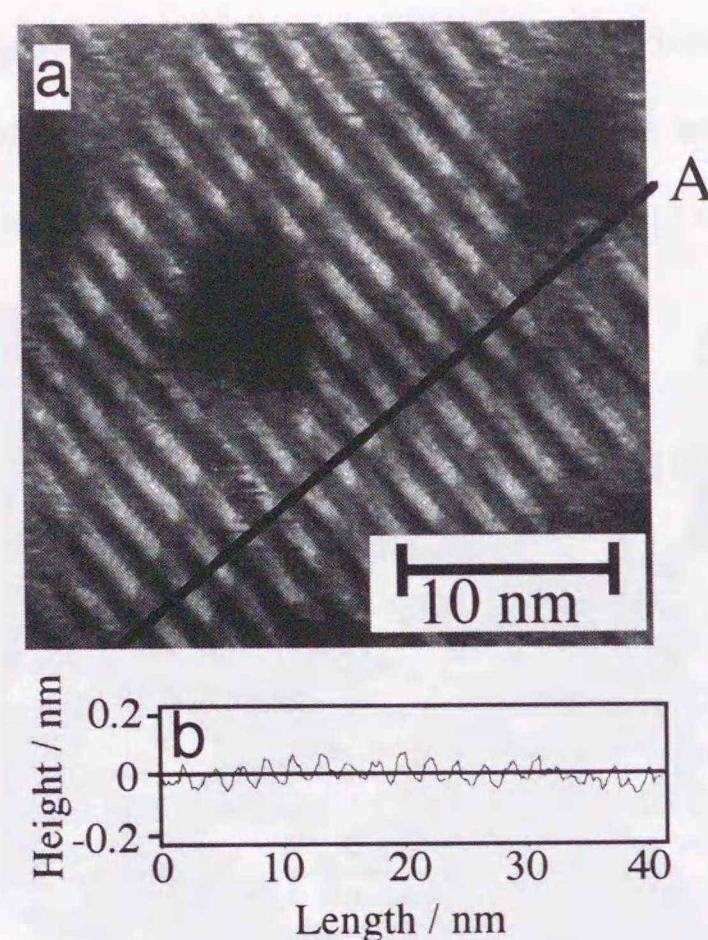


Fig. 3-2. (a) A magnified image of one of the stripe structures. (b) A cross sectional view along line "A".

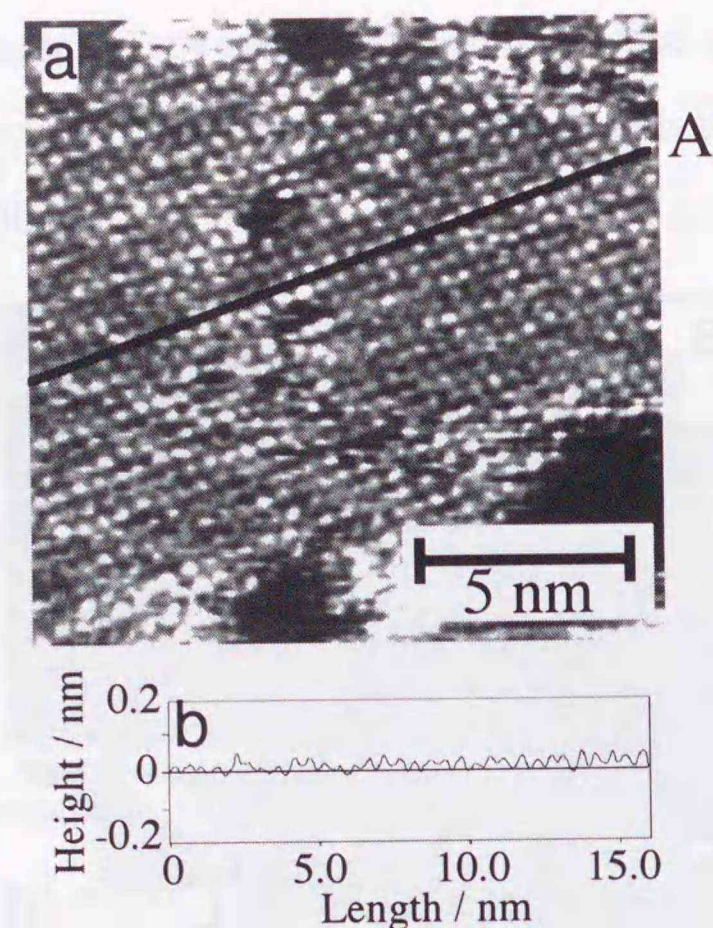


Fig. 3-3. (a) A molecularly resolved image obtained on the islands. (b) A cross sectional view along line "A".

ripening of the VIs took place in this stage. Although no preferential growth of the islands at the step edge was observed, the islands tended to grow at the domain boundary of the stripe structure. Molecularly resolved images were hardly obtained on the island at this stage, probably because molecular arrangement was not yet rigid. The islands grew two dimensionally with time (Fig. 3-1c). The molecular arrangement corresponding to the $(\sqrt{3} \times \sqrt{3})R30^\circ$ was observed on the island at this stage as shown in Fig. 3-3. The $c(4 \times 2)$ structure was still unable to be observed in solution while it was observed in air on the SAM at the saturation coverage in our group. The gold surface was almost covered with these islands 56 min after the addition of the $C_{10}SH$ solution (Fig. 3-1d).

When the SA process was monitored in the solution of lower concentration, the growth of the SAM was inhibited and the details of the SA process could be observed by the sequential addition of the dilute solution of $C_{10}SH$ into the pure heptane. After the surface of a gold substrate was observed in pure heptane to make sure that there was no surface contamination, droplets of $1 \mu M$ $C_{10}SH$ heptane solution was added into the cell while

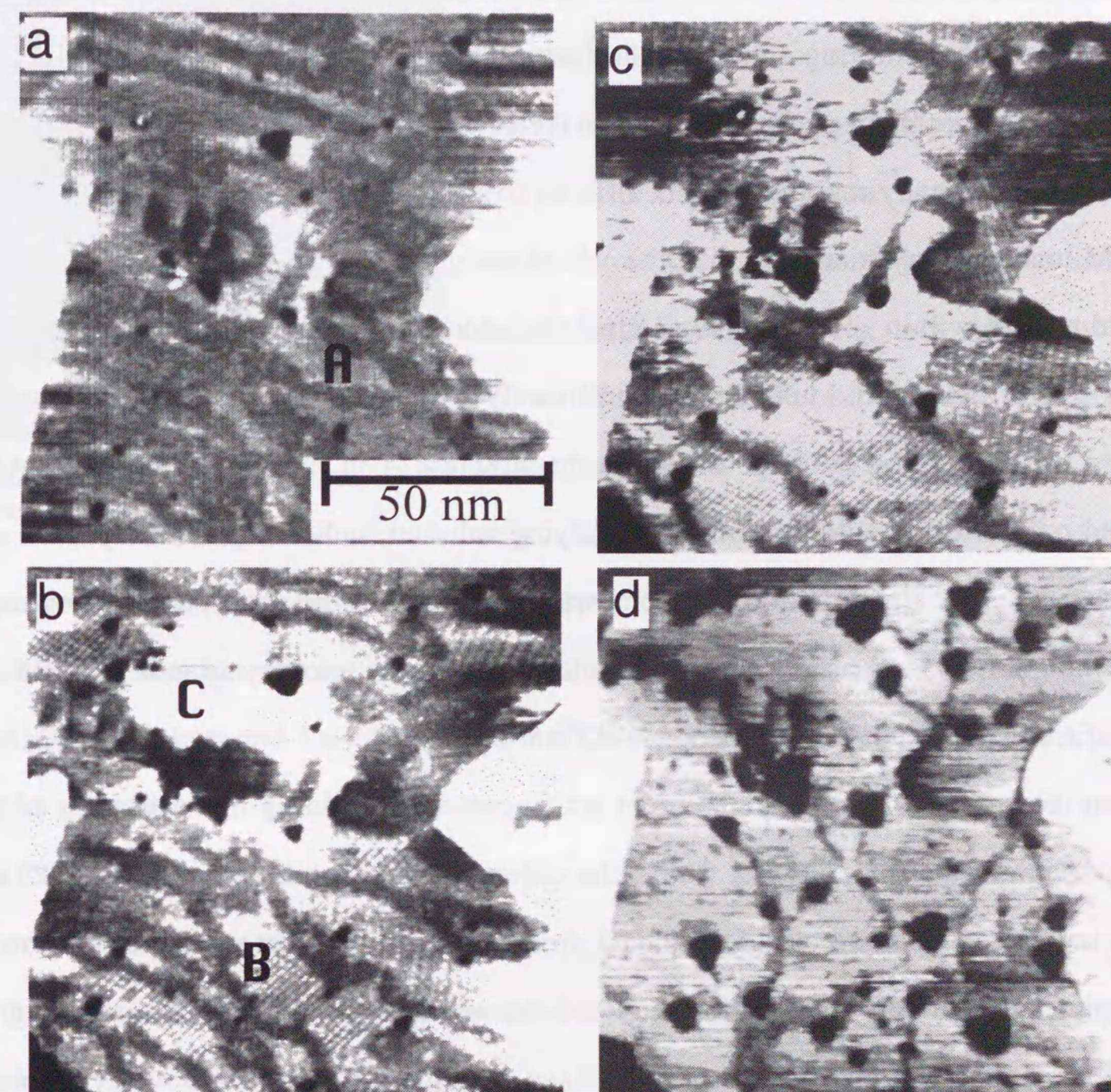


Fig. 3-4. Sequentially obtained STM images of a gold (111) surface taken after the addition of $C_{10}SH$ heptane solution ($170 \times 170 \text{ nm}^2$). (a) 2 min after the *first* addition of the thiol solution, (b) 2 min and (c) 7 min after the *second* addition of the thiol solution, (d) 2 min and (e) 12 min after the *third* addition of the thiol solution and (f) 13 min after the fourth addition of the thiol solution. Estimated concentrations of the solution in the STM cell were ca. (a) $0.1 \mu M$, (b) and (c) $0.3 \mu M$, (d) and (e) $0.5 \mu M$ and (f) $>0.5 \mu M$.

STM measurement was carried out. Figure 3-4 shows sequentially obtained STM images of the gold surface ($170 \times 170 \text{ nm}^2$) at the same position when the concentration of the modifying solution was increased. The time duration after the addition of the droplets of the solution is shown in the figure caption. The area with triangular shape at the right side observed in all the images was a gold terrace which was higher than the other portion by 0.24 nm , i. e., monoatomic step of gold. When a trace amount of the $C_{10}SH$ was existed (ca. $0.1 \mu M$) in the solution (Fig. 3-4a), two-dimensionally (2D) grown structures without

molecular features indicated "A" were observed within several minutes after the addition of the droplets of modifying solution. The featureless regions should be assigned to the bare gold surface or the regions covered with the two dimensional liquid phase of C₁₀SH which has been already reported.⁴⁷ It is difficult to distinguish these structures only from the STM image. Many triangular pits, the VIs of the gold surface, were also observed on the gold terrace within several minutes after the addition of the droplets of the solution and the size of the pits did not change significantly with time. The location of these pits seems to be restricted at the edge or within the structure A in Fig. 3-4a. These pits were observed only after the addition of the modifying solution, indicating that they were not induced by the tip. The depth of these pits was very close to the one of the monoatomic step of the gold (111) surface. Thus, these pits should be the vacancy islands (VIs) of the gold surface which was reported before.^{26,28,29, 48,49}

When the concentration of the solution was increased by adding more droplets of the C₁₀SH solution (ca. 0.3 μ M, Fig. 3-4b), the ordered stripe structures indicated "B" and islands indicated "C" were observed. These structures appeared just after the addition of the droplets of the modifying solution. Figure 3-4c, which was captured 5 min after Fig. 3-4b was taken, showed that these structures have grown with time. Molecularly resolved images were hardly obtained on the islands at this stage. This fact suggests that the molecular structure was not rigid yet and the adsorbed molecules are in dynamic equilibrium with the molecules in solution⁵⁰⁻⁵² or diffuse on the surface. In many cases, the islands seemed to grow at the domain boundary of the line shaped ordered structures. The areas of these structures increased when the droplets of the 1 μ M C₁₀SH solution were added further so that the concentration of the solution was increased to ca. 0.5 μ M (Fig. 3-4d). The growth of the areas of these structures continued for about ten minutes as shown in Fig. 3-4e, which was captured 10 min after Fig. 3-4d was taken. Molecularly resolved images were rarely obtained on the islands even at this stage.

