Studies on Synthesis and Properties of Cyclic Organosilicon Compounds and their Application to Electronic Devices

（環状有機ケイ素化合物の合成と物性に関する研究及び電子デバイスへの応用）

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General Introduction

In the past, electronic materials have mainly been dependent on inorganic materials due to their high performance and high durability. In the last four decades, however, many studies have been extensively conducted to utilize organic compounds that are lighter, rich in diversity, and less environmental burden than inorganic compounds to realize light weight and/or flexible electronic devices. Among them, organic semiconductors for thin film transistors (OTFT), organic luminescent materials for light emitting diodes (OLED) and flat panel displays and smart phones, and photoelectric material for image sensors or photovoltaics have attracted much attention. There are several organic materials with sufficient performance and durability that can be used for these devices, however, further material studies based on new ideas are required to realize enough performance same as inorganic materials. Under such circumstances, development of organic materials taking advantage of the characteristics of elements is of much attention. This concept is an unprecedented molecular design that based on electronic or structural features of elements for building entirely new skeletal organic materials.

Silicon is a positive element with a larger atomic radius and lower electronegativity compared to carbon, and its chemical properties are different though it is Group 14 element closest to carbon. Silicon-silicon σ bond has higher energy level than carbon-carbon σ bond because silicon has valence electrons in the outer shell than carbon, which is comparable to carbon-carbon π bond. Therefore, the silicon-silicon σ bond has high reactivity and is easily cleaved by reacting with halogen such as bromine. Synthesis and functionalities of compounds in which the π electron system is crosslinked or substituted by silicon atom(s) are well studied. In addition to physical effects such as increased solubility by silicon substitution, orbital interaction (σ - π conjugation) between silicon σ orbital and π electron system has been shown to have unique electronic effects such as extension of conjugation length, improvement of fluorescence emission efficiency.

Figure 1 shows the HOMO - LUMO levels of cyclopentadiene, silacyclepentadiene (silole), cyclopentadithiophene, dithienosilole, and disilanobithiophene. Comparing HOMO and LUMO energy levels of cyclopentadiene and silole, the HOMO energy level of silole is close to cyclopentadiene. On the other hand, the LUMO energy level of silole is overwhelmingly lower than that of cyclopentadiene. This is due to the interaction (σ*-π* interaction, σ*-π* conjugation) between the σ* orbital of the silicon-containing bond and the π* orbital of butadiene. A system condensed with thiophene shows the same effect. The HOMO energy level of dithienosilole is almost the same as that of cyclopentadithiophene. On the other hand, a large difference appears in the LUMO energy level due to the effect of σ*-π* conjugation. Comparing dithienosilole and disilanobithiophene, the band gap is comparable, whereas disilanobithiophene has lower energy level for both HOMO and LUMO. This result is considered to be a complex factor such as stereoscopic effect and orbit-orbit interaction. The characteristic red-shifted UV absorptions of silole derivatives would arise from their low-lying LUMO [2, 3]. The low-lying LUMO provides the chance to use silole derivatives as the functionality materials, such as semi-conductors and electron-transporting materials, and many papers concerning the synthesis and functionalities of monomeric silole derivatives as well as silole-containing polymers have been published to date [4-9].

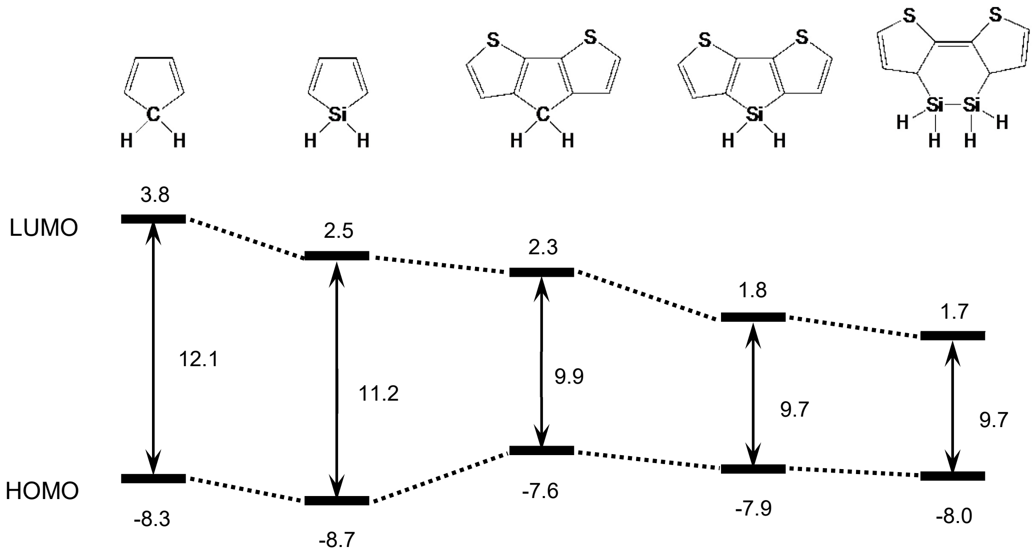


Figure 1 Relative energy levels of HOMO and LUMO base on molecular simulation at the RHF/6-31G level [1].

Corriu et al. have previously reported the formation of polymers having $Fe(CO)_3$-coordinated silole-1,1-diyl units [10]. They showed that silole derivatives may be potential ligands to transition metal centers. However, no other studies about the incorporation of metal-coordination to the silole ring in polymeric systems had appeared, until our laboratory reported the synthesis of $Fe(CO)_3$-coordinated poly(disilanylene-3,4-diethynylenesiloles) (Chart 1) [11].

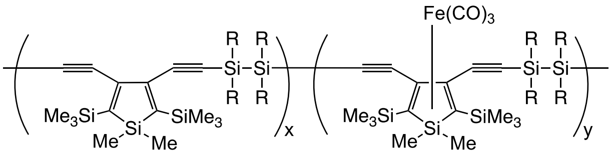
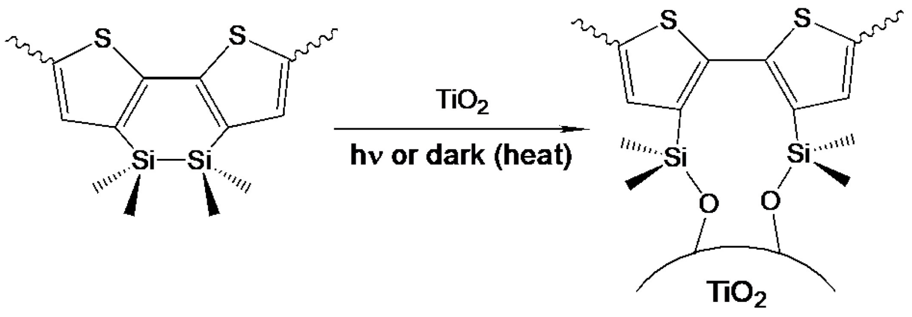


Chart 1 $Fe(CO)_3$-coordinated poly(disilanylene-3,4-diethynylenesiloles.

As expected, the coordination of $Fe(CO)_3$ to the 3,4-diethynylsilole unit leads to significant changes in the polymer electronic states and the UV absorptions move to longer wave length from those of the parent non-coordinated polymers, indicating the enhancement of π-conjugation by the $Fe(CO)_3$-coordination. This is probably due to the increase of the bond order between silole C3-C4 atoms, through which the two ethynyl groups may be conjugated more effectively.

Organic electronics have received increasing attention. In these devices, surface modification of inorganic materials (e.g, oxides) with organic modifiers is an important process in areas of surface and interface engineering. This is because electronic properties, photonic properties, durability, etc., are greatly affected by the state of the interface between substances. Organosilicon compounds having reactivity such as chlorosilanes and hexamethyldisilazane have been studied as surface modifiers [12-15]. The performance improvements have been reported by treating inorganic oxides with these compounds [16-21]. However, by-products produced during the reaction may degrade the device performance. Therefore, new surface modifier that has sufficient reactivity, easy to handle in air and does not produce reactive by-products, such as hydrogen chloride and ammonia is desired.

As mentioned above, the silicon-silicon σ bond has high reactivity. It is readily cleaved photochemically, but stable enough to handle under ambient conditions without UV irradiation. Recently, our laboratory has reported that treatment of TiO_2 surface with polymers composed of alternating Si-Si and π-conjugated units under UV irradiation resulted in attachment of the polymers on the surface through the formation of Ti-O-Si linkages. More recently, disilanobithiophene polymers reacted with TiO_2 surface even in the dark (Scheme 1), likely due to the ring strain [22-27].

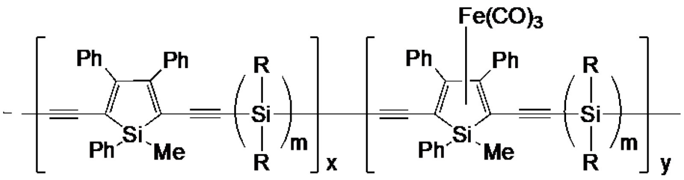


Scheme 1 Modification of TiO_2 surface with disilanobithiophene-polymers.

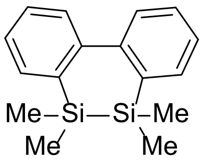
Hydrolysable Si-N bond(s) also have moderately high reactivity and allows the smooth transformation into Si-O bond(s). Aminosilanes containing Si-N bond(s) readily interact with alcohols (ROH) to form R-O-Si linkages under mild and neutral conditions, unless they are sterically congested. In addition, aminosileanes are sufficiently stable towards hydrolysis by atomospheric moisture to permit the use of them without special care [28-30]. However, aminosilanes are less used than chlorosilanes because of limited commercial sources.

In this thesis, the author describes how the regional change affects the electron states of $Fe(CO)_3$-coordinated diethynylsilole-containing polymers. Furthermore, focusing on the interface state of substances affecting the performance of electronic devices, the author also describes the development of new surface modifiers having reactive Si-Si bond or Si-N bond without producing reactive by-product.

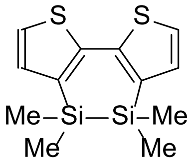
In Chapter 1, the preparation and properties of $Fe(CO)_3$-coordinated poly(organosilanylene-2,5-diethynylenesiloles) are described in comparison with those of the 3,4-diethynylsilole polymers, reported previously. The hole-transporting properties of poly(organosilanylene-2,5-diethynylenesiloles) were evaluated by the performance of EL devices containing the polymer layer as the hole-transport. The results indicated that the coordination of the $Fe(CO)_3$-unit to diethynylsilole system seems to provide an opportunity to modify the electronic states of the π-electron system. In addition, the present silole-containing 2,5-diethynylenesiloles polymers may be used as the hole-transport for OLEDs.



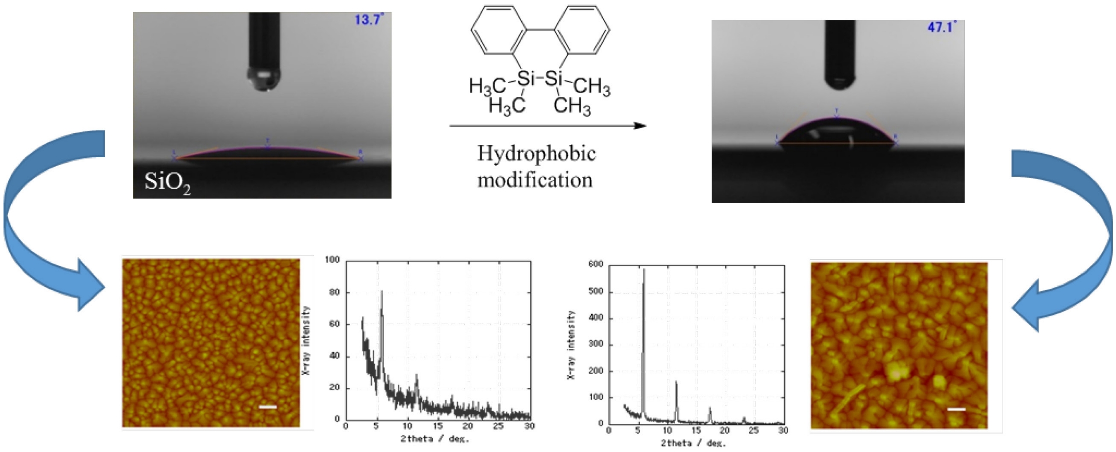
In Chapter 2, the hydrophobic modification of SiO_2 surface using tetramethyldisilanobiphenyl (DSBP) and tetramethyldisilanobithiophene (DSBT) as new modifiers are described. The modification performance of DSBP was evaluated by the performance of the top-contact p-type organic thin film transistor (OTFT) with a pentacene vapor-deposited film as the active layer. The results suggested that the modification method with DSBP can efficiently control the SiO_2 surface. DSBP and DSBT are stable and clean modifiers that can be stored without any special care and produce no byproducts.



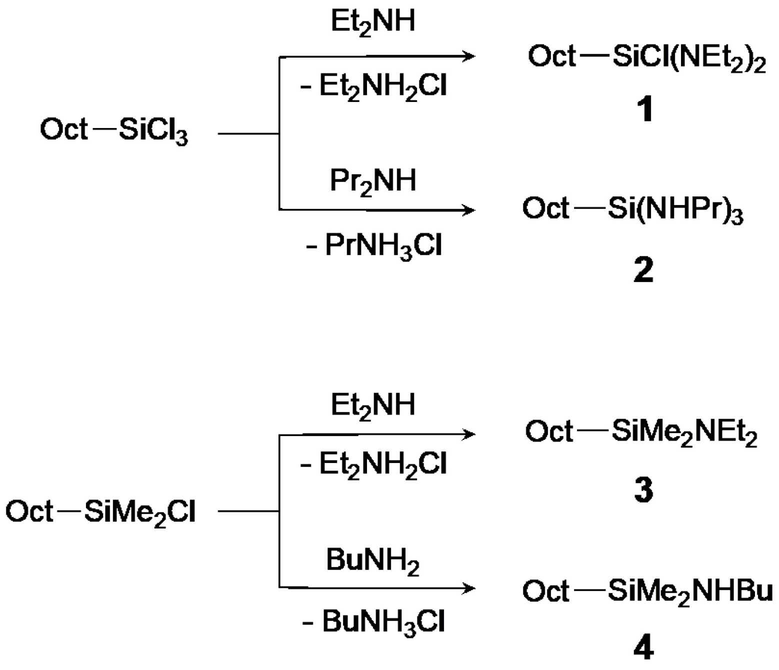
DSBP

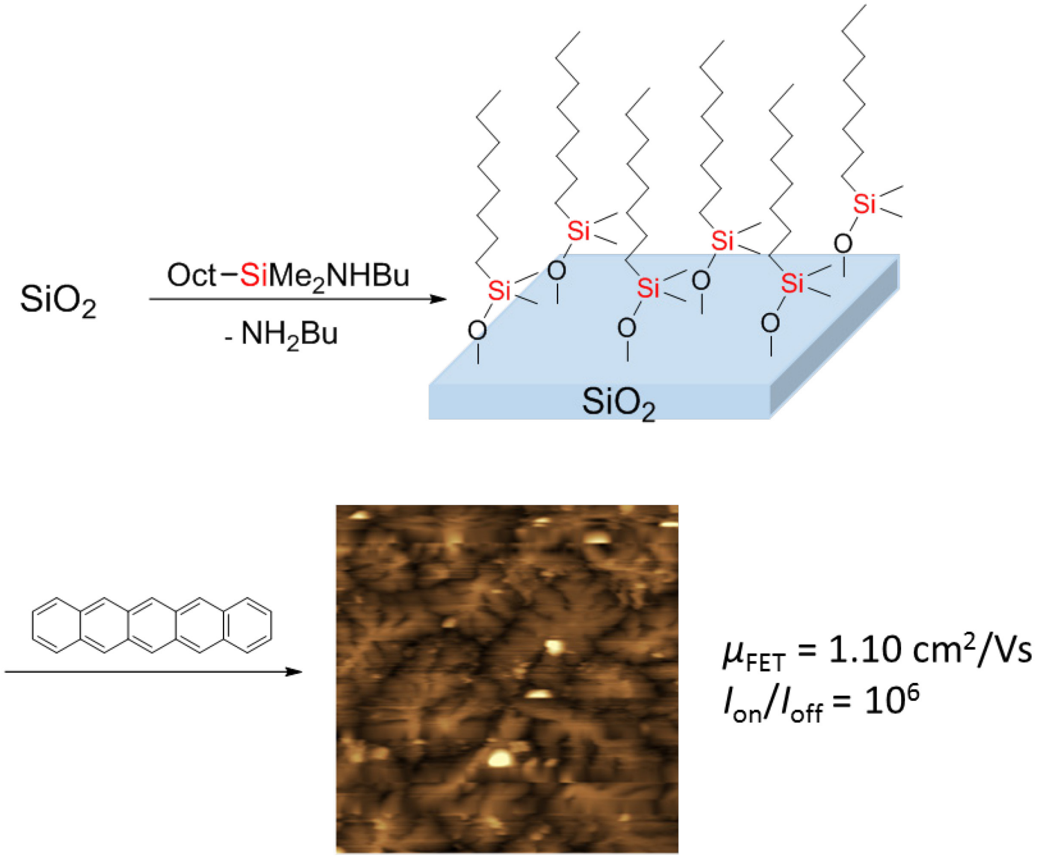


DSBT



In Chapter 3, the preparations and surface modification performance of new aminosilanes with hydrolysable Si-N bond(s) were described. The modification performance was evaluated by the performance of the top-contact p-type OTFT with a pentacene active layer. The transistor with the aminosilane-modified SiO_2 showed two- to threefold higher hole mobility than the device with bare SiO_2. The higher stability of presented aminosilanes towards moisture leads to easier-handling than the chlorosilane congeners. Surface modification by those aminosilanes liberates alkylamines as by-products. However, they are much less reactive than ammonia that is produced when inorganic surface is modified by hexamethyldisilazane that is known as a typical hydrophobic modifier with a Si-N bonds as the reactive sites.





