

# Modification of Hydrogen-terminated Si(111) Surface with Transition Metal Dithiocarbamate Complexes

NOMURA Ryôki, HATASAKA Ryûzô and SHIMOMURA Osamu

Department of Chemistry, Osaka Institute of Technology, Ô-miya, Asahi, Osaka, 535-5858, Japan.

e-mail: nomura@chem.oit.ac.jp

Formation of self-assembled monolayers of nickel (II) or zinc (II) dithiocarbamate complexes onto the surface of silicon wafers was attempted using hydrogen-terminated silicon technology. Nickel (II) dithiocarbamates with  $\omega$ -alkenyl moieties successfully reacted with hydrogen-terminated silicon and gave single molecular layers of the complexes, however, similar zinc (II) dithiocarbamates did not react with it. Such a difference is perhaps lead from the difference of the molecular geometry of nickel and zinc dithiocarbamates, *i.e.* planar 4-coordinated for nickel and tetrahedral structure for zinc.

Key words: hydrogen-terminated silicon, dithiocarbamate complexes, self-assembled monolayer, nickel complexes

## 1. INTRODUCTION

Several living bodies develop in function by accumulating a hierarchical structure comprising various biomolecules, which is often called as supramolecules. For example, ability for molecular recognition of some organs is derived from fixing some sensing parts and transducers on some substrate tissues. To realize an artificial molecular recognition device using biomolecules as sensing parts, such a hierarchical structure is necessary.

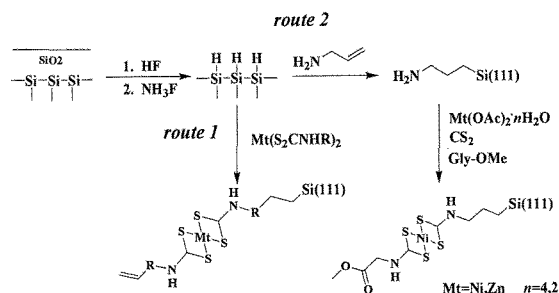
Now, technology of self-assembled monolayer (SAM) usually furnishes effective solution to assemble certain biomolecules on the surface of solid state circuits leading to sensing devices [1]. Some patterns of SAM are already known; for example, the combination of thiols with Au and Pt based on the affinity of sulfur to these noble metals [2], and the application of silane coupling reaction for the surface oxide layers of base metals [3]. These methods are considered as a modification of the metal electrodes with organic molecules and can be applied in the immobilization of enzymes onto the metal surface. Recently, it has been reported that a bio-sensor based on surface plasmon resonance (SPR) should be developed using thiol SAM [4]. Some problems are, however, known for these attempts; *e.g.*, dissociation of thiol molecules from the noble metal surface becomes significant by heating in solutions, and monolayers from silane coupling reactions are also thermally labile and hydrolyzable.

On the other hand, alkene molecules can react with hydrogen-terminated silicon (H-Si) to give a novel SAM with stable Si-C linkages. This type of SAM is attracting much attention to develop new sensing devices, because this SAM technology can offer a direct modification of semiconductor devices by organic components [5,6].

In our continuous studies on the development of the complex assemblies, it was reported that a self-organization of some nickel(II) dithiocarbamates with terminal OH group or with amino acid ester moieties leads to specific microchannel structures [7,8]. Some molecular recognition ability should be expected from such microchannel structures derived from the

complex assemblies. It is, however, necessary to immobilize them on the solid surface to realize molecular recognition devices. Consequently, we tried to immobilize such metal dithiocarbamate complexes on the surface of silicon wafers in two essential routes. The route 1 was consisting of the reaction of hydrogen-terminated Si(111) and dithiocarbamate complexes with  $\omega$ -alkenyl groups. While the route 2 was a surface reaction of aminoalkyl-terminated Si(111) with metal ions, amino acid esters and carbon disulfide as illustrated in Scheme 1.

Scheme 1 Schematic representation of the two methods for preparing complex-terminated Si(111)



## 2. EXPERIMENTAL

### 2.1 General

IR, UV-vis and <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded with a SHIMADZU FT-IR DR8500, SHIMADZU UV-3100PC spectrophotometer and a Varian UNITY300 (300 MHz) spectrometer, respectively. MS and XGT were observed using a PE Biosystems Voyager-DE PRO time-of-flight mass spectrometer and a HORIBA X-ray Analytical Microscope XGT-2700, respectively. Optical-microscope images were obtained with a KEYENCE VHX-100. Single crystal automatic X-ray structure analysis was done with a Rigaku AFC-7R four-circle X-ray diffractometer. The structure analyses of crystals were done over the reflection range within 4.0° < 2θ < 120.1° by the  $\omega$ -2θ scanning using CuK $\alpha$  radiation (1.54178 Å) at 298 K.