When the modifying solution was added more ($> 0.5 \mu$ M, Fig. 3-4f), the gold terrace was almost entirely covered with the island structure. The time required for the islands to

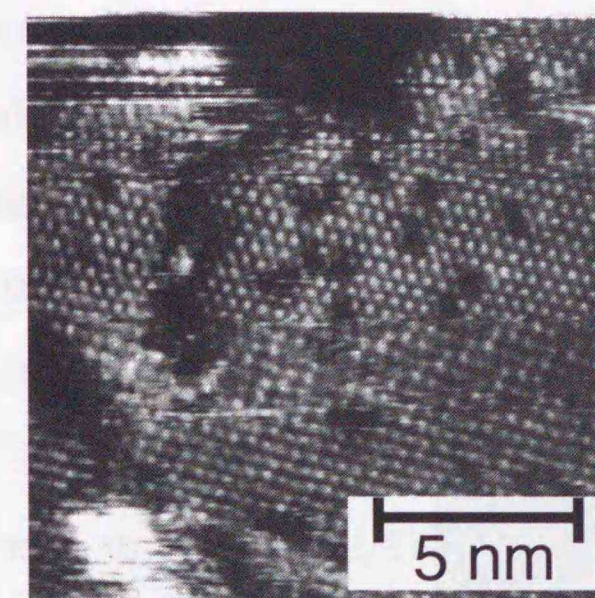


Fig. 3-5. A magnified STM image of the island seen in Fig. 3-4f.

cover the whole surface was highly dependent on the surface conditions and concentration. It took typically ca. 30 min to 1 h in ca. 0.3 μ M solution. At this stage, the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure with defects of the dimension of one or several molecules was observed on the islands as shown in Fig. 3-5. Although the $c(4 \times 2)$ structure was not observed here, this does not

mean that the $c(4 \times 2)$ structure did not exist as molecular structures observed by STM is highly dependent on the sharpness and symmetry of the tip and imaging conditions.^{53,54} Multilayer formation was not observed even in solutions of higher concentration ($\sim 5 \mu$ M).

Although Poirier and Tarlov reported that the Ostwald ripening of the pits took place,²⁷ such a phenomenon was not observed in the present study. The discrepancy is probably due to the differences in the observation period and the mobility of the gold adatom (their observation was carried out with butanethiol [CH₃(CH₂)₃SH]). Actually, the observation of the very initial stage of the VIs formation showed a traces of the ripening process as shown in the later section.

When the SA process was monitored in solutions of higher concentration, e. g., 3 μ M, the stripe structures were hardly observed and the gold surface was covered with the islands very quickly, e. g., within 5 min though the disordered phase was observed. The stripe structures were not observed since the coverage became high enough to form the island structure before the molecules formed the stripe structures.

To investigate the initially observed structures more carefully, the STM investigation was carried out in heptane containing ca. 0.2 μ M C₁₀SH so that the island growth was suppressed. Figure 3-6 shows a typical STM image of the gold surface. At least four kinds of structures, i. e., two types of stripe structure (A and B), a mesh-like structure (C) and islands (D) were observed. Higher resolution image (Fig. 3-7a) provides clearer evidence for the coexistence of the different stripe structures. Molecular rows of each structure run

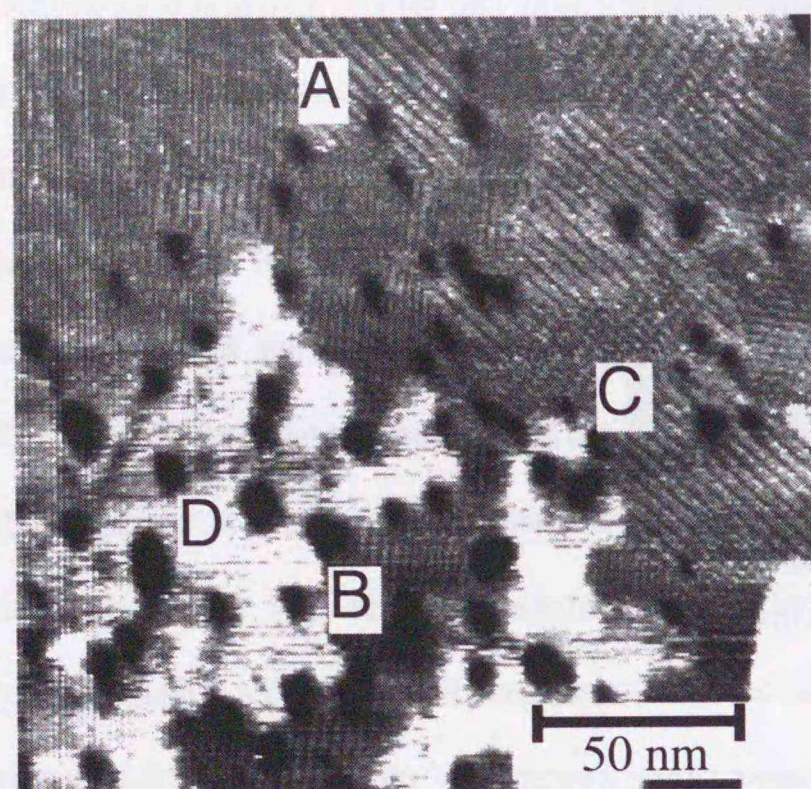


Fig. 3-6. An STM image obtained in ca. $0.2 \mu\text{M}$ solution of C_{10}SH in heptane. "A": the wide stripe structure. "B": the narrow stripe structure. "C": the mesh structure. "D": the island structure.

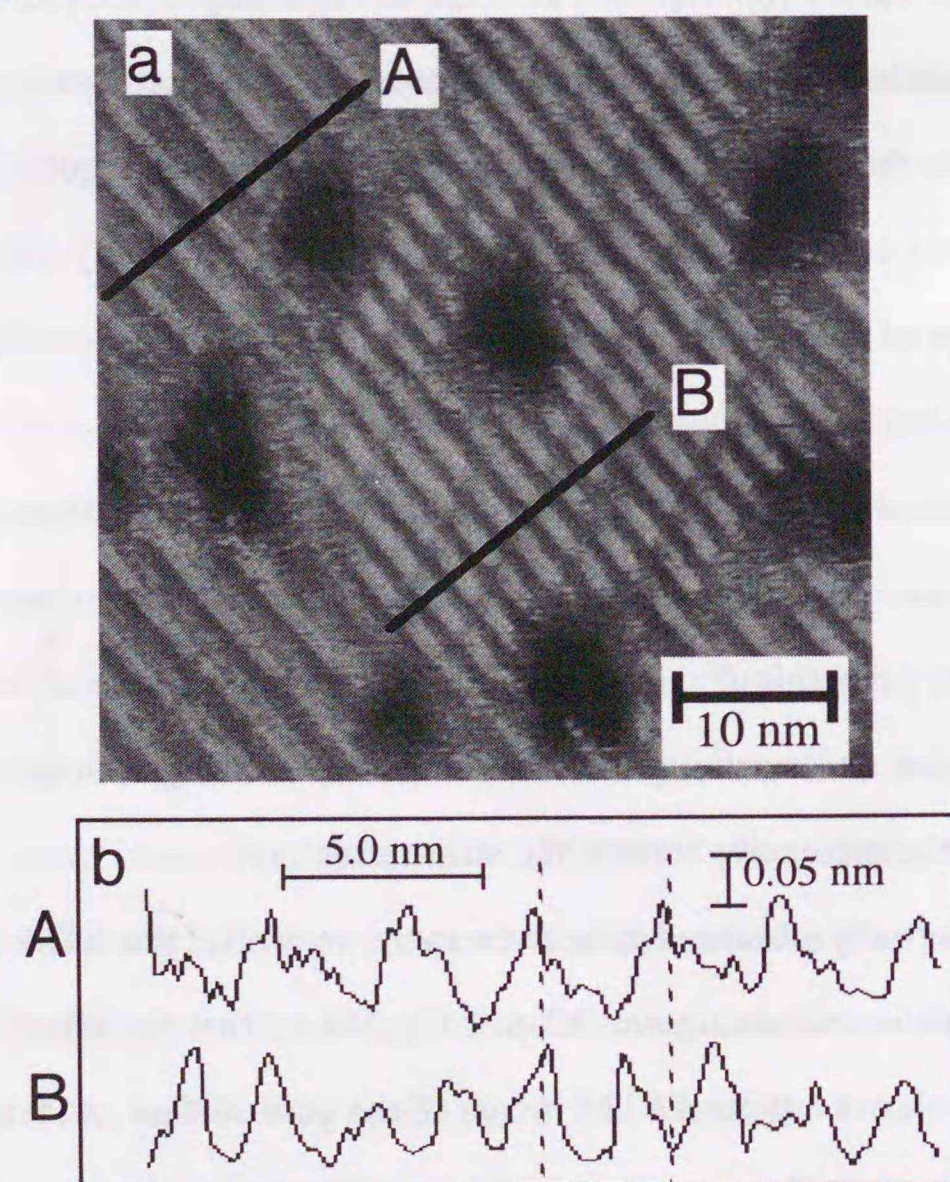


Fig. 3-7. (a) A typical closed up STM image of the region which shows the co-existence of different stripe structures. (b) Sectional views along the line A and B.

in the same direction but their separation is different (see Fig. 3-7b). Thus, these two different structures are not due to convolution with an asymmetric tip but real. These structures were observed for more than 1 hour without significant change, indicating that they were stable under this condition. In many cases, the narrow stripe and the mesh structures were dominantly observed and the wide stripe was rarely observed.