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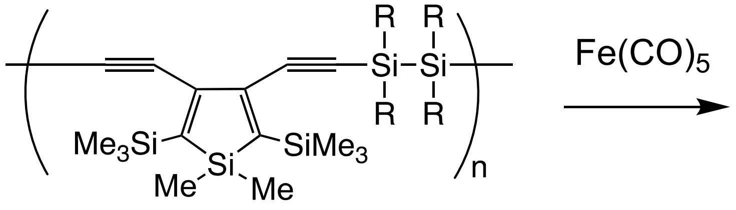
Chapter 1

Preparation of polymers containing Fe(0)-coordinated 2,5-diethynylsilole units

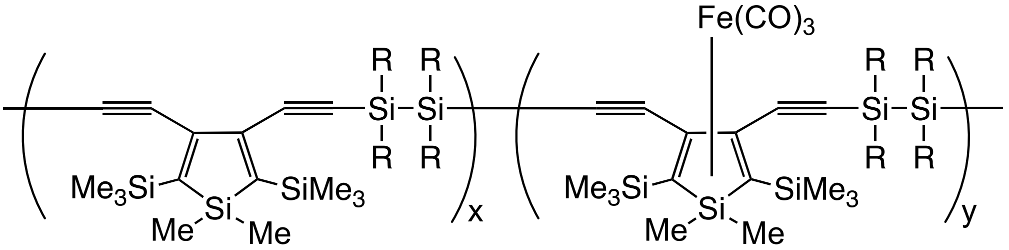
Introduction

Current interest has been focused on the chemistry of a silole ring system, because of their unique electronic states. The characteristic red-shifted UV absorptions of silole derivatives would arise from their low-lying LUMO due to the σ^*-π^* interaction between the silicon σ-orbital and the butadiene π-orbital [1,2]. The low-lying LUMO provides the chance to use silole derivatives as the functionality materials, such as semi-conductors and electron-transporting materials, and many papers concerning the synthesis and functionalities of monomeric silole derivatives as well as silole-containing polymers have been published to date. In addition, it is noted that silole derivatives may be potential ligands to transition-metal-center [3]. Corriu et al. have previously reported the formation of polymers having $Fe(CO)_3$-coordinated silole-1,1-diyl units [4]. However, no other studies about the incorporation of metal-coordination to the silole ring in polymeric systems have appeared until we have reported the synthesis of $Fe(CO)_3$-coordinated poly(disilanylene-3,4-diethynylenesiloles) (**1b** in Chart 1) [5]. As expected, the coordination of $Fe(CO)_3$ to the 3,4-diethynylsilole unit leads to significant changes in the polymer electronic states and the UV absorptions move to longer wave length from those of the parent non-coordinated polymers (**1a**), indicating the enhancement of π-conjugation by the $Fe(CO)_3$-coordination. This is probably due to the increase of the bond order between silole C3-C4 atoms, through which the two ethynyl groups may be conjugated more effectively.



R = Me, Et

1a



1b

Chart 1 synthesis of Fe(CO)3-coordinated poly(disilanylene-3,4-diethynylene¬siloles.

To know how the regional change affects the electronic states of $Fe(CO)_3$-coordinated diethynylsilole-containing polymers, we synthesized $Fe(CO)_3$-coordinated 2,5-diethynylsilole polymers by the reactions of poly(organosilanylene-2,5-diethynylenesiloles) and $Fe(CO)_5$, and studied their properties in comparison with those of the 3,4-diethynylsilole polymers [5,6]. The preparation of poly(organosilanylene-2,5-diethynylenesiloles) has been previously reported.

Polymers having an alternate arrangement of organosilanylene and π-conjugated units have been studied as novel functionality materials [8,9]. In order to elucidate the present organosilanylene-2,5-diethynylenesilole alternating polymers as the hole-transport, we fabricated double-layer EL devices with the structure of ITO/polymer film/Alq_3/Mg-Ag (ITO = indium tin oxide, Alq_3 = (tris(8-quinolinolato)aluminum (III)) and examined their performance.

Results and discussion

2.1. Preparation of a model compound

First, we examined a model reaction of 2,5-bis[(dimethylphenylsilyl)ethynyl]-1-methyl-1,3,4-triphenylsilole (**2a**) with $Fe(CO)_5$ (Chart 3). Thus, heating a xylene solution of compound **2a** at 150°C for 20 h with an excess of $Fe(CO)_5$ gave $Fe(CO)_3$-coordinated diethynylsiole (**2b**) in 66% yield. Compound **2b** was isolated as the single stereoisomer probably with the exo-configuration with respect to the Fe-coordinated silole unit (Chart 2). Although the ^1H and ^{13}C NMR spectra of the reaction mixture indicated the existence of the endo-isomer, that was removed by recrystallization. The ratio of isomers in the reaction mixture was determined approximately to be exo/endo = 3/1 by the NMR spectra.

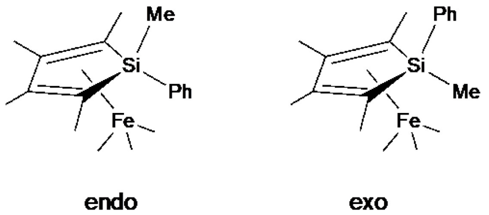


Chart 2 Endo- and exo-configuration of Fe-coordinated silole unit.

The structure of **2b** was verified by spectroscopic and elemental analysis. The ^{13}C NMR spectrum of **2b** showed a carbonyl signal at 209.2 ppm and signals at 42.9 ppm and 91.8 ppm, which are characteristics of a metal-coordinated butadiene unit [10]. On the other hand, the signals of sp carbons of **2b** appeared at 108.0 ppm and 110.6 ppm, in essentially the same region as those of the starting **2a**, indicating that no significant interaction takes place between the ethynyl units and Fe-complex center in **2b**, similar to polymer **1b** [5].

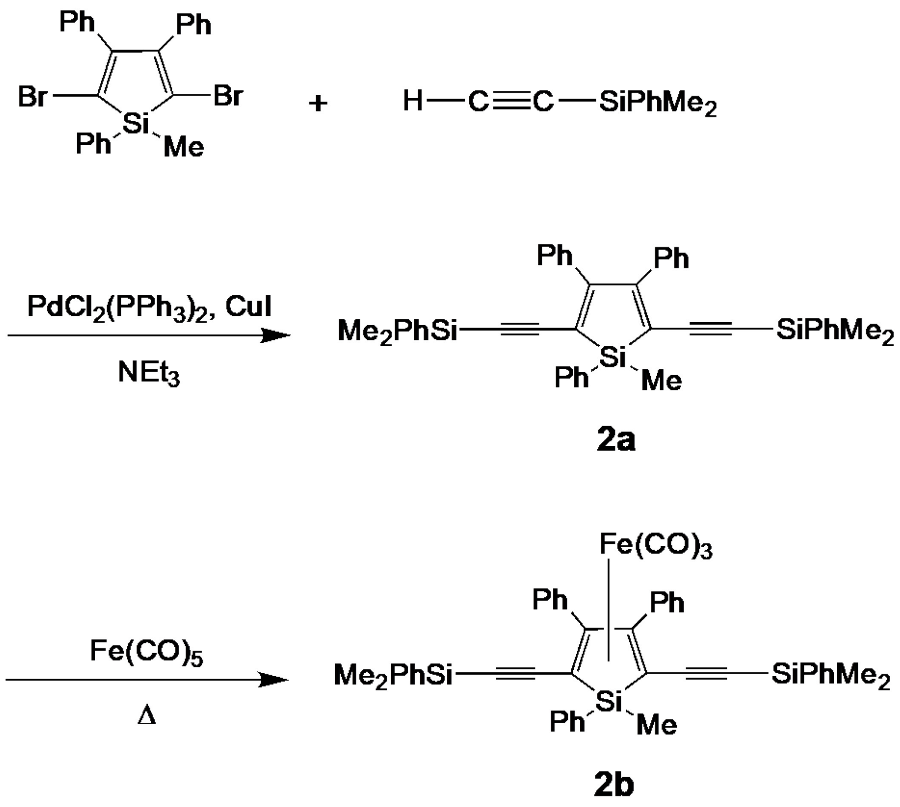


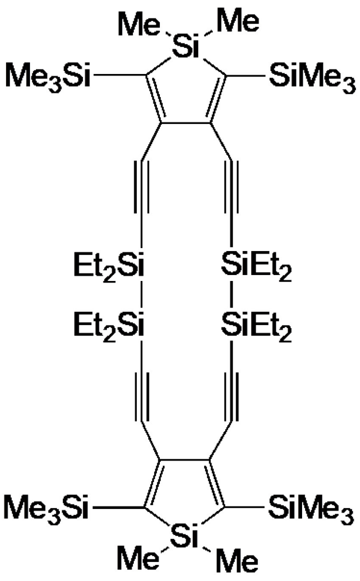
Chart 3 Model reaction of 2,5-bis[(dimethylphenylsilyl)ethynyl]-1-methyl-1,3,4-triphenylsilole (2a) with $Fe(CO)_5$.

UV spectral data for **2a** and **2b** are summarized in Table 1, together with those of $Fe(CO)_3$-corrdinated and noncoordinated 3,4-diethynylsilole derivatives reported previously (**3a** and **3b**, in Chart 4) [5]. Compound **2a** exhibited red-shifted absorptions relative to **3a**. $Fe(CO)_3$-coordination to 2,5-diethynylsilole system in **2b** led to blue-shifts of the absorption maxima, in marked contrast to 3,4-diethynylsilole **3a**, whose absorption maxima are red-shifted by $Fe(CO)_3$-coordination. Presumably, the coordination in **2b** decreases the π-bond order of C2-C3 and C4-C5, relative to those in **2a**, to suppress the conjugation in the 2,5-diethynylsilole unit.

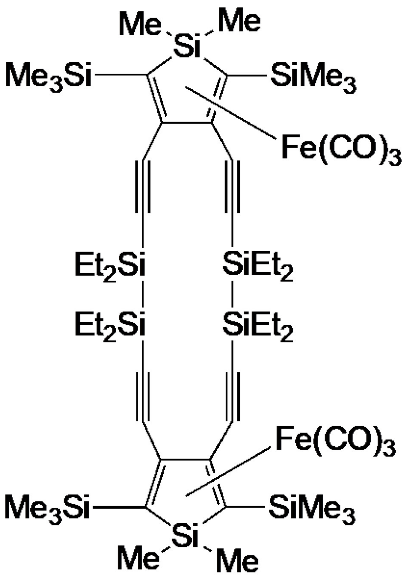
Table 1 UV spectral data for Fe-coordinated and non-coordinated diethynylsiloles in THF

compound	λ_{max}/nm	λ_{edge}/nm
2a	210, 283, 398	460
2b	210, 259 (sh[a]), 307 (sh[a])	450
3a	210, 268, 301	390
3b	210, 237, 320	430

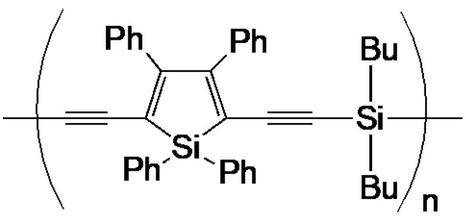
[a] Shoulder.



3a



3b

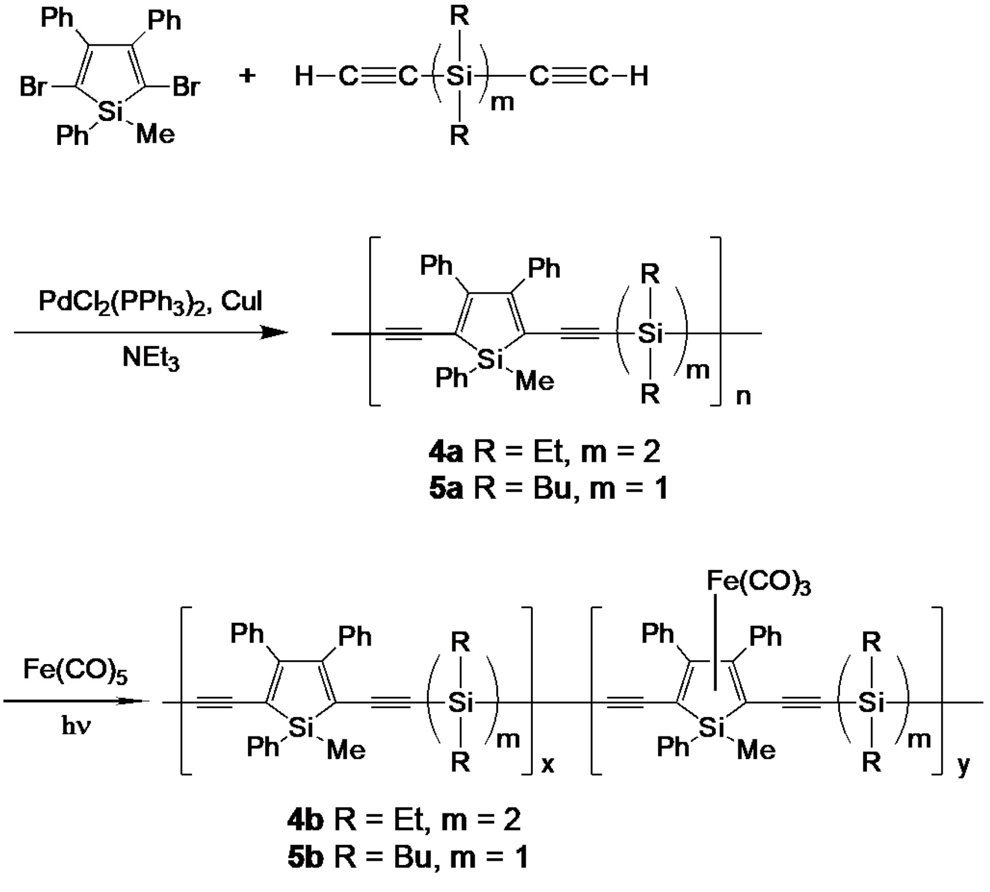


6a

Chart 4 Fe(CO)3-coordinated and noncoordinated 3,4-diethynylsilole derivatives.

2.2. Preparation of Fe(CO)$_3$-coordinated 2,5-diethynylsilole polymers

To obtain polymers with Fe(CO)$_3$-coordinated 2,5-diethynylsilole units, we first carried out the reaction of poly[tetraethyldisilanylene-(2,5-diethynylene-1-methyl-1,3,4-triphenylsilole)] (**4a**) with Fe(CO)$_5$ under the same conditions as those for the preparation of **2b**. However, when **4a** was heated at 150°C for 20 h in the presence of a 4-fold excess of Fe(CO)$_5$ in benzene, only insoluble dark-brown solids were formed and no soluble products were isolated from the reaction mixture. Although the IR spectrum of the insoluble products showed absorptions at 1984 and 2050 cm^{-1}, due to the stretching frequencies of the carbonyl ligands, no further information to characterize the products could be obtained.