In addition, the structures were solved by teXsan program [9]. We could get refined structure of complexes **1**, and **3** using Direct Methods (SIR92) [10] and Patterson Methods(DIRDIF99) [11].

## 2.2 Syntheses of dithiocarbamate complexes(**1-6**)

A mixture of the corresponding metal (II) acetate (5 mmol) and amines (10 mmol), such as allylamine, propylamine, 1-amino-10-undecylamine or 4-vinylbenzylamine in methanol (100 ml) was stirred at room temperature for 1 h. Afterwards, carbon disulfide (10 mmol) was slowly added by syringe with cooling by ice. The reaction system was stirred for another 24 h at room temperature. After the reaction ceased, methanol was removed under reduced pressure, and residual powders were washed with water several times. Thus, nickel (II) and zinc (II) complexes **1-5** were obtained in deep green or colorless as shown in Table I. Similarly mixed ligands complex **6** was prepared using the combination of allylamine(5 mmol) and glycine methyl (5 mmol) with nickel acetate (5 mmol) and carbon disulfide (10 mmol).

Identifications of the complexes were done with IR, <sup>1</sup>H- and <sup>13</sup>C-NMR spectra and TOF-MS. The results of preparation and selected spectral data of these complexes are shown in Table II.

## 2.3 Preparation of hydrogen-terminated Si(111) surface

Hydrogen-terminated Si(111) chips, H-Si(111), were prepared as following. Small cuts (10 mm square) of superficially oxidized silicon wafer of 111 direction (Shin-Etsu semiconductor, Co. Ltd.) were treated with 10% aqueous HF for 20 min and etched twice with 40% aqueous NH<sub>4</sub>F for 20 min, successively.

## 2.4 Preparation of aminoalkyl- and complex-terminated Si(111)

Typical procedure is as following; An H-Si(111) chip was immersed into 20 mL of mesitylene, then aminoalkenes or a solution of the complexes**1-6** in mesitylene were added slowly by a syringe. Heat was added to the mixture at 55-60 or 166°C under N<sub>2</sub> for 24 h, respectively. Afterwards, the silicon chip was rinsed with hexane and ethanol, successively. Then the chip was washed in methanol under an irradiation of ultrasound. These treatments were repeated twice.

## 2.5 Preparation of complex-terminated Si(111) by the surface reaction of aminoalkyl-terminated Si(111)

Aminopropyl-terminated Si(111) was immersed in 20 mL of methanol. After nickel (II) acetate (0.5 mmol) and amines (0.5 mmol) was added to them, carbon disulfide was added slowly under N<sub>2</sub> with cooling. The mixture was kept at room temperature for 72 h.

Table I Characteristics of complexes **1-6**

No.	Complexes	%-yields	color
1	Ni(S <sub>2</sub> CNHCH <sub>2</sub> CH=CH <sub>2</sub> ) <sub>2</sub>	91.7	dark green
2	Ni(S <sub>2</sub> CNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	89.2	dark green
3	Zn(S <sub>2</sub> CNHCH <sub>2</sub> CH=CH <sub>2</sub> ) <sub>2</sub>	85.4	colorless
4	Ni(S <sub>2</sub> CNH(C H <sub>2</sub> ) <sub>9</sub> CH=CH <sub>2</sub> ) <sub>2</sub>	25.0	dark green
5	Ni(S <sub>2</sub> CNHCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> ) <sub>2</sub>	40.3	dark green
6	Ni(S <sub>2</sub> CNHCH <sub>2</sub> CH=CH <sub>2</sub> )- (S <sub>2</sub> CNHCH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> )	-	dark green

Table II Selected spectral data of complexes **1-6**

Complexes	IR $\nu$ /cm <sup>-1</sup>			<sup>13</sup> C-NMR $\delta$ (S <sub>2</sub> CN)	MS M <sup>+</sup> m/z
	C=S	C=O	C=C		
1	995.3	-	1643.4	206.3	322.2(321.9)
2	995.3	-	-	205.4	326.4(326.0)
3	993.3	-	1645.3	205.8	no peak
4	993.3	-	1641.4	205.1	546.2(546.2)
5	985.6	-	1629.9	206.3	474.3(474.0)
6	983.6	1722	1643.4	206.0	354.2(353.9)