Figure 3-8a shows a typical STM image of the structure A. We refer this structure as a

wide stripe structure. The inter-row spacing is 3.2 nm (Fig. 3-8b). This inter-row spacing is close to the one of the $11\sqrt{3}$ structure observed for the SAMs at low coverage in UHV condition.^{19d,45,55} This stripe structure consists of a paired bright row. Considering the space between the strip, the wider stripe structure seems to consist of the molecules which lies down on the surface, i. e., the molecular axis is aligned with the surface plane. This structure is not expected if Au-S chemical bond was formed because sp or sp³ orbital of S atom is known to be used for a Au-S-C bond and the angle of the Au-S-C is 104°

and 180° for the former and the latter orbitals, respectively.⁵⁶ Thus, the molecules in this wide stripe structure should be physisorbed. A similar structure was reported by Cyr *et al.* for self-assembled monolayers of alkanethiols on graphite.⁵⁷ Their observation showed that alkanethiols were preferentially oriented head to head, i. e., thiol to thiol, but occasionally oriented head to tail. In the present case, however, no head to tail orientation was observed. This may be because molecules were in dimerized form, i.e., disulfide.^{20b,}

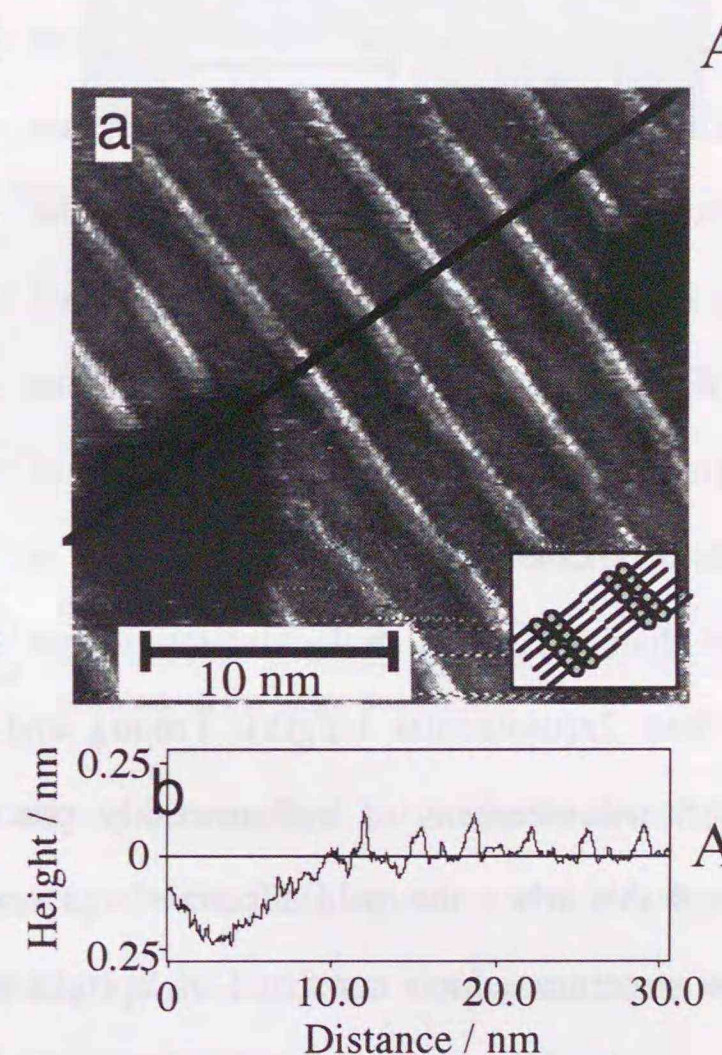


Fig. 3-8. (a) A magnified STM image ($25 \times 25 \text{ nm}^2$) of a wide stripe structure. (b) A sectional view along the line "A".

Figure 3-9a shows a typical STM image of the structure B in Fig. 3-6. We refer this structure as a narrow stripe structure as the inter-row spacing is 2.3 nm (Fig. 3-9b) which is shorter than the one of the stripe shown above. The paired structure was reproducibly observed in different experiments and thus it is not the artifact due to a double tip. The inter-row spacing of the stripe is close to the one expected for a $(5\sqrt{3} \times \sqrt{3})R30^\circ$ (or $7.5 \times \sqrt{3}$) structure which was reported to appear after thermal treatment of SAMs of alkanethiols.^{17d,32,46} This value is larger than the single molecular length but less than $2 \times (\text{molecular length})$. Troung and Rowntree carried out *ex situ* STM and IRRAS measurement of self-assembly process of butanethiol in dilute solution and showed that when the gold substrate was soaked in dilute solution for a long time, the stripe structure which consisted of upright molecules was formed.^{31,59} Although their results seemed to support that the narrow stripe structure of the present study may also consist of upright molecules, Poirier proposed the another structure based on molecularly resolved STM images.⁶⁰ He succeeded to observe the alkylchains between the bright rows and concluded that the $7.5 \times \sqrt{3}$ structure is formed when the alkylchains are piled up each other (Fig. 3-9a inset).

In addition to the stripe structures which are very similar to those reported in UHV condition,^{19d,25,27,45,47} a mesh-like structure shown in Fig. 3-10a, which has never been reported, was observed (recently, Poirier reported the similar structure in UHV⁶⁰). The unit structure has a shape of parallelogram and consists of paired rows separated by 1.3 nm. The period in short side (A) and the long side (B) is 2.5 nm and 4.5 nm, respectively

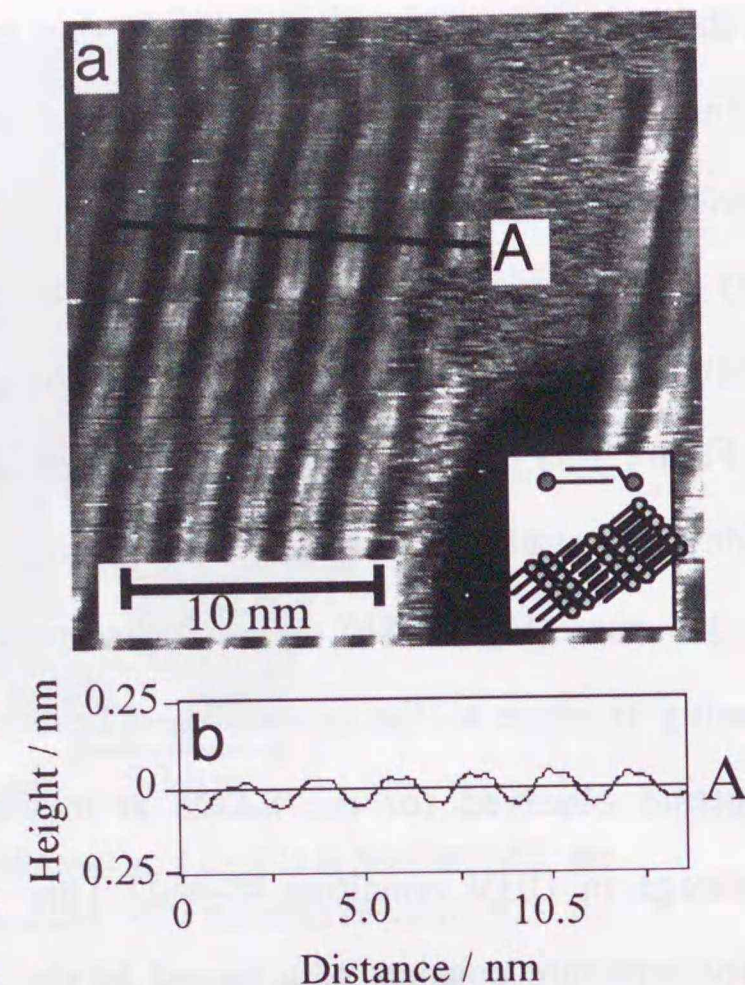


Fig. 3-9. (a) A magnified STM image ($25 \times 25 \text{ nm}^2$) of a narrow stripe structure. (b) A sectional view along the line "A".

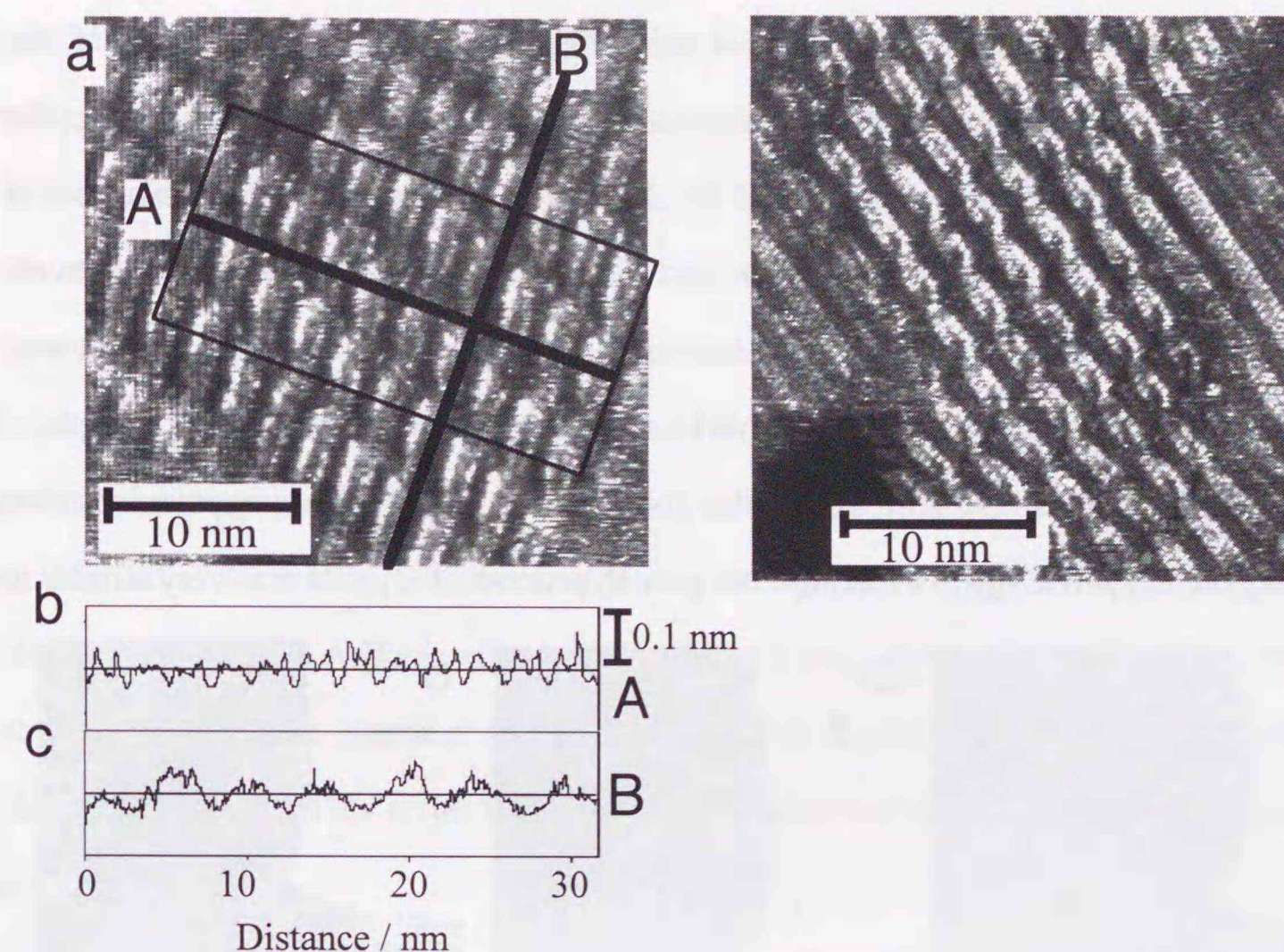


Fig. 3-10. (a) A magnified STM image ($30 \times 30 \text{ nm}^2$) of a mesh structure. (b) and (c) Sectional views along the line "A" and "B", respectively.

Fig. 3-11. A closed up STM image ($30 \times 30 \text{ nm}^2$) which shows a transitional state from the mesh structure to the stripe structure.