4a R = Et, m = 2
5a R = Bu, m = 1

4b R = Et, m = 2
5b R = Bu, m = 1

Scheme 1 Preparation of Fe(CO)$_3$-coordinated 2,5-diethynylsilole polymers under photochemical conditions.

Next, we examined the reaction of **4a** with $Fe(CO)_5$ under photochemical conditions (Scheme 1). Thus, irradiation of a benzene solution of **4a** with 8 equiv. of $Fe(CO)_5$ with a high-pressure mercury lamp bearing a Pyrex filter for 2 h, gave a dark brown mixture containing insoluble precipitates. After filtration of the precipitates, the soluble products were reprecipitated from benzene-methanol to give an $Fe(CO)_3$-coordinated polymer (**4b**) in 79% yield. The ^{1}H NMR spectrum of **4b** revealed two MeSi signals of $Fe(CO)_3$-coordinated silole ring at 0.39 and 1.31 ppm, in an integral ratio of 3/1, probably due to exo- and endo-silole units, respectively (Chart 2). Its ^{13}C NMR spectrum also showed two sets of signals due to $Fe(CO)_3$-coordinated exo- and endo-1-methyl-1,3,4-triphenylsilole units in the same region as those of the model compound **2b**. The degree of the introduction of $Fe(CO)_3$-coordination to the polymer was calculated to be $x/y = 10/90$, by the integration of the ^{1}H NMR signals.

Table 2 summarizes the properties of polymers **4a** and **4b**. The molecular weight of polymer **4b** was smaller than that calculated on the basis of the molecular weight of the starting **4a**. Probably, the higher molecular weight fraction of polymer **4a** was removed as the insoluble precipitates from the reaction mixture. Photochemical cleavage of the Si-Si bond may be also involved in this reaction [8]. UV spectrum of **4b** clearly indicated the decrease of the absorbancy of the band at about 415 nm, which may be due to a blue shift in the absorption maximum of Fe-coordinated segments in the polymer chain. The IR band due to the C≡C stretching moved to higher energy from 2109 to 2120 cm^{-1} by Fe-coordination, again indicating the suppressed conjugation between the Fe-coordinated silole and ethynylene units in **4b**.

Table 2 Properties of Fe-coordinated and Non-Coordinated 2,5-Diethynylsilole-Polymers

polymer	Mw (Mw/Mn) [a]	λ_{max}/nm (ε) [b]	Td_5/°C [c]	wt loss/% [d]
4a	21 000 (2.4)	415 (6800)	418	45
4b	11 000 (2.5)	413 (2000)	214	47
5a	31 000 (3.2)	406 (5900)	421	40
5b	7 100 (2.7)	405 (1700)	220	55

[a] Determined by GPC, relative to polystyrene standards.

[b] In THF.

[c] Temperature resulting in 5% weight loss noted by thermogravimetric analysis of the polymer at the rate of 10°C/min in a nitrogen atmosphere.

[d] Weight loss at 1000°C based on the initial weight.

Similar to **4b**, $Fe(CO)_3$-coordinated monosilanylene polymer **5b** was prepared from **5a** in 57% yield, whose properties are also summarized in Table 2. Although polymer **5b** was barely soluble in organic solvents and we could not carry out the NMR spectroscopy, the IR and UV spectra closely resemble those of **4b** (Figure 1). The IR spectrum revealed an absorption due to the C≡C stretching at slightly higher energy from that of **5a**, together with the C=O stretching bands. Furthermore, the carbon and hydrogen contents determined by combustion elemental analysis are in good agreement with the calculated values of polymer **5b** whose silole units are wholly coordinated with an $Fe(CO)_3$-unit. Polymer **6a** (see Chart 4) [6] having two phenyl groups on the silole silicon atom did not react with $Fe(CO)_5$ under both thermal and photochemical conditions. In these reactions, polymer **6a** was recovered unchanged.

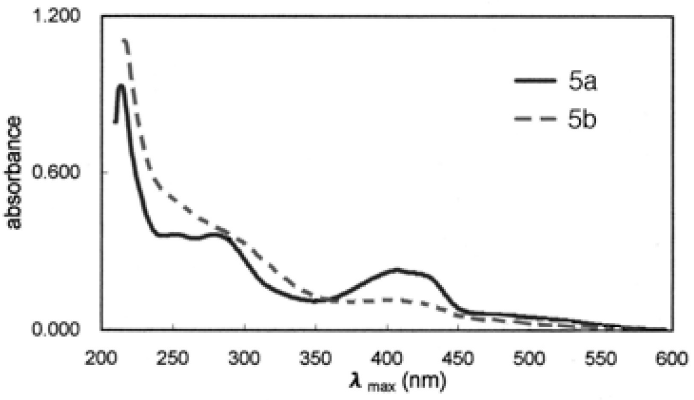


Figure 1 UV spectra of polymers 5a and 5b.

The temperatures resulting in 5% weight loss of the initial weight (T_d^5) were noted by thermogravimetric analysis (TGA) of the polymers in a nitrogen atmosphere. As listed in Table 2, the $Fe(CO)_3$-coordination resulted in a significant decrease in the T_d^5 value, indicating that thermal liberation of the $Fe(CO)_3$-units occurred during the analysis. Similar decrease in the T_d^5 value by $Fe(CO)_3$-coordination was also observed for polymers **1b** when compared with **1a** [5]. However, there can be seen no significant increase in the weight loss at 1000°C for polymers **4b** and **5b** relative to **4a** and **5a**.

2.3. Applications of poly(organosilanylene-2,5-diethynylenesilole)s to hole-transports in EL devices

Double layer EL devices having a spin-coated film of polymer **4a** and **5a** as the hole-transport and vapor-deposited layer of Alq_3 as the electron-transporting emitter were fabricated. Figure 2 represents the current density-voltage (*I-V*) and luminance-voltage (*L-V*) plots of the devices. As scan be seen in Fig. 2, the device with polymer **5a** showed lower turn-on voltage than that with **4a**, and always afforded higher current density and luminance in the applied voltage of 6-16 V with the maximum luminance of 300 cd/m^2. This is in contrast to that polymer **4a** exhibited the UV λ_{max} at lower energy than **5a**, and may be due to the higher concentration of π-conjugated unit in the film of monosilanylene polymer **5a**. Similar tendency was observed other organosilanylene-π-electron system alternating polymers [8,11].

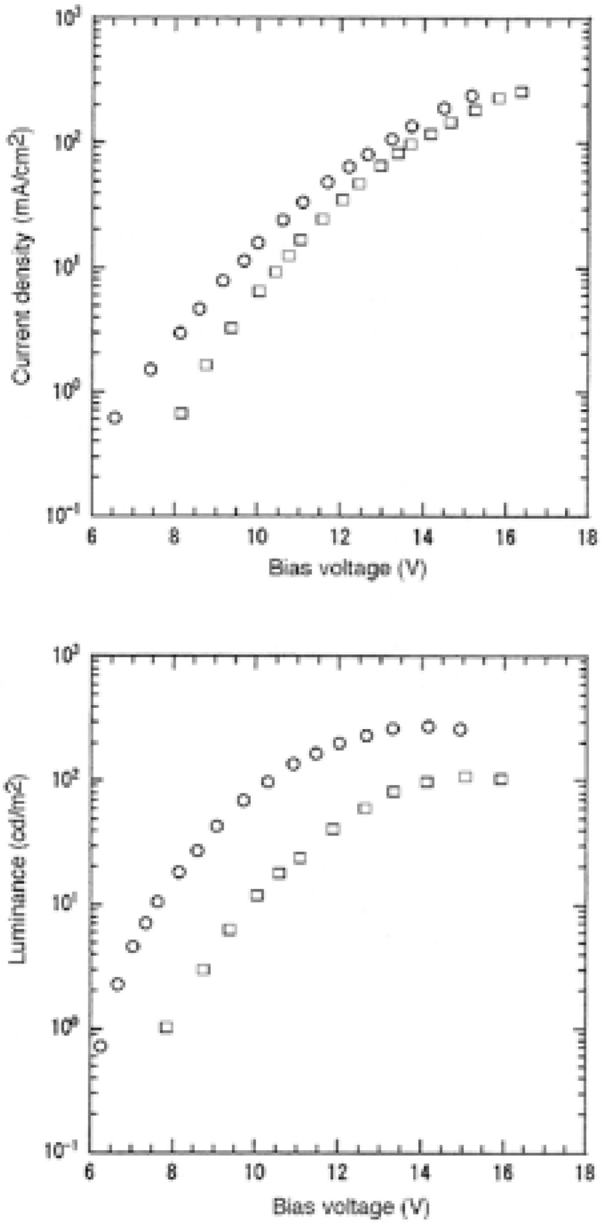


Figure 2 Current density-voltage (top) and Luminescence-voltage plots (bottom) for EL devices having a polymer film of (□) 4a and (○) 5a, as the hole-transport.

Conclusions

On the basis of the results described above, we demonstrated that 2,5-diethynylsilole unit may be used as the potential ligands to transition metal center, unless they have two sterically bulky substituents at the silole silicon atom. The coordination of the $Fe(CO)_3$-unit to diethynylsilole system seems to provide an opportunity to modify the electronic states of the π-electron system. Thus, by $Fe(CO)_3$-coordination to 2,5-diethynylsilole unit led to suppressed conjugation in this system, in contrast to 3,4-diethynylsilole system whose coordination with $Fe(CO)_3$ enhances the conjugation between the ethynyl groups through the silole π-system. In addition, we found that the present silole-containing polymers **4a** and **5a** may be used as the hole-transport for EL devices.

Experimental

4.1. General procedures

All reactions were carried out under an atmosphere of dry nitrogen. Benzene and xylene were dried over sodium-potassium alloy and sodium, respectively, and distilled just before use. Triethylamine was distilled from potassium hydroxide and stored over activated molecular sieves 4A before use. The starting compounds, 2,5-dibromo-1-methyl-1,3,4-triphenylsilole [12], ethynyldimethylphenylsilane [13], and 1,1,2,2-tetraethyldiethynyldisilane [14] were prepared as reported in the literature.

4.2. Preparation of 2a

A mixture of 0.50 g (1.04 mmol) of 2,5-dibromo-1-methyl-1,3,4-triphenylsilole, 40 mg of $PdCl_2(PPh_3)_2$, 6 mg of CuI, and 25 mL of triethylamine was stirred at room temperature for 30 min. To this was added 0.66 g (4.15 mmol) of ethynyldimethylphenylsilane and the mixture was heated under reflux for 15 h. The resulting salts were filtered and the solvent was evaporated. The residue was subjected to silica gel column chromatography eluting with hexane to give a crude product. Recrystallization of the crude product from hexane gave 0.25 g (37% yield) of **2a** in pure form as the yellow solids. Mp: 93-95°C. ^{1}H NMR ($CDCl_3$): δ 0.34 (s, 12H), 0.75 (s, 3H), 7.11-7.25 (m, 25H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 5.9, 0.7, 103.4, 106.7, 116.9, 122.6, 127.2, 127.6, 127.7, 128.2, 129.1, 129.3, 130.3, 133.7, 134.6, 137.2, 163.7 (one carbon is overlapping). *Anal.* Calc. for $C_{43}H_{40}Si_3$: C, 80.56; H, 6.29. Found: C, 80.46; H, 6.02%.

4.3. Preparation of 2b

A mixture of 89 mg (0.24 mmol) of **2a** and 0.109 g (0.555 mmol) of $Fe(CO)_5$ in 1.3 mL of xylene was heated at 150°C for 20 h, in a sealed glass tube. The resulting insoluble materials were filtered and the solvent was evaporated. The residue was subjected to preparative GPC eluting with benzene to give a crude product. Recrystallization of the crude product from ethanol gave 30 mg (66% yield) of compound **2b** in pure form as the pale brown solids. Mp: 126-128°C. ^{1}H NMR ($CDCl_3$): δ 0.36 (s, 12H), 1.26 (s, 3H), 7.25-7.52 (m, 25H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ –5.2, –0.7, 42.9, 91.8, 108.0, 110.6, 127.4, 127.6, 128.1, 129.0, 129.8, 131.8, 132.6, 133.4, 133.6, 135.2, 137.5, 139.7, 209.2. *Anal.* Calc. for $C_{46}H_{40}FeO_3Si_3$: C, 70.75; H, 5.16. Found: C, 70.52; H, 5.13%.

The NMR spectra of the reaction mixture indicated the formation of the other isomer of **2b**, which was removed by recrystallization. ^{1}H NMR ($CDCl_3$): δ 0.06 (s, 3H), 0.38 (s, 12H), 7.11-7.57 (m, 25H, overlapping with the signals of **2b**). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 1.0, 6.1, 41.4, 91.6, 108.7, 127.7, 128.0, 128.2, 129.1, 130.3, 133.6, 133.7, 133.8, 134.1, 137.5, 208.4, signals of other carbons may overlap with those of **2b**.

4.4. Preparation of dibutyldiethynylsilane

A solution of 0.40 mol of ethylmagnesium bromide in 350 mL of THF was added slowly to 400 mL of THF saturated with acetylene over a period of 4 h, to prepare ethynylmagnesium bromide. To the resulting solution of ethynylmagnesium bromide which may contain a small amount of ethynylenedimagnesium dibromide, was added 10.64 g (0.05 mol) of dibutyldichlorosilane and the mixture was stirred at room temperature for 20 h. After hydrolysis with water, organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. Evaporation of the solvent and distillation of the residue under reduced pressure gave 8.82 g (92% yield) of dibutyldiethynylsilane. Bp: 105-106°C (23 mmHg). IR: 3290, 2027 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.71-0.77 (m, 4H), 0.89 (t, 6H, J = 6.9 Hz), 1.31-1.50 (m, 8H), 2.46 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.6, 13.8, 25.5, 25.9, 84.7, 95.0. MS m/z 192 (M^+). *Anal.* Calc. for $C_{12}H_{20}Si$: C, 74.92; H, 10.48. Found: C, 75.22; H, 10.17%.

4.5. Preparation of 4a and 5a

A mixture of 0.48 g (1.00 mmol) of 2,5-dibromo-1-methyl-1,3,4-triphenylsilole, 34 mg of $PdCl_2(PPh_3)_2$, 6 mg of CuI, and 12 mL of triethylamine was stirred at room temperature for 30 min. To this was added 0.22 g (1.00 mmol) of tetraethyl-1,2-diethynyldisilane and the mixture was stirred at 50°C for 48 h. The resulting salts were filtered and the solvent was evaporated. Reprecipitation of the residue from benzene/methanol gave 0.397 g (73% yield) of **4a**. Mp: 79-86°C. IR: 2109 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.58-1.16 (23H, Et and Me), 7.08-7.81 (15H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ –5.9, 5.0, 8.3, 102.8, 108.3, 122.6, 127.1, 127.4, 128.0, 129.2, 130.2, 132.1, 134.5, 137.2, 162.7 (silole C2 and C5). *Anal.* Calc. for $(C_{35}H_{38}Si_3)_n$: C, 77.42; H, 7.05. Found: C, 76.23; H, 7.00%.

Polymer **5a** was obtained in the same fashion as above using tetraethyl-1,2-diethynyldisilane in place of dibutyldiethynylsilane in 69% yield. Mp: 85-91°C. IR: 2116 cm^{-1}. ^1H NMR (C_6D_6): δ 0.69-1.31 (m, 21H, Bu and Me), 7.08-7.81 (m, 15H, Ph).

$^{13}C\{^1H\}$ NMR (C_6D_6): δ –5.7, 13.8, 14.9, 25.9, 26.0, 101.5, 106.0, 122.5, 127.1, 127.6, 128.1, 129.3, 130.3, 131.9, 134.6, 137.1, 163.6 (silole C2 and C5). *Anal.* Calc. for $(C_{35}H_{36}Si_2)_n$: C, 81.97; H, 7.08. Found: C, 80.38; H, 6.99%.