## 3. RESULTS AND DISCUSSIONS

### 3.1 Preparation of complex-terminated Si(111) via route 1

Reactions of hydrogen-terminated Si(111) with Ni (II) and Zn (II) dithiocarbamates having  $\omega$ -alkenyl groups, complexes **1** and **3**, respectively, were carried out under several conditions. Consequently, it was found that the appearance of the surface of Si substrates altered after the reactions in mesitylene at 166 °C (Fig. 1). Some detailed studies revealed that the optimal reaction period was 24 h.

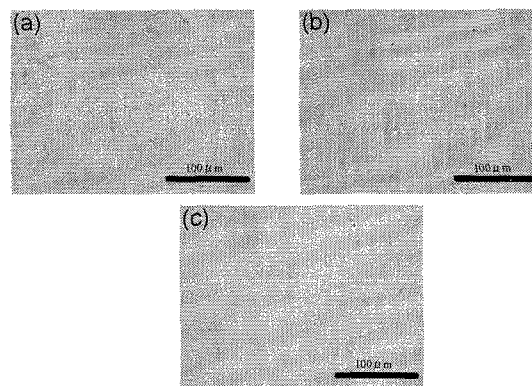


Fig. 1 Surface appearance of (a) after the reaction with complex **1**, (b) after the reaction with complex **3**, (c) original H-Si(111).

Then we tried the elemental analysis of the specimen after the 24 h reaction using XGT technique. We could detect nickel and sulfur on the surface of the specimen from the reactions with nickel dithiocarbamates **1,4**, and **5**. A typical elemental analysis charts are displayed in Fig. 2. The surface elemental distributions were also observed, and the results obtained are presented in Fig. 3. The image in Fig. 3(a) shows that the distributions both of nickel and sulfur are uniform on the surface of the substrate derived from the reaction with complex **1**.

We could observe the change of the surface appearance of the silicon surface after the reaction with zinc complex **2**. In contrast to the case of the treatment by nickel complexes, we could, however, not detect any traces of the presence of zinc and sulfur on the surface of the silicon as shown in Fig. 2 (b). These elemental analyses data may reasonably indicate that the nickel dithiocarbamate complexes were successfully immobilized. On the other hand, the zinc dithiocarbamate complex did not react with the hydrogen-terminated Si(111).

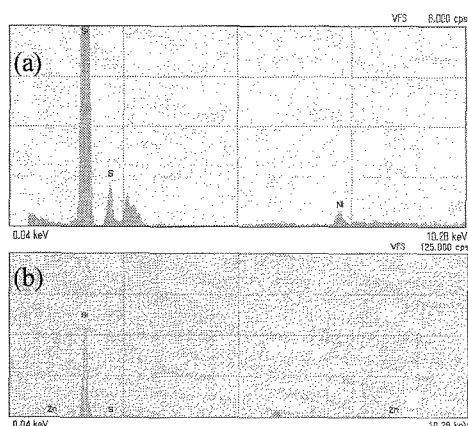


Fig. 2 Surface elemental analysis by XGT. (a) After the reaction of complex **1** with H-Si(111), and (b) after the reaction of complex **3** with H-Si(111).

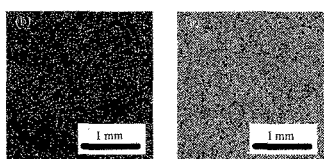


Fig. 3 Surface elemental distribution images by XGT; (a) distribution of nickel and (b) distribution of sulfur for the silicon after the reaction of complex **1**.

Next we observed the electronic spectra of the complex-terminated Si(111) to confirm the immobilization of the nickel dithiocarbamate moiety on the surface. The nickel complex **1** shows some absorption maxima within uv-vis region as shown in Fig. 4. Among the absorption maxima, very weak d-d transition band appeared at around 480 and 650 nm is a characteristic absorption for nickel (II) dithiocarbamates. In the reflection spectra of the hydrogen-terminated Si(111), we can see no peaks in uv-vis region. While, small absorption peaks could be detected the d-d band at around 480 and 650 nm for the specimen obtained from the reaction with complex **1**. Consequently, it can be said that the complex **1**-terminated Si(111) was obtained.