(see Fig. 3-10b and c). Note that Fig. 3-10b shows an averaged height in the direction of the paired rows within a rectangle drawn in Fig. 3-10a. This structure was dominantly observed at the initial stage of the SA process of C_{10}SH . There were even cases when only the mesh structure covered the gold surface. Although it is difficult to discuss the molecular arrangement of the mesh structure only from the STM image, this structure seems to be an one variation of the narrow stripe structure as a structure which seems to show a transition from the mesh to the narrow stripe structure was observed at a certain portion of the surface as shown in Fig. 3-11. At the center of the figure, the unit structures of the mesh are started to be connected each other. Stripes are also seen in the figure.

(b) Self-assembly of alkanethiols of longer alkylchain (C_{15}SH and C_{18}SH).

Figure 3-12 shows STM images of the gold surface obtained in a heptane solution containing ca. $0.5 \mu\text{M}$ C_{15}SH . The narrow stripes and pits were observed even just after the addition of the modifying solution (Fig. 3-12a). Although the STM images of the same

region obtained 1 min (Fig. 3-12b) and 4 min (Fig. 3-12c) after the addition of the modifying solution clearly showed that the pits and the stripe structure grew with time, the growth of the latter was more significant. The observed SA process was similar to that of C₁₀SH except the fact that the wide stripe and the mesh structure were rarely observed. The corrugation period perpendicular to the stripes was about 2.7 nm. This value was larger than that of the narrow stripe of C₁₀SH but shorter than the 2x(molecular) length.

Figure 3-13 shows an STM image of the gold surface observed in a heptane solution containing ca. 0.5 μ M C₁₈SH. Although the growth process of C₁₈SH was very similar to

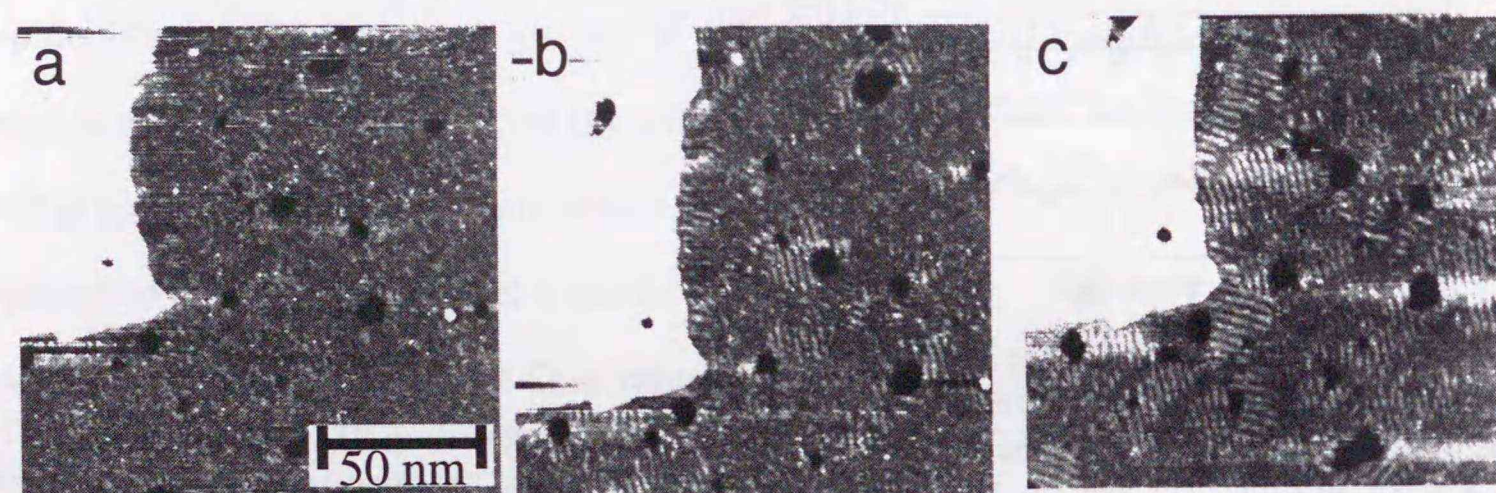


Fig. 3-12. A real time monitoring of self-assembly process of C₁₅SH in 0.5 μ M solution of C₁₅SH in heptane. Each image was obtained at (a) just, (b) 1 min and (c) 4 min after the addition of the droplets of the modifying solution (150 $\times$ 150 nm²).

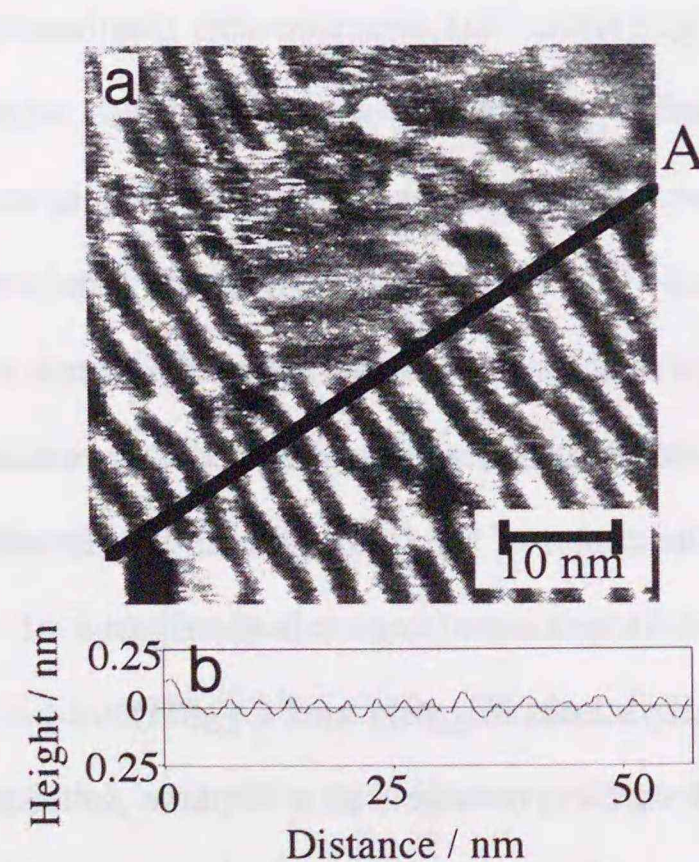


Fig. 3-13. An STM image (50 $\times$ 50 nm²) of the stripe structure of C₁₈SH. (b) A sectional view along the line "A".

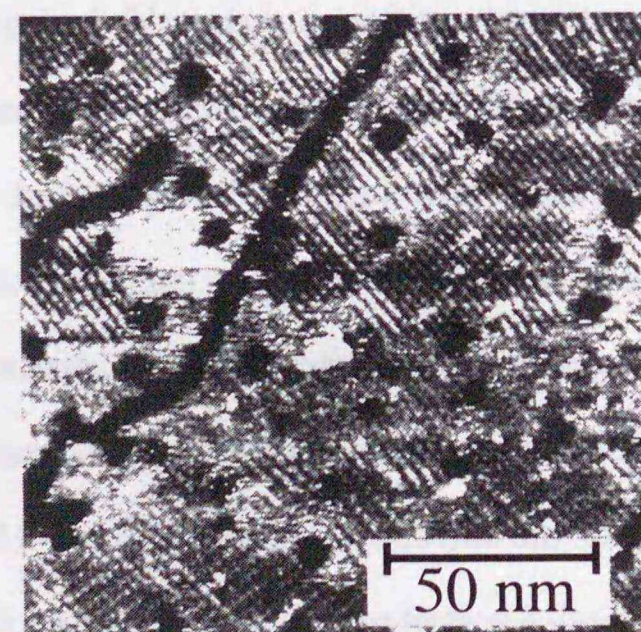


Fig. 3-14. An STM image of the Au(111) surface in 0.5 μ M solution of disulfide (C₁₀S-SC₁₀).

that of C₁₅SH, the corrugation period perpendicular to the stripe lines was 3.3 nm which is larger than those of C₁₀SH and C₁₅SH but shorter than 2x(molecular length). After the further addition of the modifying solution, the STM image became obscure and we were not able to observe the island structure in both C₁₅SH and C₁₈SH solution. This may be because the formation of the $\sqrt{3}\times\sqrt{3}R30^\circ$ structure of these molecules is not promoted in heptane as shown in the later section. or a tunneling gap impedance is not high enough to resolve the long alkanethiol tail and the tip destroyed the structure.

The initial SA structure of the dialkyl-disulfide (CH₃(CH₂)₉S-S(CH₂)₉CH₃) was also observed in a dilute heptane solution. The STM image showed that the stripe and mesh structures which are identical to those observed in C₁₀SH covered the gold surface as shown in Fig.3-14. This result indicates that the adsorbed states of the disulfide and thiol are very similar.

(c) The Formation Process of the VIs.

The very initial stage of the SA process and formation of the VIs was followed by using very dilute solution. Figure 3-15a shows an STM image of Au(111) surface taken 17 min after the injection of the C₁₀SH solution. The concentration of the C₁₀SH in the STM cell was $\sim 0.1 \mu$ M. The brighter patch-like regions should correspond to the disordered phase of the C₁₀SH as reported before. Pits were also appeared within the patch-like regions. These pits should correspond to the VIs of gold surface as the depth of them was close to 0.24 nm. Figure 3-15b shows an STM image after the second injection of the C₁₀SH solution. The concentration of the solution in the cell was still $\sim 0.1 \mu$ M. The area of the patch-like regions were apparently increased and the stripe phase of alkanethiols was observed in these patch-like regions. In addition to the SAM formation, small VIs indicated by arrows in Fig. 3-15a disappeared after the second addition of the C₁₀SH solution as shown in Fig 3-15b. Note that total number of the VIs on the surface counted in larger area was increased as new VIs were also formed in most of cases.

Poirier reported that the VIs started to be formed at the regions where the deformation of the reconstruction of the gold surface became large and the molecules did not exist

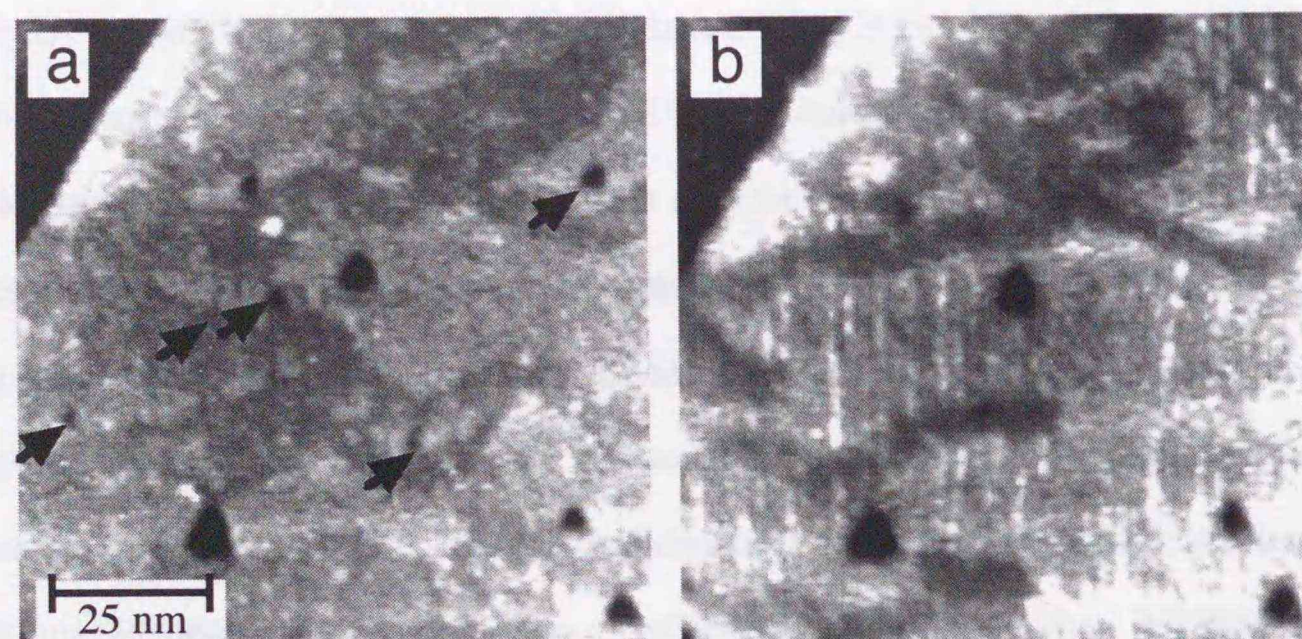


Figure 3-15. (a) STM image of Au(111) surface in heptane 17 min after the addition of the C₁₀SH solution. (b) STM image taken after the second addition of the C₁₀SH solution.