4.6. Preparation of 4b and 5b

A mixture of 150 mg (0.28 mmol) of **4a** and 0.433 g (2.20 mmol) of $Fe(CO)_5$ in 30 mL of benzene was irradiated with a high pressure mercury lamp (100 W) bearing a Pyrex filter with water-cooling for 2 h. The resulting insoluble materials were filtered the solvent was evaporated. Reprecipitation of the residue from benzene/methanol gave 0.149g (79% yield) of **4b** as the dark brown solids. IR: 2120, 2049, 1983 cm^{-1}. ^1H NMR (C_6D_6): δ 0.39 (br s, 0.7H, exo-Me), 0.80-1.11 (m, 20.3 H, Et, overlapping with the Et and Me signals of Fe-noncoordinated units), 1.31 (br s, 2H, endo-Me), 7.00-7.65 (m, 15H, Ph, overlapping with the signals of Fe-noncoordinated units). $^{13}C\{^1H\}$ NMR (C_6D_6): δ –4.9, -6.2, 5.4, 8.7, 42.7, 44.4, 91.1, 91.6, 103.1, 110.8, 127.8, 128.9, 129.1, 129.5, 129.7, 130.2, 130.8, 131.0, 132.1, 132.7, 133.9, 134.1, 134.6, 135.0, 135.8, 137.8 (Signals due to Fe-noncoordinated units were also observed). *Anal.* Calc. for $(C_{38}H_{38}FeO_3Si_3)_{0.9n}(C_{35}H_{38}Si_3)_{0.1n}$: C, 67.77; H, 5.73. Found: C, 66.79; H, 5.68%.

Polymer **5b** was obtained from **5a** in the same fashion as above in 57% yield (calculated as a wholly substituted polymer). IR: 2121, 2051, 1986 cm^{-1}. *Anal.* Calc. for $(C_{36}H_{38}FeO_3Si_2)_n$: C, 69.93; H, 5.56. Found: C, 69.88; H, 5.90%.

4.7. Preparation of EL devices

A thin film (ca 70 nm) of polymer **4a** or **5a** was prepared by spin coating from the chloroform solution on an anode, indium-tin-oxide (ITO) coated on a glass substrate (Nippon Sheet Glass Co.). An electron-transporting-emitting layer was then prepared by vacuum deposition of Alq_3 at 1×10^{-5} torr with a thickness of 60-70 nm on the polymer film. Finally, a layer of magnesium-silver alloy with an atomic ratio of 10:1 was deposited on the Alq layer surface as the top electrode at 1 $\times 10^{-5}$ torr.

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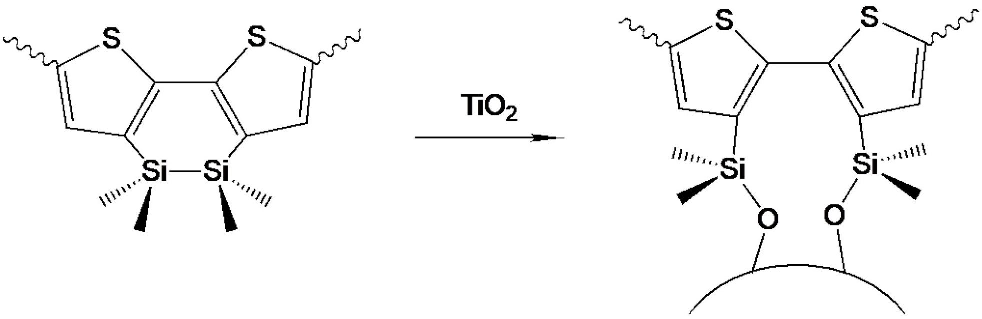
Chapter 2

Hydrophobic modification of SiO_2 surface with disilanobiphenyl and disilanobithiophene and the application to pentacene-based organic transistors

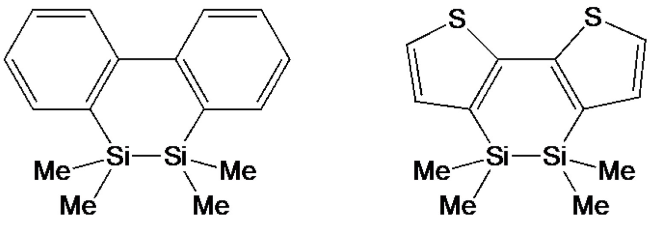
Introduction

Surface modification of inorganic oxide with organic modifiers is an important process in areas of surface and interface engineering. Several silane coupling agents, such as chloro- and aminosilanes are widely used as the modifiers [1-4]. They react readily with hydroxyl groups on the surface (M-OH) to form M-O-SiR linkages covering the surface with organic groups (R). By this process, the hydrophobicity of the surface is readily increased, making it possible to control the organic layer structure prepared on the surface. Surface modification of the SiO_2 gate electrode is of importance in organic thin film transistor (OTFT), which enhances the performance of the device [5-9]. This is ascribable to diminishing the carrier traps and changes of the interface properties. For example, modification of SiO_2 surface with trichlorosilanes, such as OTS (octadecyltrichlorosilane) results in the improved alignment of the organic molecules on the surface to enhance the semi-conducting properties of the organic layers. However, the reactions of these coupling agents with M-OH groups on the surface produce HCl as the by-product that may damage the SiO_2 surface and/or contaminate in the modified SiO_2. In addition, trichlorosilanes usually possess high tendency to undergo hydrolysis even with atmospheric moisture, making their handling difficult. Hydrolysis of trichlorosilanes must be avoided not only for storing, but also during the modification process, as their hydrolysis provides polysilsesquioxane polymers or oligomers that may stack on the surface to disturb the formation of smooth single-molecular-modified surface, introducing defects of the active layer. More stable aminosilanes including hexamethyldisilazane (HMDS) have been also used as hydrophobic modifiers. However, HMDS has only methyl groups, thereby difficult to realize highly hydrophobic surface. Although aminosilanes with longer alkyl chains have been also studied, they are still limited [10].

Recently, we demonstrated that treatment of TiO_2 surface with polymers composed of alternating Si-Si and π-conjugated units under UV irradiation resulted in attachment of the polymers on the surface through the formation of Ti-O-Si linkages (Scheme 1) [11-15]. Interestingly, the modified TiO_2 could be used as photo-electrodes of dye sensitized solar cells. More recently, disilanobithiophene polymers were introduced as more efficient modifiers, which reacted with TiO_2 surface even in the dark [16]. In this paper, we report the hydrophobic modification of SiO_2 surface using tetramethyldisilanobiphenyl (DSBP, in Chart 1) as a new modifier. They are stable under ambient conditions and can be stored for several months under room light in air without noticeable decomposition. DSBP would have larger ring strain arising from the *ortho*-H repulsion than DSBT, thus being expected to be more reactive towards inorganic oxide surface. A disilanobithiophene monomer (DSBT) was also investigated as a modifier in comparison with DSBP.



Scheme 1 Modification of TiO_2 surface with disilanobithiophene-polymers.



DSBP (X = CH=CH) DSBT (X = S)

Chart 1 Structures of DSBP and DSBT.

Results and Discussion

2.1. Modification of glass surface with disilanes

To evaluate DSBP as a hydrophobic SiO_2 modifier, we measured water contact angles of glass plates after treating with DSBP in dry argon. When glass plates that had been ozone-cleaned were irradiated in toluene solutions of DSBP with different concentrations by a low-pressure mercury lamp (254 nm) for 3 h at 20-40 °C, the contact angles increased from 2° to approximately 60°, indicating the hydrophobic modification of the glass surface by DSBP (Table 1, run 1, 2, 4, and 5). A control experiment in pure toluene under the same conditions provided the contact angle of 11°. The slight increase of the contact angle in this process would be due to some contamination of organic substances. Changes of the contact angles along increasing the irradiation time were monitored using a 3.5 M DSBP solution in toluene as shown in Figure 1. The contact angles increased rapidly and was almost saturated after only 1 h irradiation. Similar treatment with tetramethyldiphenyldisilane also provided hydrophobic surface with a contact angle of 70° (Table 1, run 6). DSBP reacted with glass surface also under thermal conditions. Thus, heating a glass plate in a DSBP toluene solution at 80 °C in the dark increased the contact angles. However, the progress of the reaction was much slower and the maximal contact angle obtained under the thermal conditions was 44°, smaller than that modified under similar conditions with irradiation (Table 1, run 3). Attempted modification of a glass plate with tetramethyldiphenyldisilane in the dark at 80 °C was unsuccessful and the water contact angle of the resulting glass plate was only 28° (Table 1, run 7). This indicates that the ring strain in DSBP is essential to promote the surface modification by disilanes in the dark.

DSBT was also applied as a hydrophobic modifier (Table 1, run 8 and 9). Similarly to the experiments using DSBP, the glass surface was more efficiently modified under irradiation, increasing the water contact angles more rapidly than in the dark. When compared to DSBP, the DSBT-modified glass plates had smaller contact angles. The increase of the contact angles in the dark was unstable and the plots were scattered to an extent, as shown in Figure 1 (bottom, square plots), likely due to the rather ineffective modification of the surface.

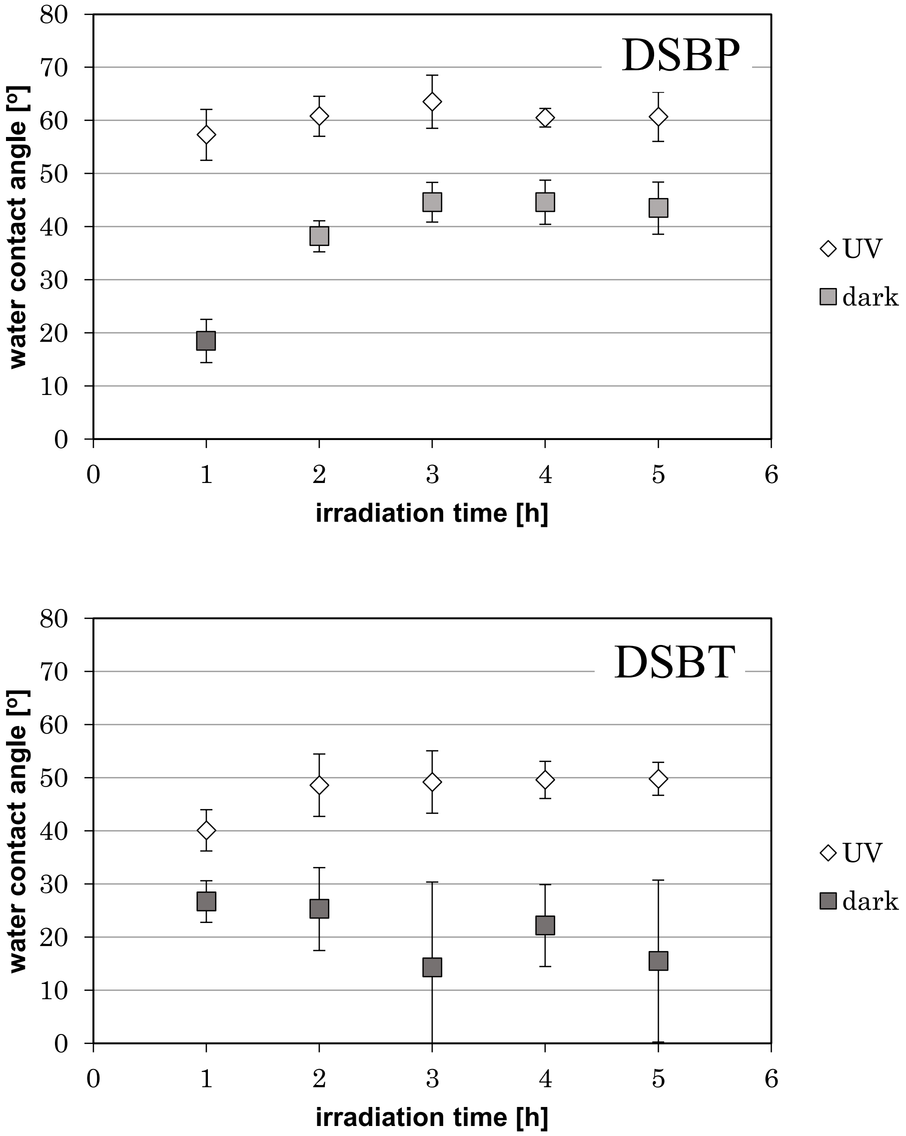


Figure 1 Plots of water contact angles versus irradiation times of glass plates in DSBP (top) and DSBT (bottom) solutions (3.5 M). The presented error bar means two-side 95% confidence interval (± 2σ) based on measurements of twenty independent points of the glass surface.

Table 1 Water contact angles of glass plates after modification with disilanes in toluene for 3 h

run	disilane	conc/M	conditions[a]	contact angle/°
1	DSBP	1.9	P	58
2		3.5	P	63
3			T	44
4		5.9	P	63
5		13.2	P	65
6	$(PhMe_2Si)_2$	5.3	P	70
7			T	28
8	DSBT	3.5	P	50
9			T	48
10	non[b]		P	11

[a] P: under irradiation (254 nm); T: in the dark at 80 °C. [b] In pure toluene without disilane.

2.2. Applications of modified SiO_2 to OTFTs

As hydrophobic modification of SiO_2 surface is of important process for the fabrication of organic thin film transistors, we examined DSBP as a modifiers of SiO_2 surface. Although modification under irradiation resulted in higher hydrophobicity of the glass surface, SEM images of the surfaces revealed the existence of small particles (< 1 μm). These particles were not soluble in organic solvents and could not be removed by washing with toluene. The EDX analysis of those formed from DSBT under irradiation showed that they contained sulfur, indicating that the particles had arisen from photochemical reactions of DSBT, leading oligomers and/or polymers that aggregated to form insoluble substances. On contrary, much less particles were found to be formed on the thermally modified-surface. On the basis of those observations, we concluded that thermally modified SiO_2 would be more suitable for organic device fabrication.

When an ozone-cleaned gate electrode of SiO_2/Si was dipped in a 3.5 M DSBP solution in toluene at room temperature for 1 h, the contact angle of the SiO_2 surface was increased from 14° to 56° (Figure 2). Pentacene was vapor-deposited on the modified surface as the active layer then gate and source electrodes were deposited on the pentacene surface to complete a top-contact OTFT. We also prepared a similar device without surface modification for comparison. As summarized in Table 2, the modification did not show drastic changes of the OTFT performance parameters. The AFM surface images and XRD patterns of the pentacene layers on modified and non-modified SiO_2 are shown in Figure 3a and 3b. In contrast to our expectation, the grain size was decreased by using the modified SiO_2. This may be due to that the SiO_2 surface was not sufficiently covered by DSBP. When a DSBP solution with a higher concentration (6.0 M) was employed for the modification, the grain size was increased and the crystallinity was enhanced, as presented in Figure 3c. Similar effects of hydrophobic modification affecting the pentacene morphologies on the surface have been often reported [5-9,21,22]. This is ascribable to the changes of interaction between the surface and pentacene, which affect the formation seed crystals and diffusion of pentacene molecules. Although the OTFT parameters were not significantly changed (Figure 4), an enhanced mobility was obtained by this modification. Increased crystalline size is known to improve the carrier mobility mainly by reducing boundaries. Capping the carrier trapping hydroxyl units with the modifier may also be a reason for the improved mobility of the device [5-9].

DSBT was also examined for OTFT preparation. As shown in Table 2, however, modification by DSBT (3.5M) led to inferior device performance to that prepared using DSBP as the modifier at the same concentration, although the water contact angles were similar regardless of the modifiers (DSBT or DSBP). The AFM and XRD analysis of the pentacene surface showed smaller grain size and lower crystallinity as compared with those of the DSBP-based OTFT, as shown in Figure 5.

Table 2 OTFT parameters with pentacene as active material, using SiO_2/Si gate electrode with and without thermal modification by disilane

disilane (conc/M[a])	water contact[b] angle /°	μ_{FET}[c] /$cm^2V^{-1}s^{-1}$	V_{th}[c] /V	I_{on}/I_{off}[c]	XRD[d] d-space/Å
DSBP (3.5)	56	0.14	-18	10^4	15.4
(6.0)	47	0.21	-17	10^5	15.1
DSBT (3.5)	55	0.11	-11	10^4	15.2
non	14	0.16	-20	10^5	15.3

[a] In toluene. [b] Measured for the SiO_2 surface. [c] OTFT performance parameter. [d] Measured for the pantacene layer.