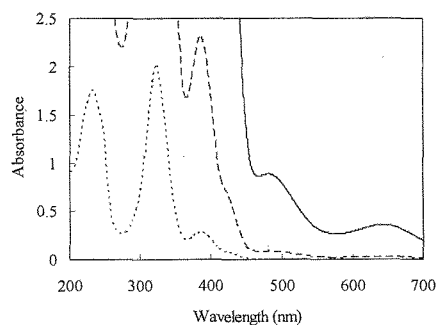


Fig. 4 Uv-vis spectra of complex **1** of (a)  $5 \text{ mmol dm}^{-3}$  solution in solid line, (b)  $0.5 \text{ mmol dm}^{-3}$  solution in dotted line, and (c)  $0.05 \text{ mmol dm}^{-3}$  solution in thin dotted line.

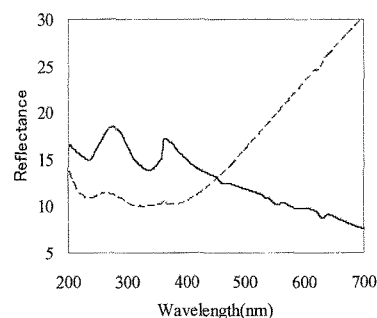


Fig. 5 Uv-vis spectra (reflection) of (a) complex **1**-Si(111) in solid line, and (b) H-Si(111) in dotted line.

Similarly nickel dithiocarbamate complexes **4** and **5**, which also possessing  $\omega$ -alkenyl part, gave complex-terminated Si(111). Consequently we obtained monolayer of Ni (II) dithiocarbamate complex on the surface of Si(111). A treatment of H-Si(111) with nickel (II) bis(dipropyldithiocarbamate) having no alkenyl part could not offer complex-terminated Si(111).

In our knowledge, symmetrical alkyl- or alkenyl dithiocarbamate complexes can not form any assemblies in solid state, because of the lack of the key for the aggregation, such as proton donor and acceptor part. Therefore, we next tried to immobilize certain mixed ligands dithiocarbamates (**6**) possessing both alkenyl group to react with the surface of H-Si(111) and glycine methyl group as a proton acceptor aiming at assembling nickel complexes on the surface of silicon to the step towards the sensing devices.

We can obtain complex **6** from the equimolar combination of allylamine and glycine methyl. Isolation of complex **6** was difficult, because it readily engaged redistribution of the ligand through an intermolecular ligand exchange. Thus we could not measure its melting point. The reaction with H-Si(111) with complex **6** was carried out and the optical microscope image of the surface of silicon after the reaction is presented in Fig. 6. Thus, similar change of the appearance of the surface to the case of complexes **1, 4** and **5** could be observed. Data of elemental analysis and distribution are also displayed in Figs. 7 and 8. These results can suggest that we can also obtain the complex-terminated Si(111) from the mixed ligand complex **6** that is self-organizable to form supramolecular structures.

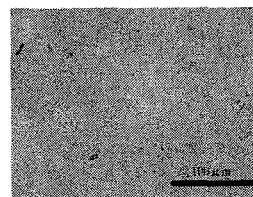


Figure 6 Optical microscope image of complex **6**-terminated Si(111).

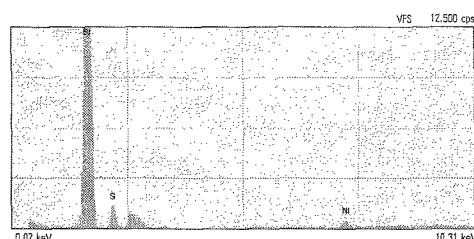


Fig. 7 Surface elemental analyses of complex 6-terminated Si(111).

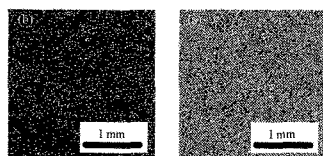


Fig. 8 Surface elemental distribution images by XGT; (a) distribution of nickel and (b) distribution of sulfur for the silicon after the reaction of complex 6-terminated Si(111).

### 3.2 Preparation of complex-terminated Si(111) *via* route 2

We, then attempted to prepare complex 6-terminated Si(111) with the different approach such as route 2 as shown in Scheme 1. At first, aminopropyl-terminated Si(111) was prepared with the reaction of allylamine with H-Si(111). Next, the reaction of aminopropyl-terminated Si(111) with nickel ions and carbon disulfide in the presence of glycine methyl as described in 2.5. Then we could obtained the complex 6-terminated Si(111), which was spectrally confirmed with XGT and uv-vis. Consequently we could obtain the monolayer of mixed ligand Ni (II) dithiocarbamate complex on Si(111) in two route.