there. This formation process of the VIs may also be applicable for the present case. Thus, the VIs were formed on the bare gold surface around the regions where the thiols were adsorbed and then totally surrounded by the thiols. As a result, the VIs were located at the boundary of the disordered phase in the STM images. In addition, the migration of the gold atoms seems to be enhanced in the region covered with the disordered phase of the thiols, since the ripening of the VIs took place in these regions. Although the ripening of the VIs was not observed clearly after the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure was constructed in the present study, Cavalleri *et al.* observed the one even after the gold surface was covered with the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure at higher temperature,⁶¹ indicating that the gold atoms covered with the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure are still able to migrate on the surface. It should be reasonable to assume that degree of the ripening is affected by the temperature and the effect of the temperature of the solvent is shown in Section 3-4.

Most of the VIs observed in heptane solution was in triangular shape with its side directed to $\langle 1\bar{1}0 \rangle$, i.e., the step of the gold substrate as seen in Fig. 3-15a while the ones observed on the SAM prepared in UHV or in ethanol solution is circular. These results seem to indicate that the diffusion of gold atoms on the surface is faster in the heptane solution than the one in the ethanol solution. The different diffusion rate of gold atom may

related to the difference of the one of gold atoms covered with the disordered thiol phases. The solvent should play an important role in this step as it is possible that the solvent is also included in the disordered phase. The solvent effect on the structure of the SAM is shown in Section 3-3.

3-2-3 Conclusion

The present results have shown that there are at least three steps in the SA process of alkanethiols of various chain length on Au(111). At the initial stage, adsorbed molecules does not arrange in ordered structure. The VIs of the gold surface are created at this stage. At the same time, the VIs ripen in the disordered phase of alkanethiols. Further adsorption of the molecules leads to the initial ordered self-assembled structures such as mesh and stripe, i. e., the $p \times \sqrt{3}$ structure ($p = 7.5$ and 11 for C₁₀SH) when the concentration of the solution is low. The SA process of alkanethiols shown above indicates that the lateral surface pressure in the molecular layer is one of the important driving forces for the formation the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. At a first glance, it seems to be unfavorable for the alkanethiols to form the lying down structure on the gold surface in the heptane solution since the heptane is expected to show good affinity with the alkylchain of the alkanethiols. However, it is natural that the alkanethiols, which were anchored on the gold surface by the sulfur-gold interaction, were laid down even in the heptane solution since the interaction between the gold surface and the alkylchains is stronger than that among the alkanes even in neat liquids as shown in Chapter 2. As a result, surface pressure is required to form the upright- $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. The size of VIs does not change significantly after this stage, suggesting the etching is minor effect on VIs formation. Finally, the islands on which molecules arrange in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, grow and the monolayer formation is completed. The dynamic equilibrium state exists at the early stage of the island growth. The $p \times \sqrt{3}$ structures, whose values of p are not consistent with the surface aligned molecular model, also exist at the early stage of self-assembly of C₁₅SH and C₁₈SH. These results seems to be consistent with the model based on the

results from macroscopic measurements which have shown that there are at least two steps in the SA process, i. e., the initial faster step and following slower step.^{3,33,34,38,41,43,44} It seems that the formation of the preformed structures and the islands corresponds to the initial faster and following slower step, respectively.

3-3 Solvent Effect on the Structure of the Self-Assembled Monolayer of Alkanethiol

3-3-1 Experimental

Preparation of the chemicals and the gold substrates were the same as described in Section 3-2-1. Electrochemical measurements were carried out with an Au(111) electrode made by the Clavilier's method⁶² with hanging meniscus technique in a 0.5 M KOH aqueous solution. The electrode potential is referred to Ag/AgCl. Modification of the gold substrate for both STM and reductive desorption (RD) measurements was carried out by immersing the substrate into 10 μ M C₁₀SH solution for 1 h. The surface were rinsed with the pure liquid of the solvent used in the modification and, then, dried with Ar gas.

3-3-2 Results and Discussions

Figure 3-16a shows an STM image of a gold substrate, which was modified in 10 μ M C₁₀SH ethanol solution for 1 h, obtained in air. Flat regions corresponding to the SAM layer with the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure and many pits of 0.25 nm deep corresponding to VIs of gold surface were observed as reported before.^{23,24} Figures 3-16b and c show STM images of the Au(111) substrate after the modification in DMF and toluene solution containing 10 μ M C₁₀SH, respectively. The gold surface again showed the existence of the monolayer with the VIs of the gold surface. When the modification was carried out in DMF (Fig. 3-16b), the the VIs of the gold surface were tend to be connected each other and the density of the missing-row-defect was very low, resulting in very large domains. The area of each the VIs of the gold surface seemed to be larger and missing-row-defects running between the VIs of the gold surface were seen when the SAM was prepared in

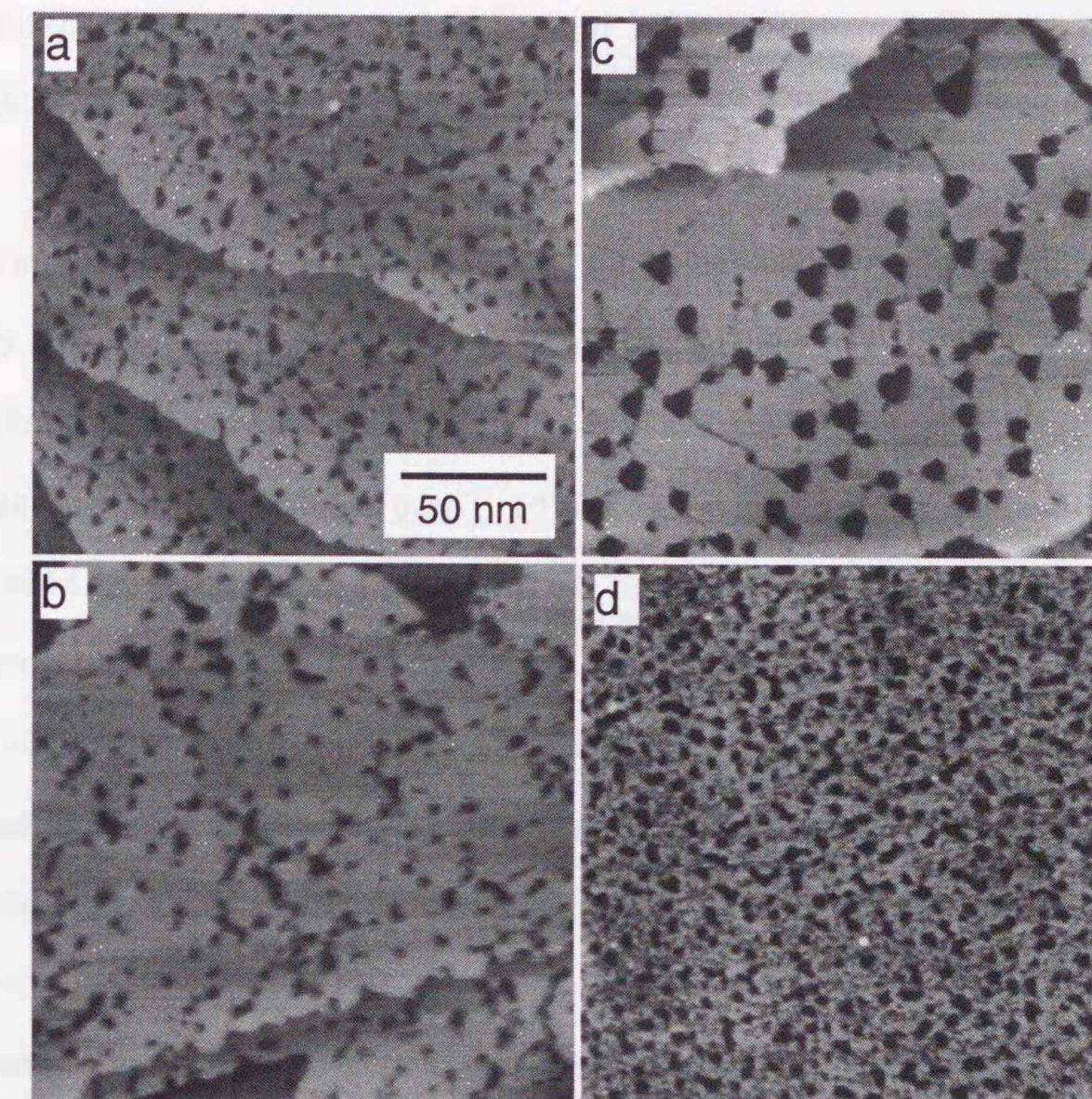


Figure 3-16. STM images of Au(111) surface modified in 10 μ M solution in (a) ethanol, (b) DMF, (c) toluene and (d) heptane for 1 h.

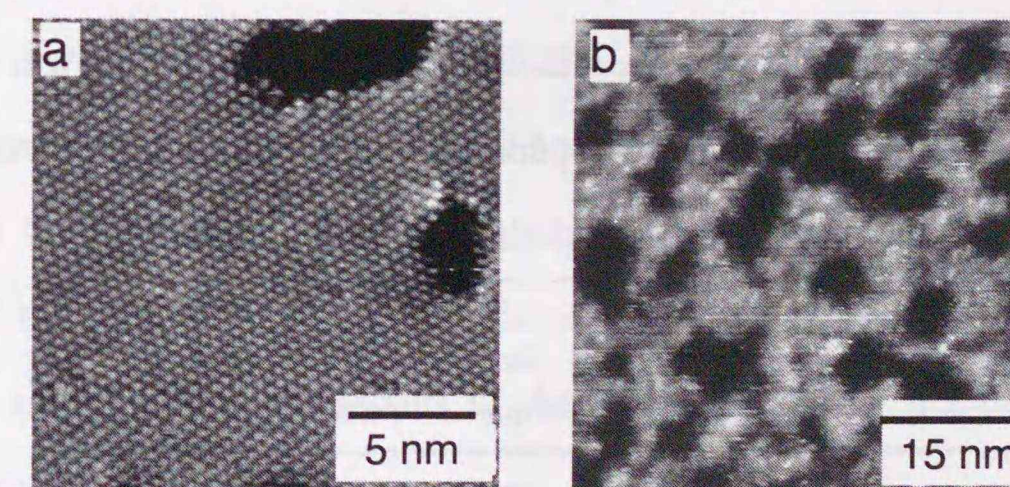


Figure 3-17. STM images of Au(111) surface modified in 10 μ M solution in (a) toluene and (b) heptane for 1 h.

toluene (Fig. 3-16c). The magnified STM images of the Au(111) surface covered with SAM prepared in DMF and toluene also revealed the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure as shown in Fig. 3-17a.