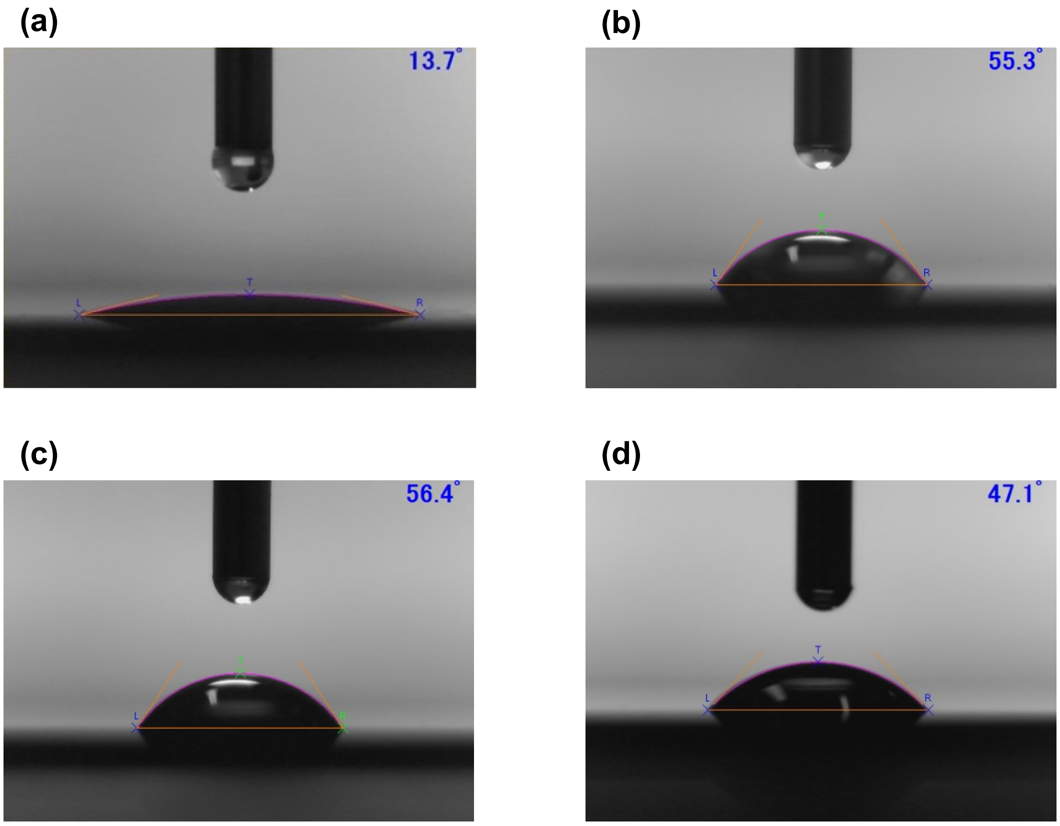


Figure 2 Water contact angle measurements of bear SiO_2 (a), and SiO_2 modified by 3.5 M DSBT (b), 3.5 M DSBP (c), and 6.0 M DSBP (d).

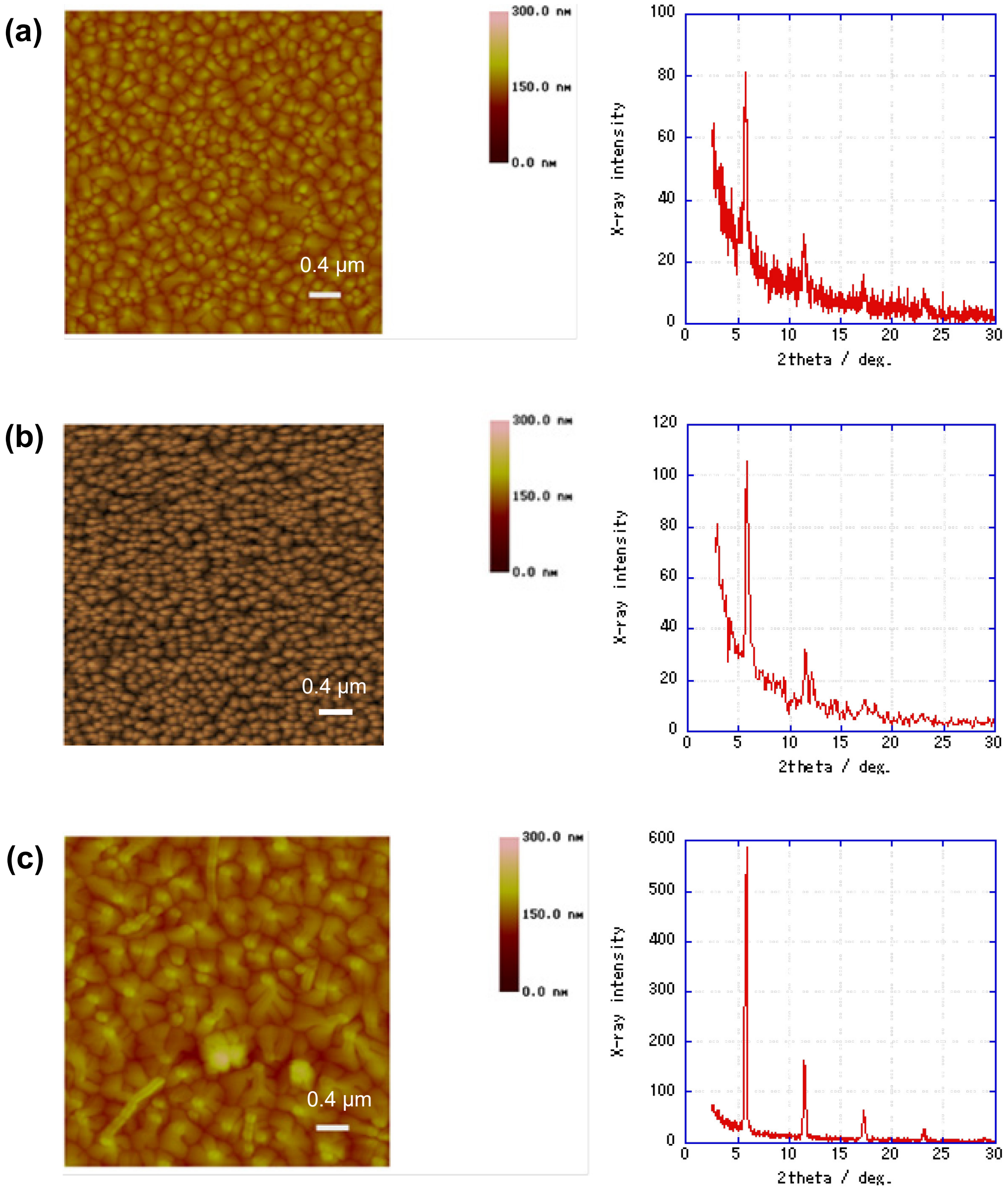


Figure 3 **AFM surface images and XRD patterns of the pentacene layers prepared on non-modified SiO_2 (a), and that modified with 3.5 M DSBP (b) and 6.0 M DSBP solutions (c).**

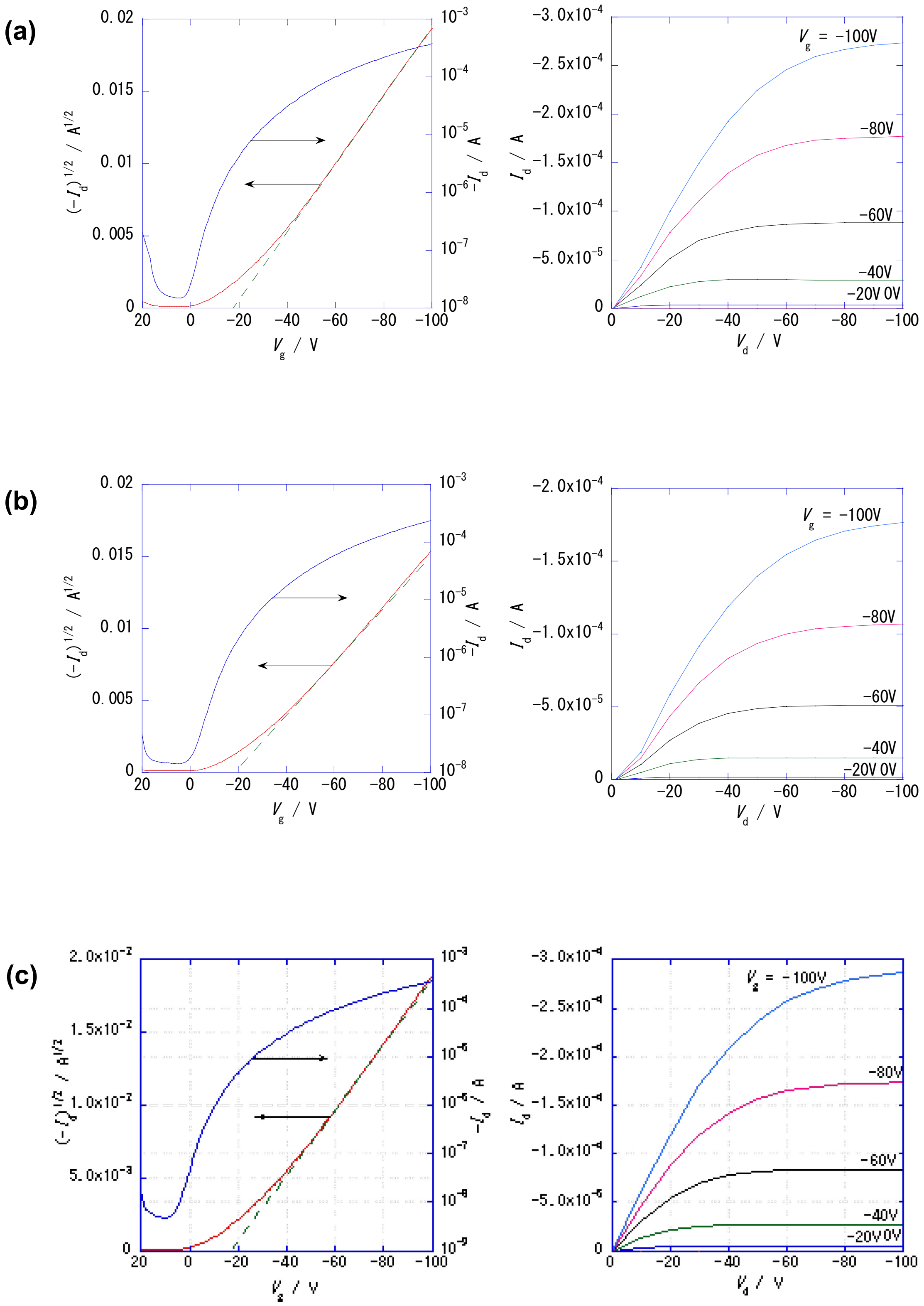


Figure 4 **Characteristics of the OTFT using bare SiO_2 (a) and that modified with 3.5 M DSBP (b) and 6.0 M DSBP solutions (c).**

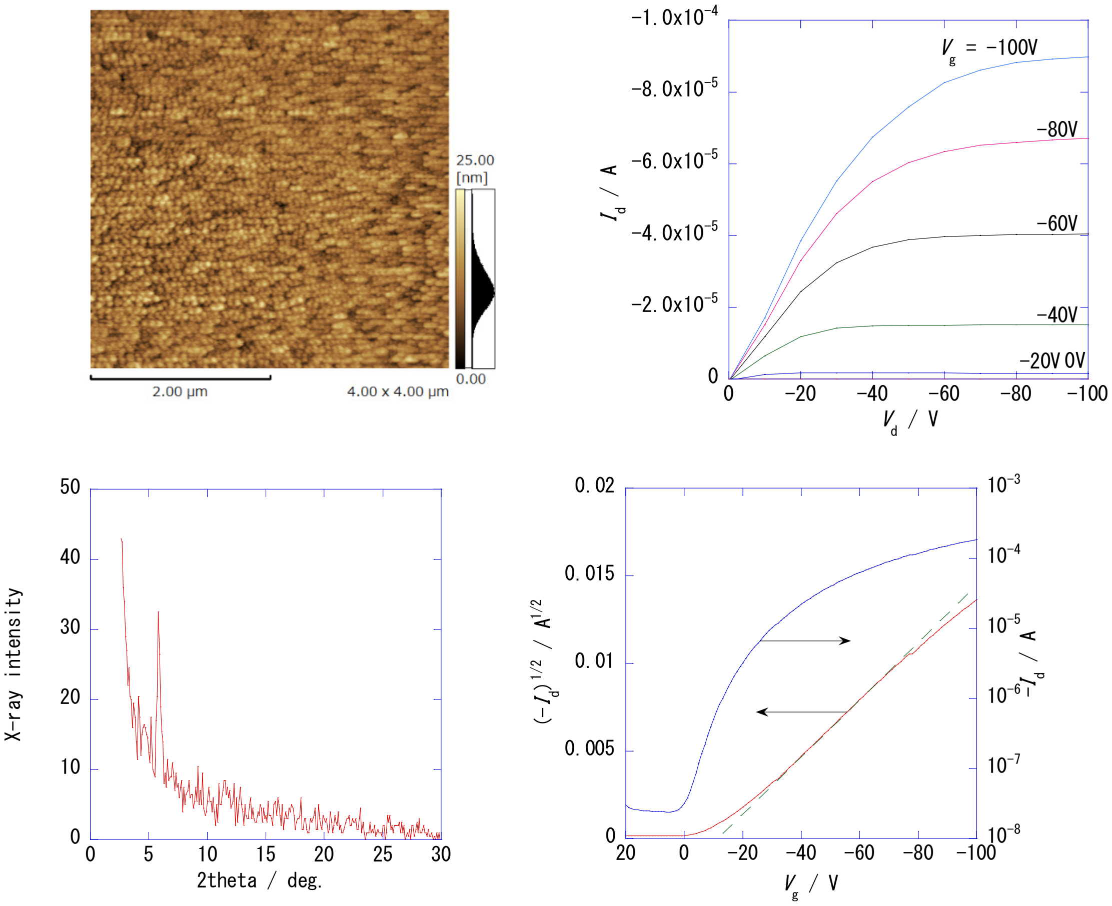


Figure 5 AFM surface image and XRD pattern of the pentacene layer prepared on SiO_2 modified with a 3.5 M DSBT solution, and Characteristics of the OTFT based on the DSBT-modified SiO_2.

2.3. XRF and XAFS measurements of modified SiO_2

To confirm the modification of SiO_2 surface by the disilanes, we carried out XRF and XAFS measurements of the DSBT-modified glass plate. XRF and XAFS analyses of DSBT and a bare glass plate were also carried out for comparison. As shown in Figure 6 (a), the XRF spectrum of DSBT-glass indicated the sulfur signal. Although the bare glass also contained sulfur, significant amount of sulfur was deposited onto the SiO_2 surface. XAFS spectra of the DSBT-glass and the reference were shown in Figure 6 (b), and the similarities of the spectra confirmed that the framework of DSBT was maintained on the SiO_2 surface after the modification.

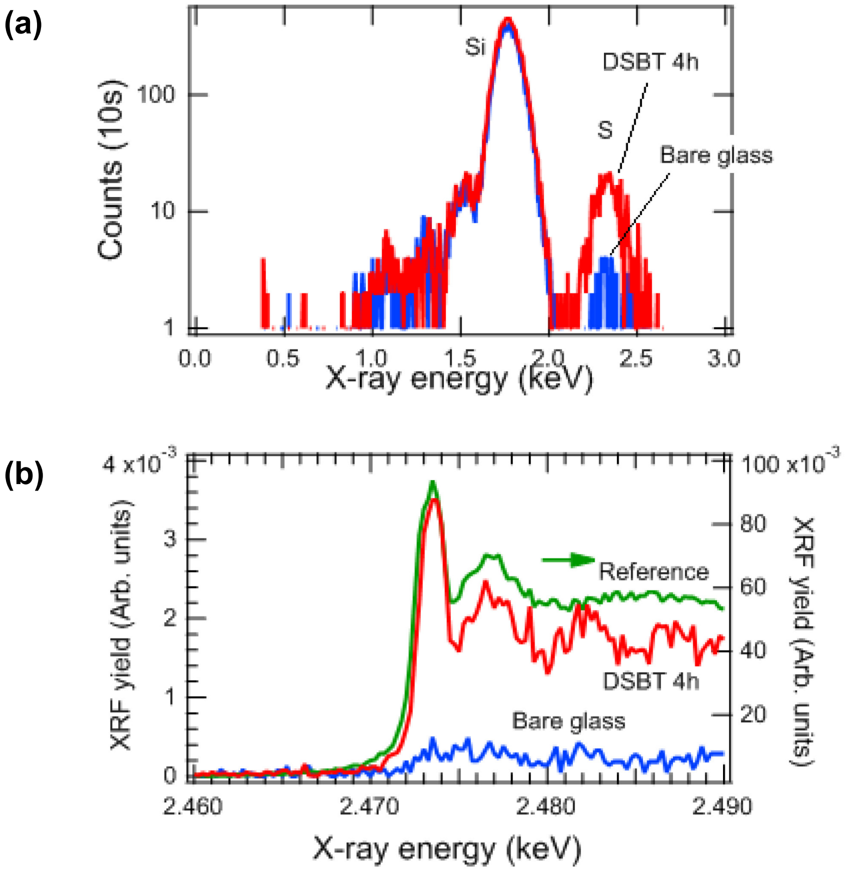


Figure 6 XRF (a) and XAFS (b) spectra of DSBT-modified glass plate (DSBT 4h) and bare glass plate. Reference XAFS spectrum obtained from a powder of DSBT was imposed in Figure 4(b).