### 3.3 Molecular structure of complexes 1 and 3

Zinc complex 3 did not react with the silicon surface. It is thought that this is resulted from the molecular structure of complex 1 and 3. Thus, their single crystals were prepared, and X-ray structural analysis of them was performed. The results obtained are illustrated in Figs. 9 and 10. Fig. 9 indicated nickel complex 1 is monomeric and is existed in a planar 4-coordinated geometry. On the other hand, Fig. 10 shows the zinc complex 3 is dimeric with bridging dithiocarbamates and is existed in a tetrahedra structure. We tentatively concluded that such dimeric structure of zinc complex interrupt the reaction by a steric hindrance.

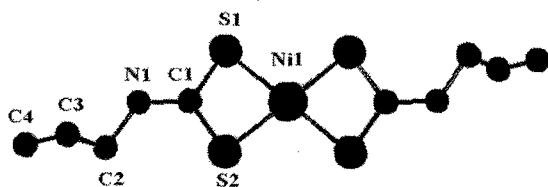


Fig. 9 An ORTEP drawing of complex 1.

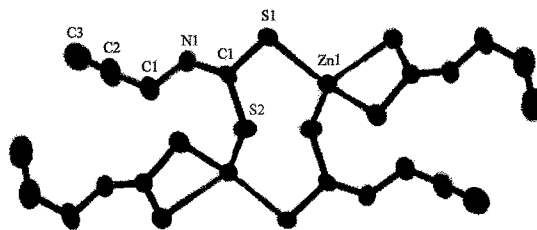


Fig. 10 An ORTEP drawing of complex 3.

## 4. CONCLUSION

Formation of self-assembled monolayers of Ni (II) and Zn (II) dithiocarbamate complexes was on Si(111) was extensively surveyed, assessing with two essential routes. The reactions of hydrogen-terminated Si(111) with Ni (II) alkenyl-substituted dithiocarbamates 1, 4, and 5 successfully gave the complex-terminated Si(111). Further, the mixed ligands complex of Ni (II) 6, in which one of two ligands contained propenyl group and the other possessed glycine methyl moiety can also react with hydrogen-terminated Si(111) to give complex 6-terminated Si(111). While analogous Zn (II) complex 3 did not react with the silicon surface. Such low reactivity of the zinc complex should be derived from steric factors from its aggregated structure.

On the other hand, amino-functionalization on the surface of silicon wafer by the reaction of hydrogen-terminated Si(111) with propenylamine was found to be also applicable to immobilize the nickel complexes.

## REFERENCES

- [1] A. Ulman, *Chem. Rev.*, **96**, 1533 (1996).
- [2] R. G. Nuzzo, and D. L. Allara, *J. Am. Chem. Soc.*, **105**, 4481 (1983).
- [3] J. Sagiv, *J. Am. Chem. Soc.*, **102**, 92 (1980).
- [4] L.A.Lyon, *Sens. Actuators. B. Chem.*, **54**, 118(1999)
- [5] M. R. Linford, and C. E. D. Chidsey, *J. Am. Chem. Soc.*, **115**, 12631 (1993).
- [6] M. R. Linford, and C. E. D. Chidsey, *J. Am. Chem. Soc.*, **117**, 3145(1995).
- [7] R. Nomura, and S. Nakamoto, *Trans. Mater. Res. Soc. Jpn.*, **26**, 483 (2001).
- [8] R. Nomura, and K. Fujiwara, *Trans. Mater. Res. Soc. Jan.*, **28**, 529 (2003).
- [9] A. C. Larson, *Crystallographic Computing*, 291-294 (1970). F. R. Ahmed, ed. Munksgaard, Copenhagen (equation 22, with V replaced by the cell volume).
- [10] SIR92: A. Altomare, G. Cascarano, C. G. Giacovazzo, W. P. Bosman, R. de Gelder, R. Israel, and J. M. M. Smits, *J. Appl. Cryst.*, **27**, 435 (1994).
- [11] DIRDIF99: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, and J. M. M. Smits, *The DIRDIF-99 program system*, Technical Report of the Crystallography Laboratory, 1999, University of Nijmegen, The Netherlands.