The structure of the C₁₀SH SAM prepared in heptane was quite different from the ones prepared in ethanol, DMF and toluene as shown in Fig. 3-16d. There were no clear flat regions on the gold surface while the VIs of the gold surface existed and a magnified STM image showed no ordered structure (Fig. 3-17b). These results were in contrast to our recent reports of *in situ* STM observation of the formation process of the SAM in heptane where the formation of the island leading to the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure was observed.⁵ The islands observed *in situ* was obscure in many cases indicating that the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure is not firmly formed in heptane. Thus, when the solvent is removed, the fragile islands were destroyed and disordered phase, which was observed in *ex situ* observation, was formed.

The quantitative analysis of the domain and pit sizes were carried out as summarized in Table 3-1.⁶³ The averaged domain size of the SAM prepared in DMF was very large as mentioned before. The domain size of the SAM prepared in toluene, where the domain boundary was clearly defined, was 7 times as large as that of the SAM prepared in ethanol. The fraction of the integrated pit area to the total surface area was, however, almost uniform regardless of the solvent, although the averaged pit size was dependent on the solvent. This result indicates that the dependence of the pit size on solvent arises from

Table 3-1. Size of domains and the VIs estimated from STM images.

Solvent	Domain Size / nm ²	VIs		
		Size / nm ²	σ^{*1} / nm ²	Fraction ^{*2} / %
Ethanol	250	25	26	14
DMF	> 5000	42	56	12
Toluene	1700	55	42	12
Heptane	—	25	27	15

*1. Standard deviation of the pit size.

*2. Ratio of the integrated pit area to the total surface area.

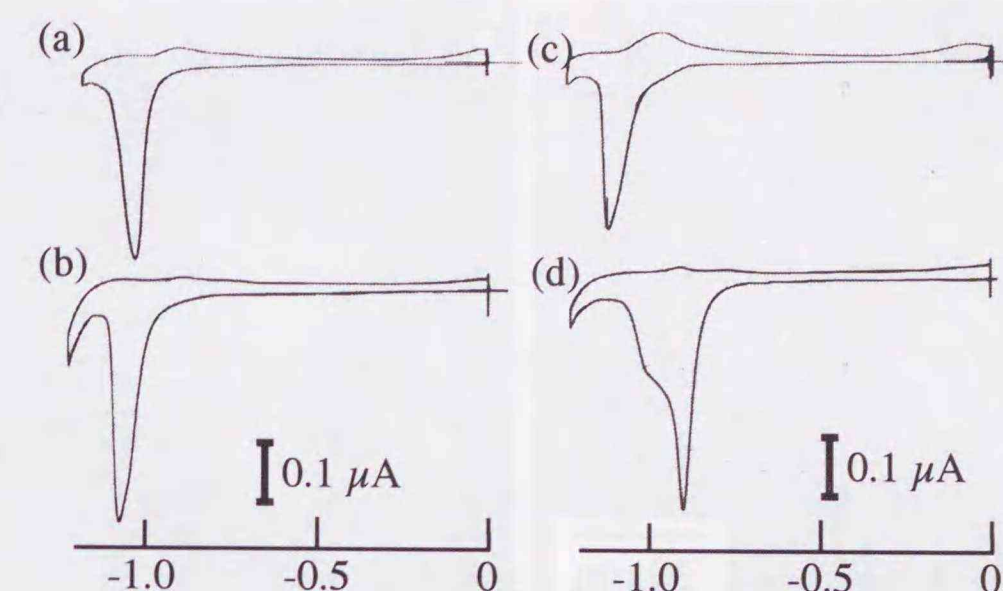


Figure 3-18. Cyclic voltammograms of Au(111) electrode obtained in 0.5 M KOH aqueous solution at 10 mVs⁻¹. Gold electrode was modified with C₁₀SH in (a) ethanol, (b) DMF, (c) toluene and (d) heptane solution.

the difference in the rate of migration process of gold atoms.²⁷ Although Edinger *et al.* reported that the density and averaged size of the VIs of the gold surface were low and small, respectively when modification was carried out in hexane for 24 h compared to the SAM prepared in ethanol,⁶⁴ we were not able to reproduce their results.⁶⁵

Figure 3-18 shows cyclic voltammograms of the gold electrode covered with the C₁₀SH SAM prepared in (a) ethanol, (b) DMF, (c) toluene and (d) heptane. A sharp cathodic current peak was observed around -1.0 V at all electrodes except for the electrode modified in heptane which gave the peak at more positive potential. These peaks were attributed to the reductive desorption of C₁₀SH SAM.⁶⁶ It is interesting to note that the structural difference observed by STM does not affect the desorption behavior. It seems to be reasonable to attribute the positively shifted current peak seen in Fig. 3-18d to the desorption of the molecules in the disordered phase which was observed in the STM examination and therefore, the results of the RD measurement are consistent with the STM examination.

The structure at the initial stage of the SA process in these solvents was also examined by *ex situ* STM measurement. Figure 3-19 shows STM images of Au(111) surface subjected to the modification in 1 μM solution of C₁₀SH for 30 s. The stripe and mesh structures which correspond to the $5\sqrt{3} \times \sqrt{3}$ structure were observed on the Au(111)

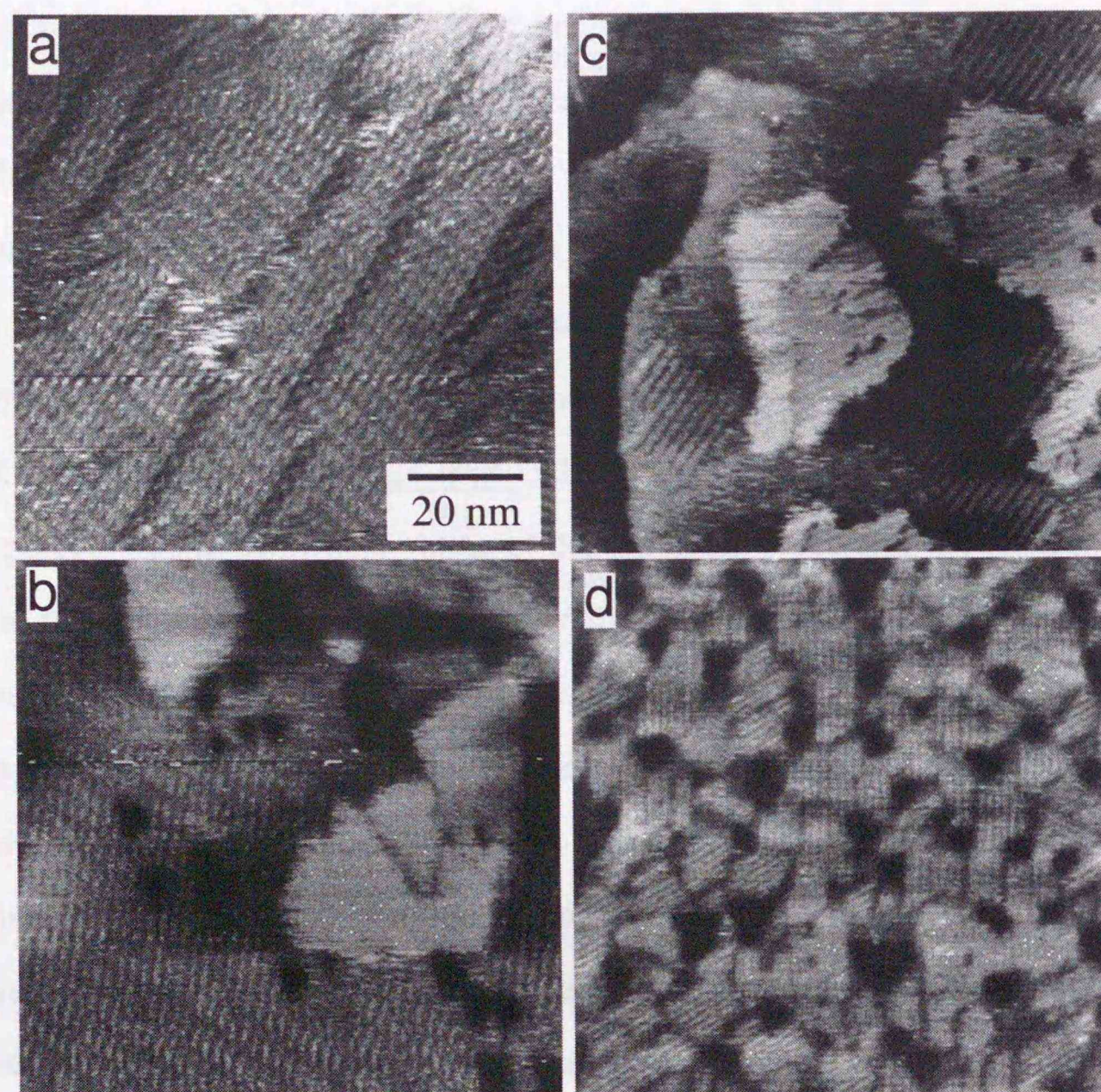


Figure 3-19. STM images of Au(111) surface modified in 10 μ M solution in (a) ethanol, (b) DMF, (c) toluene and (d) heptane for 30s.

surface modified in (a) ethanol, (b) toluene and (c) DMF solution while the islands which was higher than the other region were also imaged on the Au(111) surface modified in toluene and DMF, indicating that the island formation was faster than that in ethanol and heptane. The stripe structure observed on the Au(111) surface modified in heptane was different from the one previously observed. The inter-row spacing of the stripe observed here corresponded to a single molecular length and, thus, the stripe consists of the molecules with their molecular axis parallel to the surface plane and arranged in tail to head, i.e., the thiol group are located at the end of the alkyl chain of the neighbor molecules. The reason why this type of stripe was observed is not clear. One possible reason is that the physisorbed molecules are rearranged when the solution is removed and

surface is rinsed. It should be noted that the number of the VIs were also dependent of the solvent at the early SA process, indicating that the rate of ripening of the VIs is dependent on the solvent. The details of the SA process is not clear since the *ex situ* measurement is poor in reproducibility and *in situ* STM observation is not available in these solvent except for heptane since the leak current flows through the tip.

3-3-3 Conclusion

It was shown that solvent used for the modification affected the structure/order of the SAMs such as sizes of the domains and the VIs. The modification in DMF solution resulted in the construction of large domains while the VIs were small and connected each other. The modification in toluene also resulted in the formation of the large domains and large VIs. The RD measurement was not sensitive to such differences. The fraction of the integrated area of the VIs to the surface area was uniform regardless of the solvent. The SA process seemed to be fundamentally the same in all solvents, i.e., the stripe structure was formed before the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure while the detailed structure of the stripe and the VIs and the rate of the formation was dependent on the solvent.