Conclusions

In summary, we demonstrated that DSBP and DSBT were efficient hydrophobic modifiers for SiO_2 surface. Thermal modification of SiO_2 with DSBP was applied for the fabrication of OTFTs and the modification was found to affect the pentacene grain size and crystallinity, indicating the effective control of the SiO_2 surface. They are stable and clean modifiers that can be stored without any special care and produce no byproducts on reacting with the surface, and thus are useful for device technology. It should be also noted that the modification leads to the formation of the surface attached almost directly by aromatic units. This may exert influence on the formation of active layers composed of accumulated π-conjugated molecules, in contrast to conventional modifiers like OTS and HMDS that introduce aliphatic groups on the surface. Recently, it has been demonstrated that phenyl- and phenethyltrichlorosilane are efficient surface modifiers of SiO_2/Si to improve the OTFT performance [23,24]. It should be mentioned that hydrophobic modification of inorganic surface is of important process not only for OTFT but also for other organic electronic devices like organic photovoltaic cells. Studies on applications of DSBP and DSBT to organic devices other than pentacene-based OTFTs are in progress.

Experimental

4.1. Materials

DSBP was prepared as reported in the literature [17,18]. Toluene used for modification of glass plates was distilled from CaH_2 and stored over activated molecular sieves until use.

4.2. Preparation of DSBT

DSBT was prepared in a fashion similar to that of 2,7-bis(trimethylsilyl)-4,4,5,5-tetramethyl-4,5-disilanobithiophene [19]. To a solution of 1.23 g (3.78 mmol) of 3,3'-dibromo-2,2'-bithiophene in 125 mL of dry ether (distilled from CaH_2 under argon) was added 4.88 mL (7.56 mmol) of a 1.60 M *n*BuLi in *n*-hexane at -80 °C over a period of 1 h. After the resulting mixture was stirred for 3 h at this temperature, 0.71 g (3.78 mmol) of a 20 mL ethereal solution of 1,2-dichlorotetramethyldisilane was added to the mixture. The mixture was stirred at room temperature overnight then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted two times with chloroform. The organic layer and the extracts were combined and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was subjected to silica gel column chromatography, followed by preparative GPC (gel-permeation chromatography) eluting with toluene to give 0.32 g (30 %) of DSBT as a light yellow solid: MS *m/z* 268 (M^+); ^1H NMR (δ in $CDCl_3$) 0.32 (s, 12H, Me_3Si), 7.10 (d, 2H, $J = 5.0$ Hz, thiophene), 7.15 (d, 2H, $J = 5.0$ Hz, thiophene).

4.3. Glass surface modification

A glass plate (2.5 × 2.5 cm^2) was washed with acetone under ultrasonic irradiation, then ozone-cleaned for 15 min using a PL16-110 photo surface processor (SEN LIGHTS Corp). The plate was then dipped in a disilane solution in toluene in a dry argon atmosphere and irradiated with a 6 w low-pressure mercury lamp bearing a Vycor filter with a distance from the glass plate of approximately 10 cm. The solution temperature was controlled to approximately 20-40 °C during irradiation. After irradiation, the plate was thoroughly washed with toluene and dried in air. The water contact angle was measured on a DM-300 contact angle meter (Kyowa Interface Science Co., Ltd.).

4.4. Top contact OTFT fabrication [20]

A thermally oxidized and heavily doped silicon substrate SiO_2/Si where 200 nm-thick gate oxides had been grown on n-type CZ Si(100) (~0.1 Ω cm) in pyrogenic H_2O atmosphere at 1000 °C for 33 min was dipped in a DSBP toluene solution at room temperature. Pentacene was vapor deposited on the resulting disilane-modified SiO_2 gate insulator (deposition rate = 0.1 nm/s, operation pressure = 2×10^{-3} Pa, ambient temperature) to provide an active layer (80 nm thick). Finally, gold source and drain electrodes were deposited on the pentacene layer through a shadow mask with the channel width and length of 50 μm and 1.5 mm, respectively. The *p*-type transistor activity was measured at room temperature in vacuum with an Agilent 4155C semiconductor parameter analyzer.

4.5. XRF and XAFS measurements

X-ray fluorescence (XRF) and X-ray absorption fine structure (XAFS) measurements were carried out on the BL11 of Hiroshima synchrotron light source (HiSOR). Samples were placed in the He chamber, and a commercial silicon drift detector (Amptek, Super SDD) was utilized for detecting S Kα lines from the sample. Monochromatized 2.490 keV X-rays were used for XRF measurements, and incident X-ray energy was scanned from 2.460 keV to 2.469 keV for S K-edge XAFS measurements. The S K-edge XAFS spectra of DSBT-modified glass plate were obtained with X-ray fluorescence yield (XFY) method.

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Chapter 3

Hydrophobic modification of SiO_2 surface by aminosilane derivatives

Introduction

Aminosilanes with hydrolysable Si-N bond(s) are useful reagents for the silylation of hydroxyl groups because they readily interact with alcohols (ROH) to form R-O-Si linkages under mild and neutral conditions, unless they are sterically congested. It is also known that aminosilanes react with inorganic oxide surface for hydrophobic modification [1]. The moderately high reactivity of the Si-N bond allows the smooth transformation into a Si-O bond. In addition, aminosilanes are sufficiently stable towards hydrolysis by atmospheric moisture to permit the use of them without special care. However, aminosilanes are less used than chlorosilanes, which are widely employed as silylating reagents of hydroxyl groups [2,3], because of limited commercial sources.

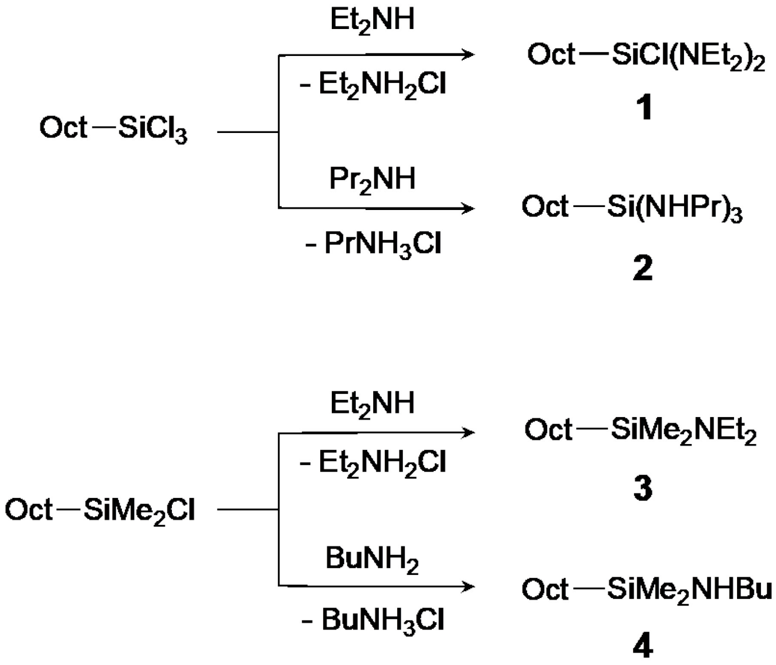
Organic electronics have received increasing attention because they are lightweight and flexible and can be fabricated easily at a low cost. Organic thin-film transistors (OTFTs) have been intensively studied as organic integrated circuits for flexible displays, radiofrequency tags, and biological sensors. A typical OTFT is composed of an organic semiconductor, a gate dielectric, and three electrodes (source, drain, and gate). When voltage is applied between the source and drain electrodes, current flows through the organic semiconductor layer associated with charge carrier transport. Although OTFTs have many advantages as mentioned above, they have significantly lower carrier mobility than silicon-based ones because of the hopping conduction mechanism and the defects present at the interface between the organic semiconductor layer and the gate insulator. Improving the field-effect characteristics of OTFTs is required so that they can be used to replace silicon-based thin-film transistors. For the improvement of carrier mobility, controlling the interface between the organic semiconductor layer and the gate dielectric layer is crucial because the interface is a critical part of field-effect devices. Alkyltrichlorosilanes, such as octadecyltrichlorosilane (OTS), are widely used as modifiers of inorganic oxide surface [4-8]. It has been proposed using the OTS and other trichlorosilane modifiers between the SiO_2 gate dielectric and the semiconducting layer to improve field-effect characteristics [9-12]. The proposed method is effective because the active molecules, such as pentacene, on an alkyltrichlorosilane self-assembled monolayer formed on the SiO_2 gate dielectric are easily oriented. However, making an ordered surface of the interface is marred by difficulty because chlorosilanes are easily hydrolyzed. In addition, HCl generated as a by-product may react with the SiO_2 surface to negatively influence OTFT characteristics. Hexamethyldisilazane (HMDS), which is less prone to hydrolysis than chlorosilanes, is also used to make an ordered surface of the interface. However, it is difficult to achieve sufficient hydrophobicity because HMDS has only short methyl chains. Therefore, a surface modifier that is easy to handle in air and does not produce reactive by-products, such as HCl, is needed.

In this paper, we report the synthesis of new stable aminosilane compounds that have long alkyl chains and liberate only amines that are much less reactive than HCl. To confirm the effects of treatment with the new aminosilane compounds, we investigated the field-effect characteristics of OTFTs consisting of the SiO_2 gate insulator treated with aminosilane modifiers. Carrier mobility was improved considerably by more than twofold by utilizing an aminosilane-modified SiO_2. Recently, Roh *et al.* reported the application of similar silazanes ($RMe_2SiNHSiMe_2R$, R = methyl, propyl, butyl, octyl) as hydrophobic modifiers of the SiO_2 surface for OTFT fabrication [13]. However, the silazanes were used in the vapor form in a vacuum oven under careful temperature control. Our aminosilanes are easy-handled and can be used as a modifier in the solution form in air under ambient conditions, thereby presenting the advantage of high processability.

Results and Discussion

2.1. Synthesis of aminosilanes

In general, bulky amino substituents are desired to improve the stability of aminosilanes towards atmospheric hydrolysis. However, bulky substituents lead to less reactivity of the aminosilanes with the SiO_2 surface and thus, careful choice of the amino substituents is essential. The new aminosilanes for the present study were prepared, as shown in Scheme 1. The reaction of trichlorooctylsilane with diethylamine at room temperature gave chlorobis(diethylamino)(*n*-octyl)silane (**1**). The attempted preparation of tris(diethylamino)(*n*-octyl)silane in the presence of a large excess of diethylamine without solvent was unsuccessful. Elevating the reaction temperature did not change the results and compound **1** was always obtained as the sole volatile product. To prepare triamino(*n*-octyl)silane, we carried out a similar reaction with less hindered primary *n*-propylamine and obtained tri(*n*-propylamino)(*n*-octyl)silane (**2**). Monoamino(*n*-octyl)silanes were also prepared in a fashion similar to **1** and **2**. Thus, with chlorodimethyl(*n*-octyl)silane, (diethylamino)dimethyl(*n*-octyl)silane (**3**) and (*n*-butylamino)dimethyl(*n*-octyl)silane (**4**) were readily obtained, as shown in Scheme 1. These aminosilanes were readily purified by distillation from the reaction mixtures. They were sufficiently stable to allow handling in air. For example, aminosilanes left to stand in air under ambient conditions for several minutes showed no detectable decomposition. Although exposure to air for a long period resulted in gradual decomposition into the corresponding silanols and siloxanes, as illustrated in Figure 1 for compound **3**, ca. 80% of starting **3** remained unchanged even after standing in air for 2 h (Figure 1 (left)). No decomposition products other than the corresponding silanol and siloxane were detected by GC-MS analysis of the reaction mixture. We also compared the rate of hydrolysis of **3** with that of the corresponding chlorosilane. As presented in Figure 1 (right), compound **3** was hydrolyzed more slowly than chlorodimethyl(*n*-octyl)silane. However, **3** suddenly disappeared after 2 h, likely due to the accelerated hydrolysis by diethylamine liberated by hydrolysis of **3** acting as a base catalyst.



Scheme 1 Synthesis of aminosilanes.

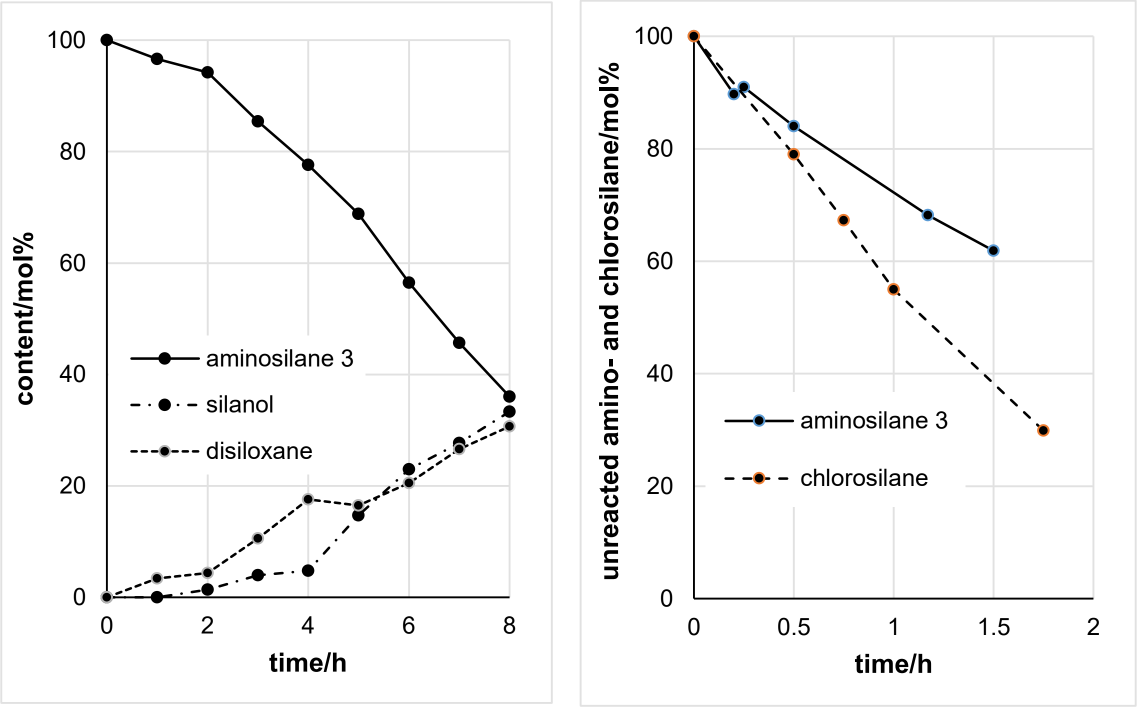


Figure 1 Stability test of compound 3 and the corresponding chlorosilane in air at 20-22 °C and 55-60% humidity. Standing the neat sample (3 0.2 mL) (left) and stirring solutions of 3 and chlorodimethyl(*n*-octyl)silane (0.3 mL in 1 mL of THF, 100 rpm) (right) in open vessels (45 mm high, 18 mmϕ bottom, and 10 mmϕ mouth) led to hydrolytic decomposition of the Si-N and Si-Cl bonds. The composition was determined by GLC.

2.2. Application of modified SiO2 to OTFTs

As the hydrophobic modification of SiO_2 surface plays a key role in the high performance of OTFTs, we examined compounds **1-4** as the surface modifiers of SiO_2. To know how the concentration of modifiers affect the surface properties, we carried out modification of glass surface using compound **3** as an example. Glass plates pre-treated by an ozone-cleaner were immersed in a 0.1 M or 0.01 M toluene solution of **3** in dry argon and the changes of the surface hydrophobicity were monitored by water contact angle measurements. As shown in Figure 2, the contact angles increased along the immersion time with a higher rate for the 0.1 M solution. However, the maximal contact angles were essentially the same, regardless of the modifier concentration. We therefore employed 0.1 M solutions of the modifiers for the following experiments, to achieve the saturated modification easily. It should be also advised that 0.01 M solutions appeared to be too diluted to store them without non-neglisible hydrolytic decomposition under ambient conditions.