3-4. Effect of the Temperature on the Structure of the SAMs of Alkanethiols

3-4-1 Experimental

Preparation of the chemicals was the same as described in Section 3-2-1. The Au(111) facet of a single crystal prepared by Clavilier's method⁶² was used as the substrate. The gold substrate was placed on a Pt sheet to be fixed in a STM cell. The Au surface was subjected to flame-annealing and cooled in air for several tens of seconds and then immersed in pure ethanol which was kept at the same temperature as the solution for the modification. The modification was carried out by immersing the substrate into 1 mM solution of C₁₀SH in ethanol at -20°C (in a freezer), 5°C (in a refrigerator), 25°C (in oil bath), 60°C (in oil bath) and 78°C (boiling point, reflux with stirring). After the

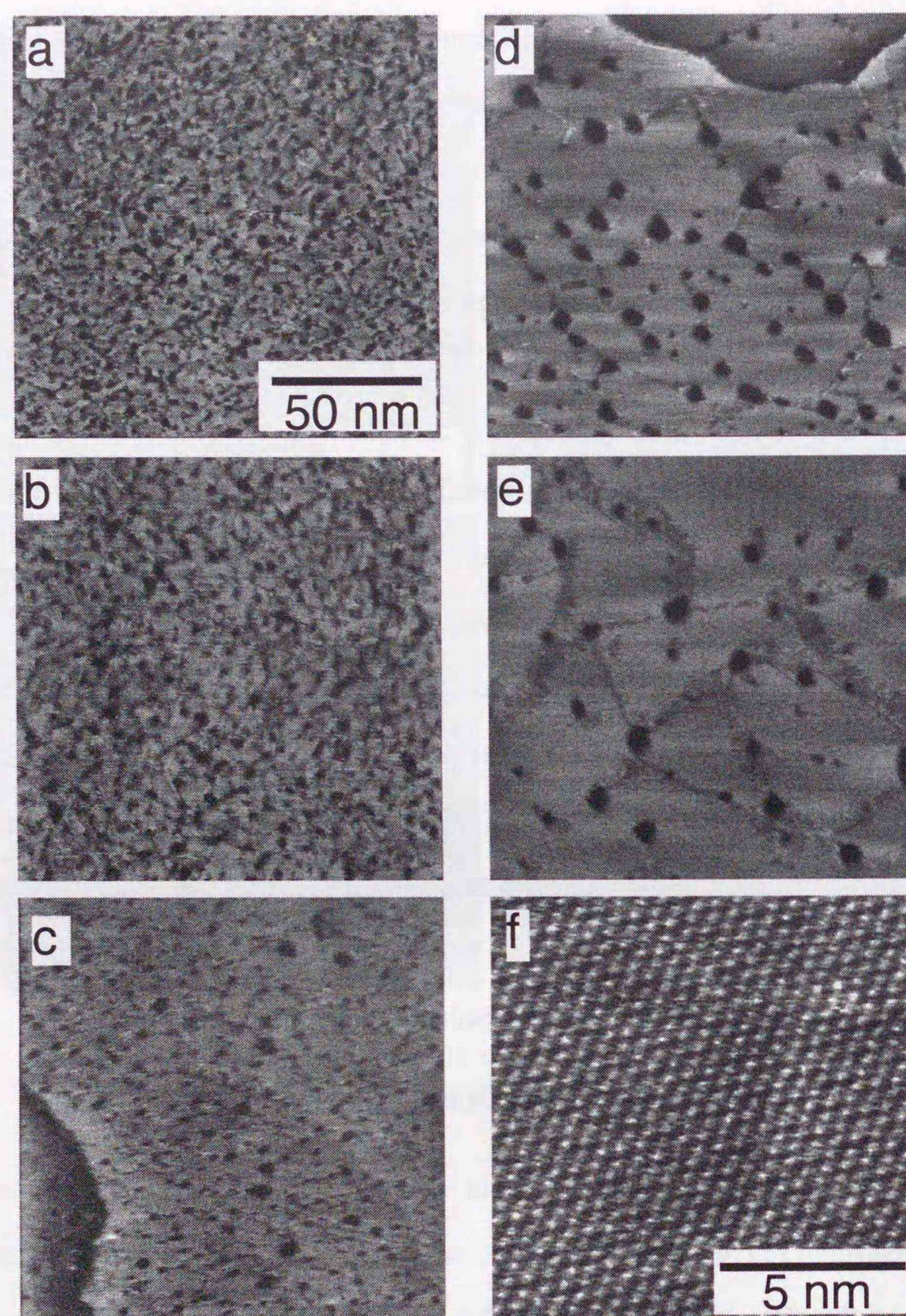


Figure 3-20. STM images of Au(111) surface (150 nm square) after the modification at (a) -10°C , (b) 5°C , (c) 25°C , (d) 60°C and (e) 78°C . (f) Typical magnified image (12 nm square) of Au(111) surface after the modification.

modification, the substrate was rinsed with pure ethanol and dried with Ar gas.

3-4-2 Results and Discussions

Figure 3-20 shows STM images ($150 \times 150 \text{ nm}^2$) of the Au(111) surface subjected to the modification at (a) -20°C , (b) 5°C , (c) 25°C , (d) 60°C and (e) 78°C for 1h. All the images show the typical features of a gold surface covered with the SAM of the

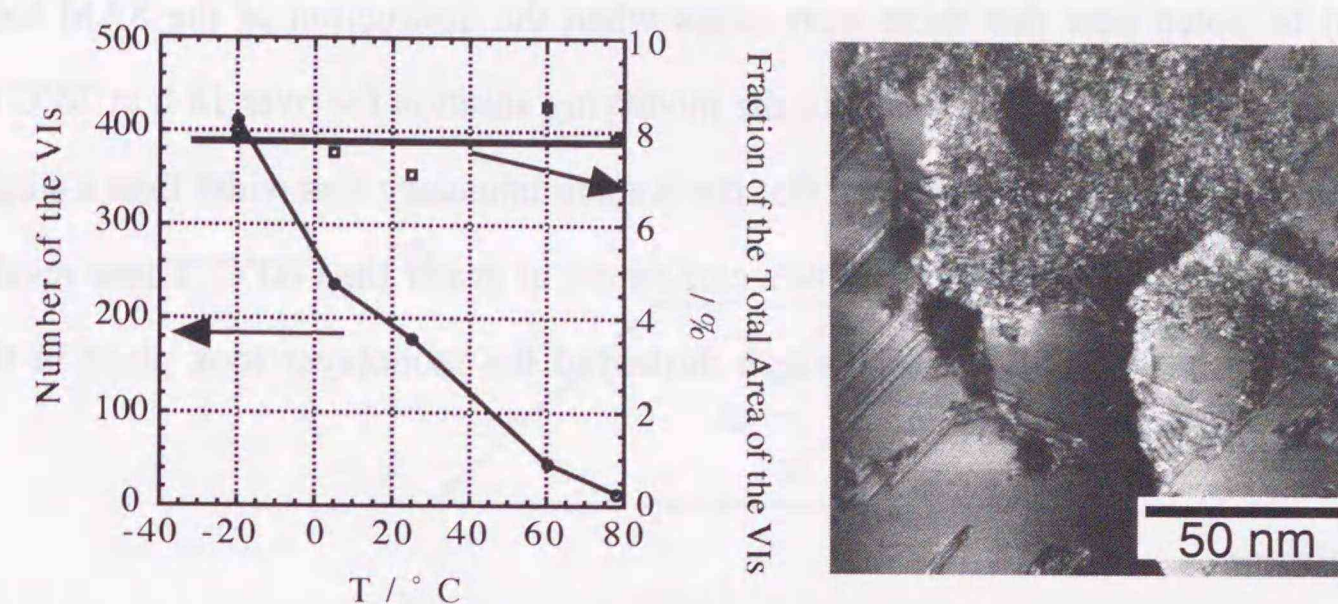


Figure 3-21 The number of the VIs and Fraction of the total area of the VIs.

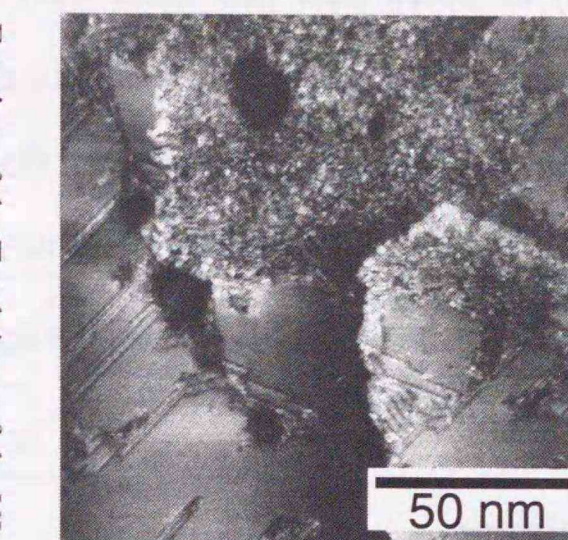


Figure 3-22. STM image of Au(111) surface after the modification for 20 h at 78°C .

alkanethiol such as pits and domain boundaries.^{23,24} The depth of the pits was ca. 0.24 nm which is close to the monoatomic step height of the Au(111) surface and, therefore, these pits were assigned to the VIs of the gold surface.^{23,24} In the all cases, the magnified STM image ($12 \times 12 \text{ nm}^2$) of the Au(111) surface showed the $(\sqrt{3} \times \sqrt{3})\text{R}30^{\circ}$ structure, which is known to be a typical structure of the SAM of alkanethiols, as shown in Fig. 3-20(f). It is clear from Figs.3-20(a) to (e) that the size of the domain and the VIs were larger and the number of VIs was smaller when the temperature of the solution was higher. Figure 3-21 shows the average number and the fraction of areas of the VIs found in the 100 nm square images.⁶⁷ While the number of the VIs almost linearly decreased with temperature, the fraction of the areas of the VIs to the total surface area was constant at ca. 8%. This value is in fair agreement with that previously reported, i.e., 10~15%.²⁷ The fact that the fraction of the areas of the VIs to the total surface area was constant regardless of the temperature suggests that the observed difference in the size of the individual VIs are the result of the Ostwald ripening, as proposed in the previous studies.^{18,68-70} The size and number of the VIs did not change when the modification time was changed to 15 min and 18 h at all temperatures, suggesting that the ripening of the VIs reached equilibrium within 15 min. It is clear that the temperature of the solution at the very initial stage of the self-assembly (SA) has a strong influence on the defect density of the SAMs.

It should be noted here that there were cases when the destruction of the SAM took place when the substrate was immersed in the modifying solution for over 18 h at 78°C as shown in Fig. 3-22. It was also observed that the domain boundary was wider than a single molecular space when the modification was carried out at greater than 60°C. These results seem to indicate that the sub-reaction which destroyed the monolayer took place in the higher temperature solution.

3-4-3 Conclusion

It was shown that temperature of the solution affected the size of the domains and the VIs. The modification in the solution of high temperature resulted in the formation of the large domain and the VIs. The total area of the VIs were uniform, ca. 8% of the surface, regardless of the temperature of the solution, supporting the Oswald ripening process of the VIs.

3.5 Conclusion

The *in situ* STM observation of the SA process of alkanethiols showed that three steps were existed in the SAM formation (Fig. 3-23). In the first step, the disordered structure of the alkanethiols was formed on the gold surface and the VIs of the gold surface were also created and underwent ripening (Fig. 3-23a). When the growth rate was slow, the stripe structures were formed (Fig. 3-23b). The one of the stripe structures consisted of the molecules with their molecular axis parallel to the surface plane and the others consisted of the molecules with their alkylchains piled up with each other. The further adsorption of the alkanethiols lead the formation of the islands in which the $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure was formed (Fig. 3-23c). Finally, the islands covered the surface and monolayer formation was completed (Fig. 3-23d). The solvent significantly affected the size of domain and the VIs, probably because the surface diffusion is affected. The fraction of the total area of the VIs were uniform, ca. 12%, independent of the solvent, indicating that the formation mechanism of the VIs were not affected by the solvent while a degree of the ripening of

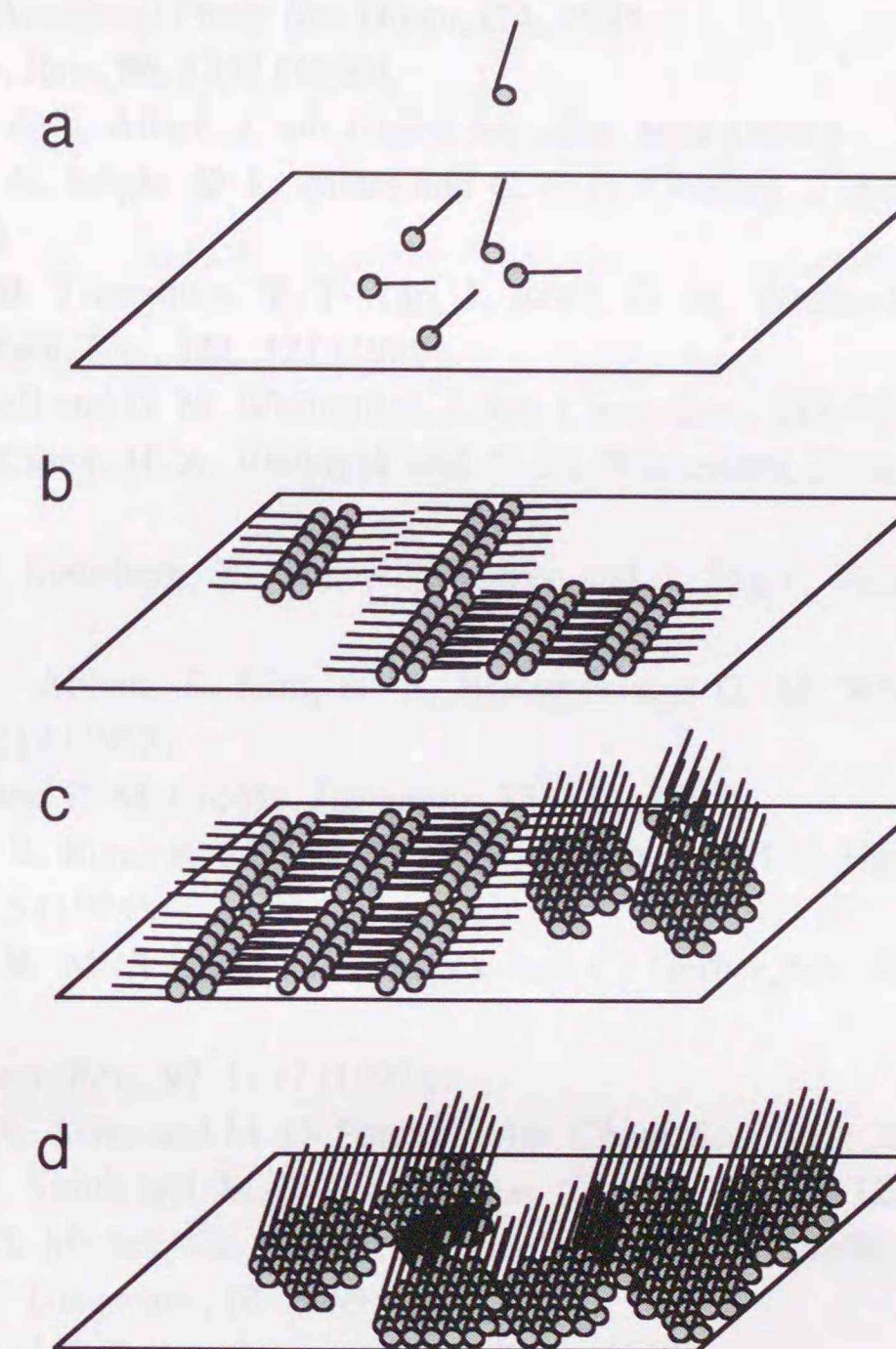
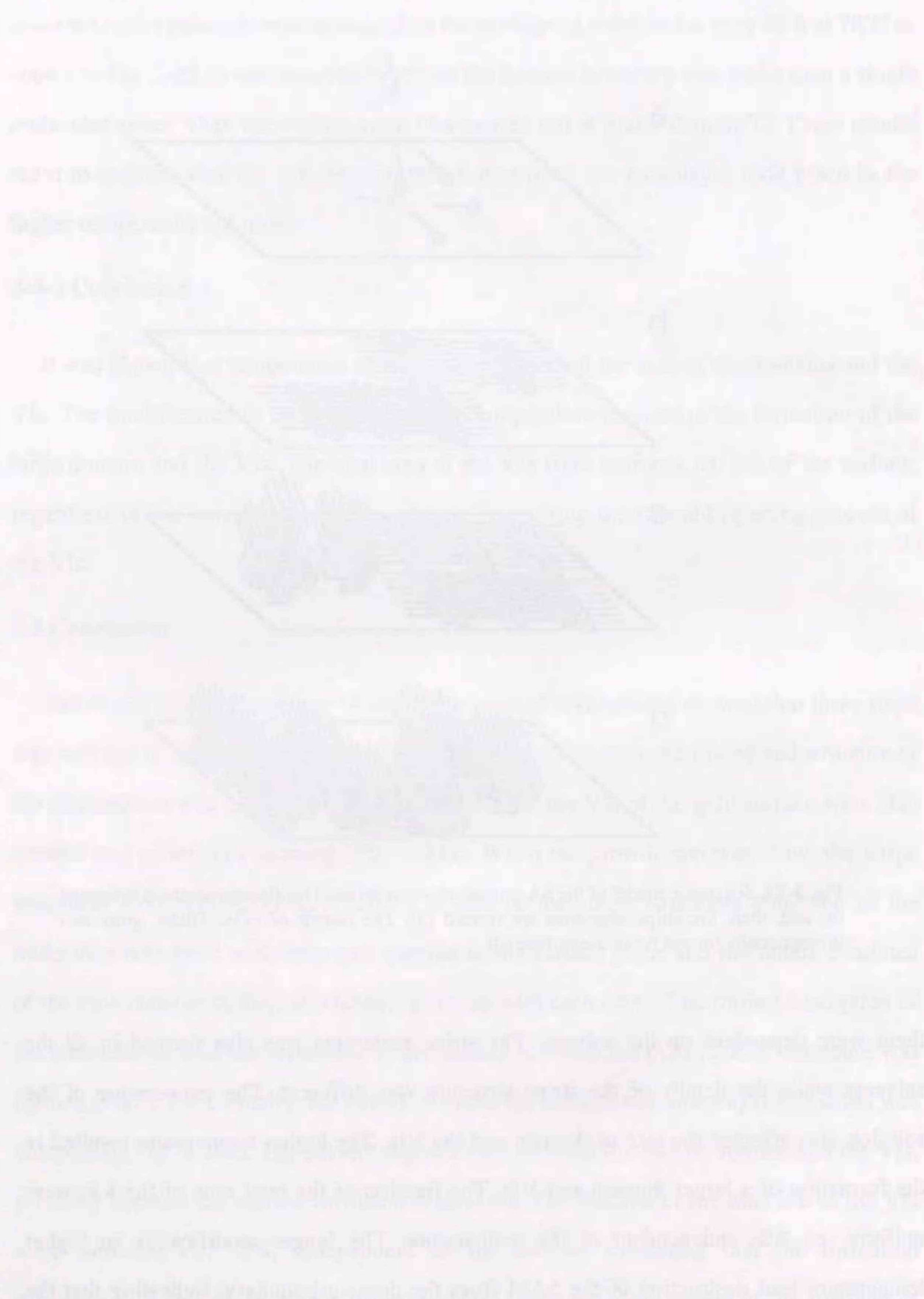


Fig. 3-23. Schematic model of the SA process of alkanethiols. The disordered phase is formed (a) and, then, the stripe structures are formed (b). The islands of $(\sqrt{3}\times\sqrt{3})R30^\circ$ grow two dimensionally (c) and cover the surface (d).

them were dependent on the solvent. The stripe structures was also formed in all the solvents while the details of the stripe structure was different. The temperature of the solution also affected the size of domain and the VIs. The higher temperature resulted in the formation of a larger domain and VIs. The fraction of the total area of the VIs were uniform, ca. 8%, independent of the temperature. The longer modification in higher temperature lead destruction of the SAM from the domain boundary, indicating that the

initial stage of the SAM formation is important in forming the large domain.



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Chapter 4

General Conclusion

In this thesis, the formation of the physisorbed and chemisorbed ordered organic layers in solution was studied by *in situ* STM.

In Chapter 2, the formation of the physisorbed two-dimensionally (2D) ordered layers, i.e., the 2D crystals, of alkanes on Au(111) and (100) surfaces in neat liquids was observed for the first time. *In situ* STM measurements revealed that the structure of the 2D crystal of alkanes on the Au(111) surface showed odd-even effect, while the one of the 2D crystal on the Au(100) surface did not show it. The r-phase of the even alkanes was also discovered on the Au(111) surface when the 2D crystal was formed at 65°C, indicating that the symmetry of the molecule plays an important role in forming the 2D crystal. These results clearly showed that the molecular-molecular interaction was the predominant factor in forming the 2D crystals of alkanes on the Au(111) surface. In addition, it was also shown that the molecular orientation was very sensitive to the structure of the substrate since the preferential orientation of the alkanes with respect to the structure of the reconstructed Au(111) and (100) surface was observed. The surface corrugation due to the reconstruction should be one of the reasons why the 2D crystal of alkanes did not show the odd-even effect on Au(100) surface since molecular packing should be disturbed by the corrugation of the substrate.

In Chapter 3, the self-assembly (SA) process of the chemisorbed 2D ordered organic layers of alkanethiols on Au(111) surface was investigated by *in situ* STM. It was revealed that there were three stages in the SA process of alkanethiols when the concentration of the solution was low, $\sim 0.5 \mu\text{M}$. In the initial stage, the disordered phase of the alkanethiols was formed on the surface. The vacancy islands (VIs) of gold surface were also formed and ripened at this stage. The alkanethiols, then, formed first ordered structures, the stripe and the mesh structure, at the low coverage. One of the stripe structures consisted of the molecules with molecular axis parallel to the surface plane and arranged in tail-to-tail, i.e.,

thiol groups were faced each other and the other structures, the narrow stripe and mesh structures, seemed to be consisted of the molecules with their molecular axis parallel to the surface plane and with alkylchains piled up with each other.

After these stripe structures covered the surface, the island structure, leading to the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, was formed and grew two dimensionally.

The effect of the solvent and the temperature of the modifying solution was also examined and it was revealed that the self-assembled monolayer (SAM) prepared in the DMF and toluene solution showed the larger domains and VIs than those of the SAM prepared in the ethanol solution. The higher the temperature of the solution, the larger the domains and the VIs became. These results indicate that the surface diffusion of the alkanethiols and gold atoms is the important factor to reduce the defects in the SAMs.

The present study showed that the 2D ordered molecular layers can be easily formed at the metal/organic-solution interface and the structure of the 2D molecular layer is controlled by the surface-molecule and molecule-molecule interactions, geometry of the substrate, solvent and temperature. The present result should provide a fundamental and valuable knowledge of the origin of the formation and the structure of the 2D ordered molecular layers and contribute to control the structure of them.