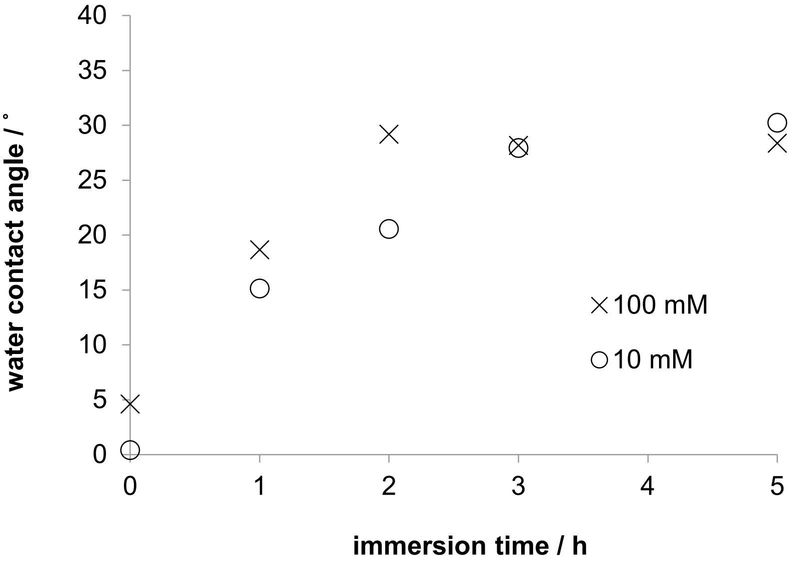


Figure 2 Changes of water contact angles of glass plates treated with 0.1 M and 0.01 M toluene solutions of compound 3 in dry argon.

SiO_2 was treated with toluene solutions of the presently prepared aminosilanes in air at room temperature for 24 h (method A) or at 60 °C for 20 min (method B) and the resulting modified SiO_2 was washed with dry toluene. The performance of top-contact OTFTs using the modified SiO_2 as the gate insulator and vapor-deposited pentacene film as the active layer is summarized in Table 1, together with that of OTFTs bearing bare SiO_2 and HMDS-modified SiO_2 as the gate insulators for comparison. As listed in Table 1, all the devices fabricated in the present study exhibited good p-type activity. When the SiO_2 gate insulator was modified by HMDS at room temperature in toluene, a mobility of $\mu_{\mathrm{FET}} = 0.44$ $cm^2V^{-1}s^{-1}$ was obtained, which was slightly higher than that based on bare SiO_2 by 10%. A sufficiently high $I_{\mathrm{on}}/I_{\mathrm{off}}$ ratio was retained (10^5), suggesting that the silylamine modification improved the device performance. However, the mobility was nearly the same as that previously reported for an OTFT with SiO_2 modified by HMDS vapor ($\mu_{\mathrm{FET}} = 0.46$ $cm^2V^{-1}s^{-1}$) [13]. Using compound **1** as the modifier further improved the device performance and modification at a higher temperature led to an even higher performance with $\mu_{\mathrm{FET}} = 1.02$ $cm^2V^{-1}s^{-1}$. Similar effects of the alkyl chain lengths of silazane [13] and chlorosilane modifiers [14] on OTFT performance have been reported. In contrast, compound **2** exhibited negative effects as the modifier. The device performance was suppressed with lowered mobility regardless of treatment temperature. With compounds **3** and **4**, we again observed improved device performance with mobility as high as 1 $cm^2V^{-1}s^{-1}$. It is noteworthy that modification of the SiO_2 gate electrode proceeded nicely with compound **3** even at room temperature; the mobility is slightly higher than that reported for the OTFT with SiO_2 modified by silazane $OctMe_2SiNHSiMe_2Oct$ vapor ($\mu_{\mathrm{FET}} = 0.84$ $cm^2V^{-1}s^{-1}$) [13]. The $I_{\mathrm{on}}/I_{\mathrm{off}}$ ratios were also improved to 10^6 with **3** and **4**, although direct comparison of the performance was difficult for devices prepared by different research groups due to differences in the detailed fabrication conditions. The deposition of the pentacene layer on SiO_2 heated at 60 °C did not significantly affect the results but slightly suppressed the performance, although this procedure is often employed to enhance the ordered aggregation of pentacene molecules.

Table 1 OTFT parameters based on modified and non-modified SiO_2 gate insulators

Modifier	Method	μ_{FET}/cm^{2}V^{-1}s^{-1}	V_{th}/V	I_{on}/I_{off}
Non		0.40	-15	10^5
HMDS	A	0.44	-4	10^5
1	A	0.53	-10	10^5
	B	1.02	-12	10^6
2	A	0.12	-10	10^5
	B	0.28	-22	10^5
3	A	0.98	-13	10^6
	B	0.40	-11	10^6
4	B	1.10	-13	10^6

[a]A: at room temperature for 24 h; B: at 60 °C for 20 min.

An optical microscope image of SiO_2 surface modified by compound **2** is presented in Figure 3, showing the formation of aggregates as small dots. Presumably, hydrolytic polymerization forming insoluble solids occurred during the surface modification process. As shown in Scheme 2, it is speculated that tri-functional compound **2** undergoes hydrolysis/condensation polymerization to yield network polymers that are insoluble in toluene (**B**), competing with the expected single-layer modification of the SiO_2 surface (**A**). This seems to be responsible for the lowered performance of the device with SiO_2 modified by compound **2**. Polymerization on the surface may also be involved (**C**). In contrast, compounds **3** and **4** formed flat surfaces and no formation of insoluble aggregates was observed in the microscope images. These mono-functional compounds should lead to only silanols or dimeric siloxanes as the by-products that are soluble in toluene and can be easily removed by washing the modified SiO_2 with toluene, even though hydrolysis/condensation takes place during the modification process. This is similar to dichloro- and trichloroalkylsilanes whose reactions with SiO_2 surface competed with the self-oligomerization depending on the conditions [15]. Compound **1** also provided a flat surface despite its tri-functionality. It is likely that only the Si-Cl bond is reactive in compound **1** under the conditions, because of the steric bulkiness of the bis(diethylamino) substitution, leading to the formation of silanol and siloxane only with two diethylamino groups on the silicon atom remaining unchanged. It is also likely that the formation of aggregates from **2** can be avoided by carrying out the modification under an inert atmosphere, e.g. in dry argon. However, this makes the process complicated and difficult to perform.

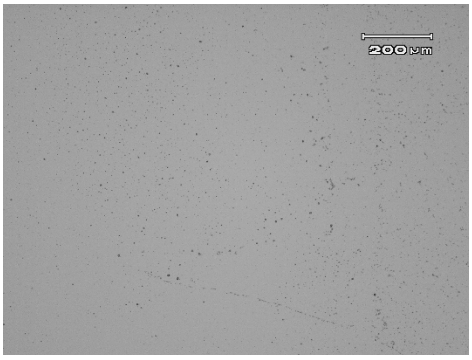
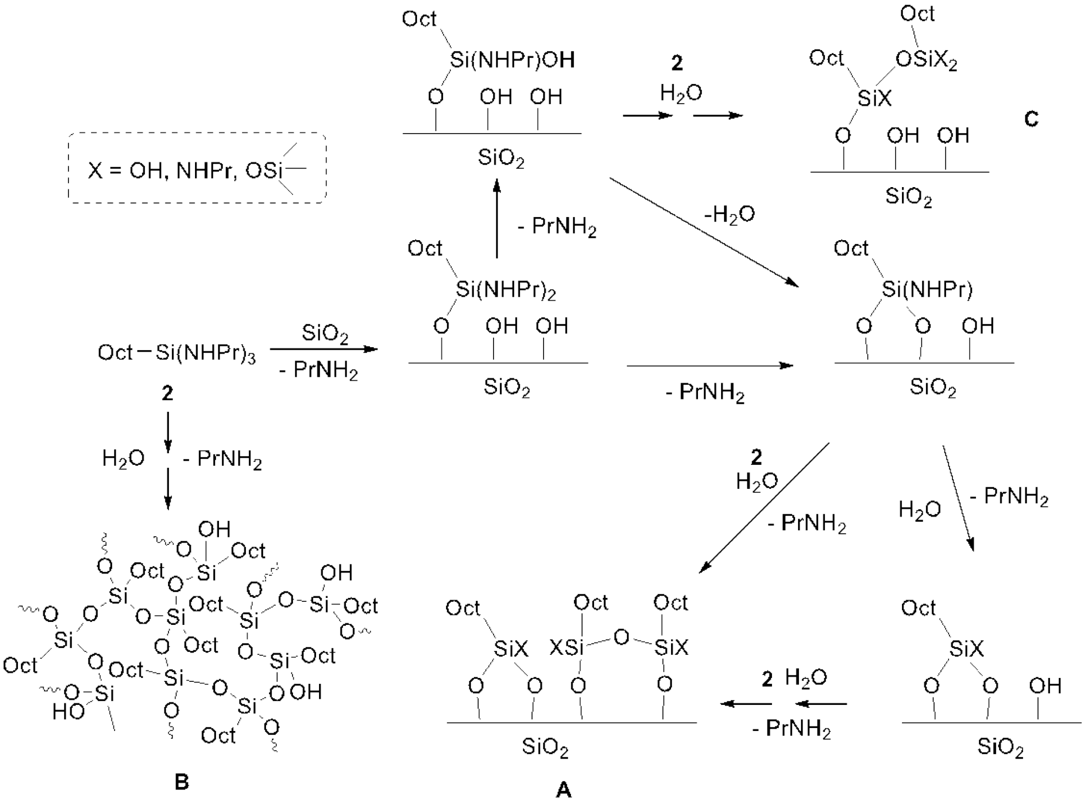
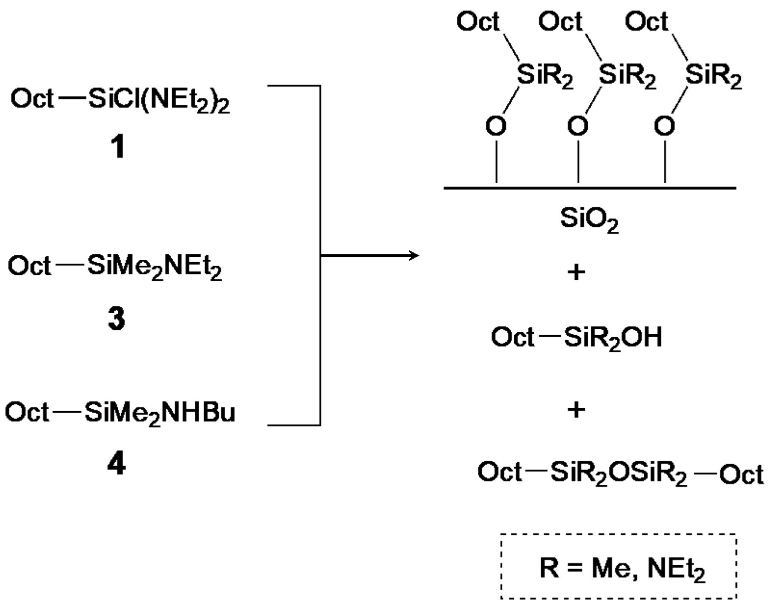


Figure 3 Optical microscope image of SiO_2 surface modified by compound 2.



Scheme 2 Reactions of compound 2.



Scheme 3 Reactions of compounds 1, 3, and 4.

The hydrophobic modification of the SiO_2 surface was confirmed by water contact angle measurements. The contact angle increased from 13.7° for bare SiO_2 to 102.5° for that modified by compound **4** at 60 °C (Figure 4). We conducted AFM analysis of the pentacene layer, as presented in Figure 5, to clarify the influence of modifiers and modification conditions (A or B in Table 1) on the morphology. In general, larger grain size leads to fewer boundaries to enhance the mobility. AFM measurements of the pentacene layer prepared on compound **2**-modified SiO_2 were difficult to perform, because of the large gaps due to the insoluble aggregates. Images of rather flat areas were obtained, as presented in Figures 5b and 5c, showing the formation of small grains for both conditions A and B. When modified by compound **3**, condition A provided larger grains than condition B, as shown in Figures 5d and 5e. This matches the fact that condition A gave a higher mobility than condition B for the modification by compound **3**, although we have no explanation as to why condition A resulted in a larger grain size than condition B. Even larger grains are seen when compound **4** was used as the modifier (Figure 5f), in accordance with the fact that compound **4** yielded the highest OTFT mobility. Pentacene formed a rather heterogeneous surface consisting of small and large grains when deposited on bare SiO_2 (Figure 5a). In contrast, the AFM images of pentacene layers that provided high mobility (Figures 5d-5f) revealed the formation of large grains with narrower size distribution. Figure 6 depicts the response curves of the OTFT based on SiO_2 modified by the present aminosilanes. XRD patterns of the pentacene layers prepared on bare SiO_2 and that modified by **4** are presented in Figure 7, which indicates higher crystallinity for the layer on bare SiO_2. It is known that enhanced crystallinity usually leads to higher carrier transporting properties. In the present case, however, narrower grain size distribution seems to play a more important role on the device performance.

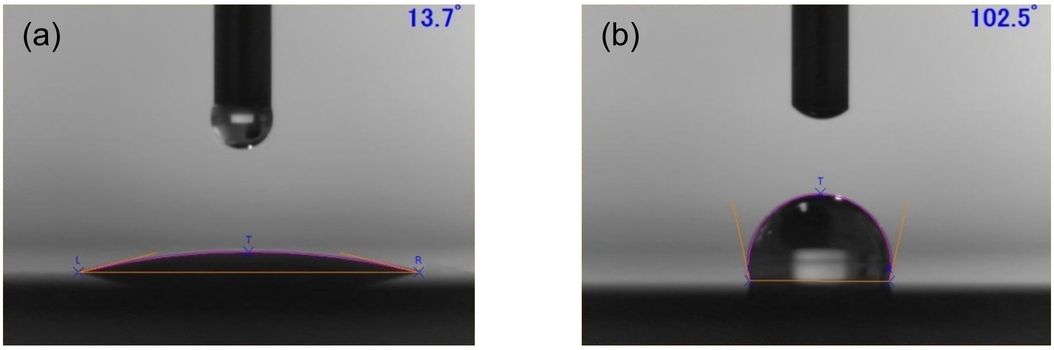


Figure 4 Water contact angle measurements for bare SiO_2 (a) and that modified by compound 4 at 60 °C.

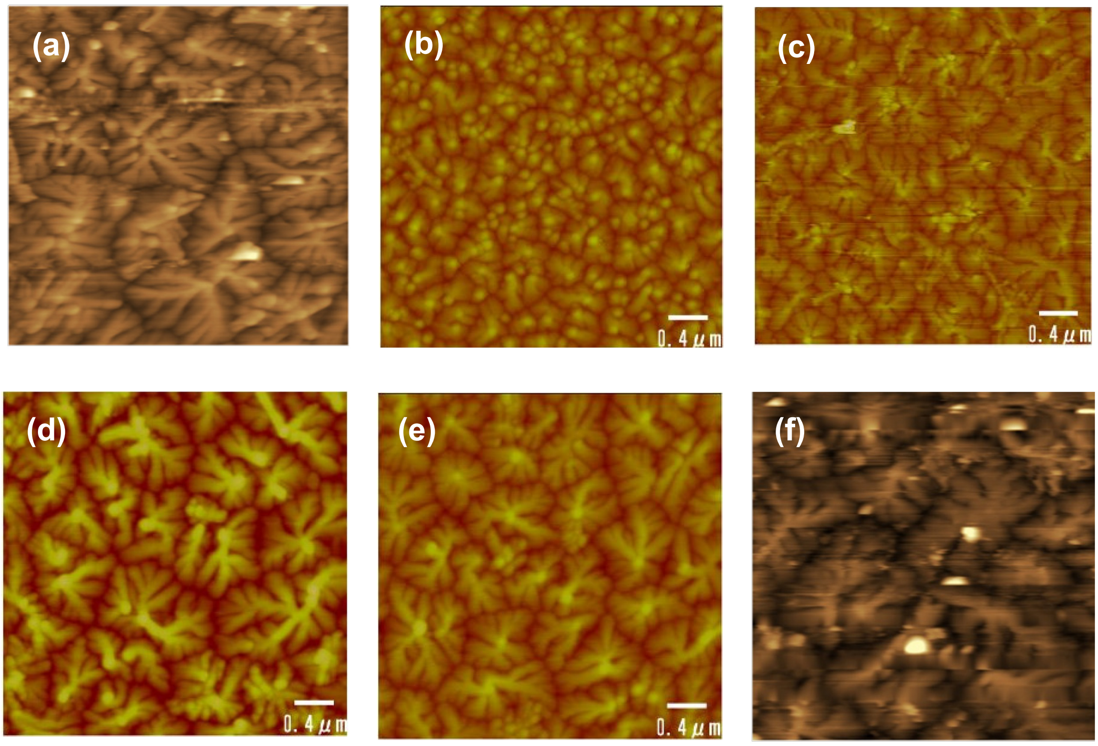


Figure 5 AFM surface images of pentacene layers prepared on bare SiO_2 (a) and modified SiO_2 by compound 2 under conditions A (b) and B (c), by compound 3 under conditions A (d) and B (e), and by compound 4 under conditions B (f).

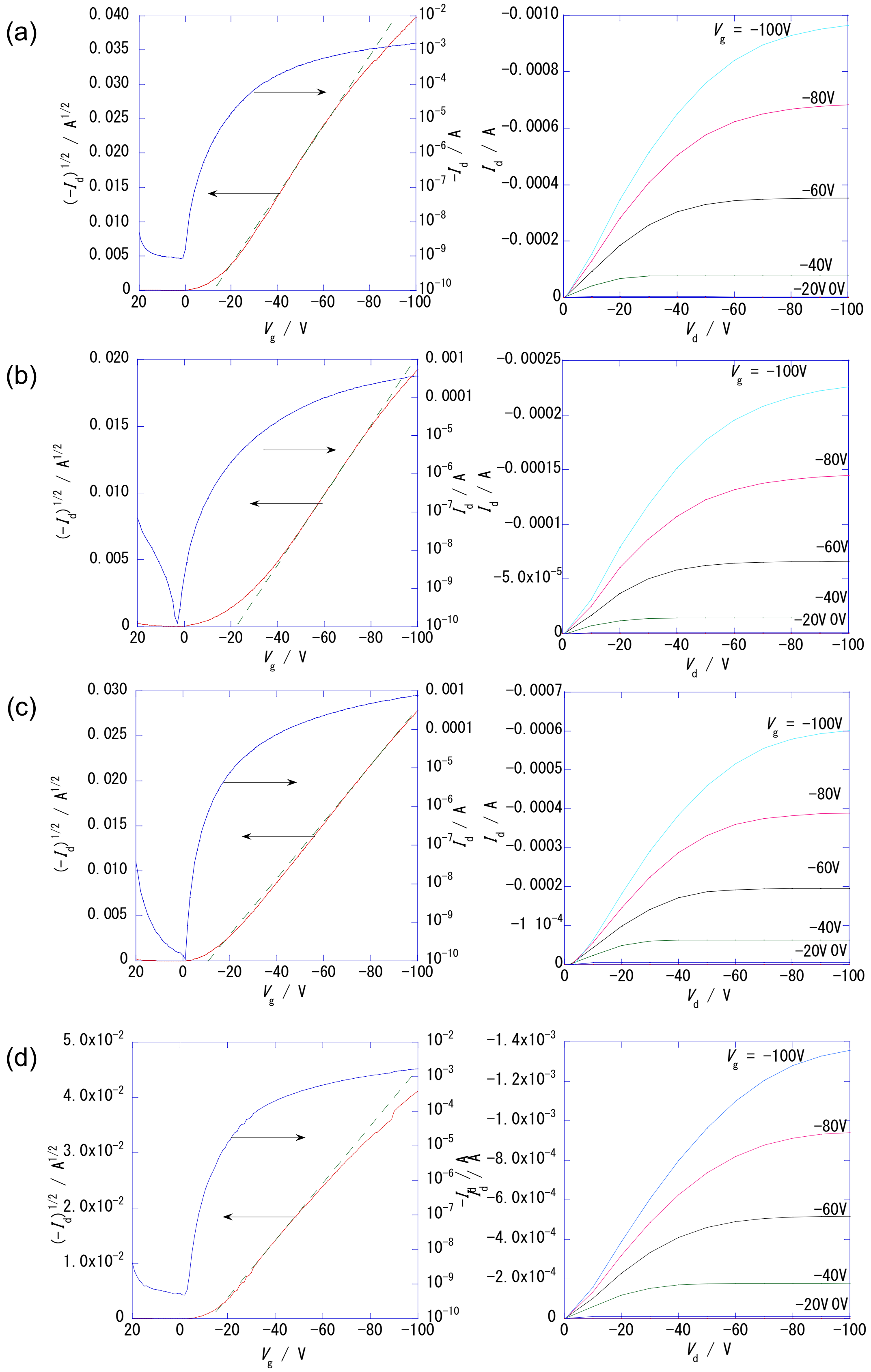


Figure 6 Characteristics of OTFT using SiO_2 modified by compounds 1-4 (a-d).

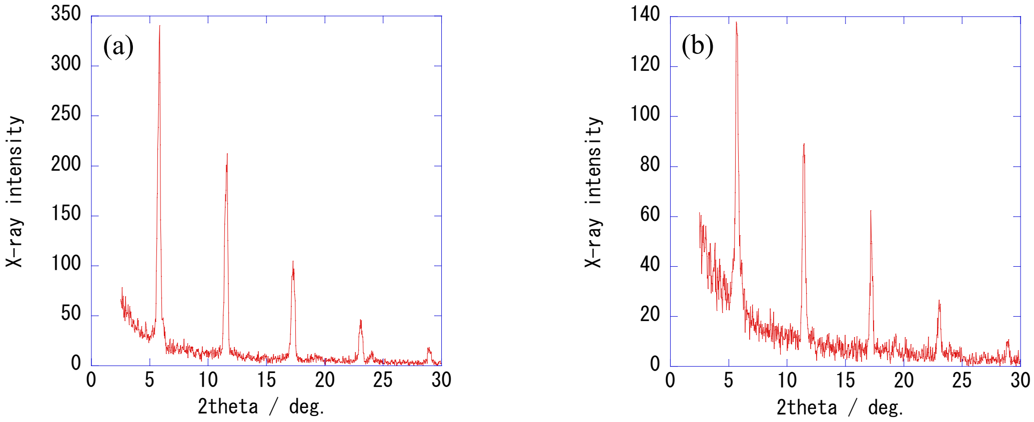


Figure 7 XRD patterns for pentacene layer prepared on bare SiO_2 (a) and that modified by compound 4.

Conclusions

In summary, we demonstrated that aminosilanes with long alkyl chains were efficient hydrophobic modifiers of the SiO_2 surface. To explore the application of the modified SiO_2, we fabricated OTFTs using the modified SiO_2 as the gate insulator and a vapor-deposited pentacene film as the active layer and evaluated the activity of the resulting OTFT in comparison with that based on bare SiO_2 as the reference device. OTFT with SiO_2 modified by triaminosilane **2** showed suppressed OTFT activity compared with the reference device. Aminosilanes **1**, **3**, and **4** exhibited excellent ability as modifiers for OTFT applications and the device performance was remarkably improved to provide 2.4- to 2.8-fold higher mobility. This is likely due to the longer alkyl chains of **1**, **3**, and **4**, in contrast to HMDS, a typical aminosilane surface modifier, which improved the mobility by only 10%. The present aminosilane modifiers do not emit HCl as the by-product and the modification can be carried out in air, in contrast to well-established chlorosilane modifiers, which give them distinct advantage for use as electronic device materials. The higher stability of aminosilanes towards moisture leads to easier-handling of aminosilanes than the chlorosilane congeners.

In particular, compound **3** reacts with SiO_2 even at room temperature to provide a sufficiently modified surface, proving the high potential of this compound as an efficient modifier. Mono-functional aminosilanes with a long alkyl chain can be a better structure-design, which generate only the corresponding silanols and disiloxanes that are readily removed by washing with organic solvents, giving rise to a certain advantage as compared to multi-functional compounds, like **2**, that form cross-linked insoluble aggregates, unless it is used under carefully controlled dry conditions.

Experimental

4.1. General procedures

All synthetic reactions for new amionosilanes **1**-**4** were carried out under an atmosphere of dry nitrogen. Diethyl ether and toluene were distilled from calcium hydride and stored over activated molecular sieves until use. Starting reagents, *n*-butylamine, diethylamine, and *n*-propylamine, were distilled from potassium hydroxide and stored over activated molecular sieves 4A until use. NMR spectra were measured on Varian 400-MR and Varian System 500 spectrometers at ambient temperature. EI-MS spectra were obtained on a Shimadzu QP5050A spectrometer. AFM images were obtained in the "tapping mode" with Digital Instruments NanoScope IIIa. Water contact angles on the modified glass plates were measured on a Kyowa DM300 contact angle meter.

4.2. Preparation chlorobis(diethylamino)(n-octyl)silane (Compound 1)

To a solution of 21.0 g (84.8 mmol) of trichloro(*n*-octyl)silane in 250 mL of Et_2O/THF = 1/4 was added slowly 60.0 mL (0.575 mol) of diethylamine at 0 ºC and the mixture was stirred at room temperature for 10 h. To the resulting mixture was added 60 mL of hexane to complete precipitation of the resulting by-product diethylammonium chloride (Et_2H_2NCl). After filtration, the solvent was evaporated and the residue was distilled under reduced pressure to provide 8.10 g (30% yield) of compound **1**: bp 94 ºC (0.4 mmHg). GC-MS *m/z* 320 (M^+ for ^{35}Cl). ^1H NMR (δ in $CDCl_3$) 0.80-0.83 (m, 2H, -CH_2Si), 0.88 (t, 3H, $C\underline{H}_3$-octyl, *J* = 5.6 Hz), 1.01 (t, 12H, $C\underline{H}_3CH_2N$, *J* = 5.6 Hz), 1.12-1.42 (m, 12H, CH_2-octyl), 2.89 (q, 8H CH_2N, *J* = 5.6 Hz). ^{13}C NMR (δ in $CDCl_3$) 14.8, 15.5, 17.6, 23.4, 23.7, 29.91, 29.93, 32.6, 33.9, 39.4.

4.3. Preparation of tri(n-propylamino)(n-octyl)silane (Compound 2)

To a solution of 8.0 mL (35 mmol) of trichloro(*n*-octyl)silane in 80 mL of THF was added slowly 21.0 mL (0.256 mol) of *n*-propylamine at 0 ºC and the mixture was stirred at room temperature for 10 h. To the resulting mixture was added 30 mL of hexane to induce the complete precipitation of the resulting by-product *n*-propylammonium chloride (*n*-$PrNH_3Cl$). After filtration, the solvent was evaporated and the residue was distilled under reduced pressure to provide 7.89 g (72% yield) of compound **2**: bp 116-119 ºC (1 mmHg). GC-MS *m/z* 315 (M^+). ^1H NMR (δ in $CDCl_3$) 0.46 (t, 2H, CH_2Si, *J* = 8.0 Hz), 0.57 (br s, 3H, CH_3-octyl), 0.84-0.91 (m, 12H, CH_2-octyl), 1.25-1.31 (m, 12H, NH and CH_3-Pr), 1.37 (sept, 6H, CH_2-Pr, *J* = 6.8 Hz), 2.68 (t, CH_2N, *J* = 6.8 Hz). ^{13}C NMR (δ in $CDCl_3$) 11.4, 14.10, 14.13, 22.7, 23.9, 27.9, 29.29, 29.35, 32.0, 33.7, 43.4.

4.4. Preparation of diethylamino-1,1-dimethyl(n-octyl)silane (Compound 3)

To a solution of 10.0 mL (42.3 mmol) of chlorodimethyl(*n*-octyl)silane in 80 mL of THF was added slowly 10.5 mL (0.101 mol) of diethylamine at room temperature and the mixture was stirred for 10 h. To the resulting mixture was added 30 mL of hexane to induce the complete precipitation of the resulting by-product diethylammonium chloride (Et_2H_2NCl). After filtration, the solvent was evaporated and the residue was distilled under reduced pressure to provide 7.80 g (76% yield) of compound **3**: bp 65-69 ºC (1 mmHg). GC-MS *m/z* 243 (M^+). ^1H NMR (δ in $CDCl_3$) 0.03 (s, 6H, CH_3Si), 0.51-0.55 (m, 2H, CH_2Si), 0.90 (br t, 3H, CH_3-octyl), 0.98 (t, 6H, CH_3-ethyl, J = 7.2 Hz), 1.23 (br s, 12H, octyl), 2.80 (t, CH_2N, J = 7.2 Hz). ^{13}C NMR (δ in $CDCl_3$) -1.8, 14.2, 15.9, 17.0, 22.8, 24.0, 29.4, 29.5, 32.1, 33.9, 40.0.

4.5. Preparation of (n-butylamino)-1,1-dimethyl(n-octyl)silane (Compound 4)

Into a three-necked flask fitted with a dropping funnel were added 3.38 g (46.2 mmol) of *n*-butylamine and 20 mL of diethyl ether. To this was added 4.25 g (15.2 mmol) of dimethyloctylchlorosilane at 0 °C. After the resulting mixture was stirred at 0 °C for 2 h, it was warmed to room temperature and stirred overnight. After the mixture was filtered to remove the by-product *n*-butylammonium chloride (*n*-BuH_3NCl) and the solvent evaporated, the residue was distilled under reduced pressure to give 2.45 g (49% yield) of compound **4** as a colorless liquid: bp 124 °C (7.4 mmHg). EI-MS *m/z* 243 (M^+). ^1H NMR (δ in $CDCl_3$) 0.00 (s, 6H, Si-Me), 0.48 (s, 1H, N-H), 0.50 (t, 2H, J = 7.2 Hz), 0.86-0.91 (m, 7H, Pr, J = 7.2Hz), 1.26-1.28 (m, 15H, hep, J = 7.2 Hz), 2.68 (q, 2H, NH-CH_2, J = 7.2 Hz). ^{13}C NMR (δ in $CDCl_3$) 1.78, 13.95, 14.12, 16.79, 19.98, 22.69, 23.69, 29.29, 29.37, 31.96, 33.65, 37.00, 41.62.

4.6. Top-contact OTFT fabrication

A thermally oxidized and heavily doped silicon substrate SiO_2/Si where 200 nm-thick gate oxides had been grown on *n*-type CZ Si(100) (~0.1 Ωcm) in pyrogenic H_2O atmosphere at 1000 ℃ for 33 min was dipped into a dry toluene solution of a surface modifier (0.1 M) in a covered Petri dish in air at room temperature for 1 day (method A) or at 60 °C for 20 min (method B). Onto the surface-modified SiO_2 gate insulator (210 nm thick) was vapor-deposited a pentacene layer (80 nm thick) at the deposition rate of

0.1 nm/s under the reduced pressure of 2×10^{-3} Pa at ambient temperature. Finally, gold source and drain electrodes were deposited on the pentacene layer through a shadow mask with the channel width and length of 50 μm and 1.5 mm, respectively. p-Type transistor activity was measured at room temperature in vacuum with an Agilent 6155C semiconductor parameter analyzer.

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Summary

In the thesis, the author described the synthesis and reactivity of silicon-containing compounds, optical and electrical properties, and applicability to electronic devices.

The author prepared polymers containing Fe(0)-coordinated 2,5-diethynylsilole units and discussed them compared to their properties of the 3,4-diethynylsilole polymers. The 2,5-diethynylsilole unit can form complex with $Fe(CO)_5$ and the bond order of C2-C3 and C4-C5 of silole changes and affects the conjugation length. The 2,5-diethynylsilole unit may be used as the potential ligands to transition metal center. The author indicated that the coordination of the $Fe(CO)_3$-unit to diethynylsilole system seems to provide an opportunity to modify the electronic states of the π-electron system.

The author described the hydrophobic modification of SiO_2 surface using tetramethyldisilanobiphenyl (DSBP), tetramethyldisilanobithiophene (DSBT), and n-octylaminosilane derivtives as new modifiers.

DSBP and DSBT can react with inorganic oxide surface by UV irradiation. Hydrophobic modification of the gate insulator (SiO_2) with DSBP affects the crystal grain size and crystallinity of pentacene and the carrier mobility. The author showed that DSBP and DSBT are stable and clean modifiers that can be stored without any special care and produce no byproducts on reacting with the surface, and thus are useful for device technology.

Aminosilanes were found to be also effective hydrophobic modifiers that do not emit HCl as the by-product. The modification can be carried out in air, in contrast to well-established chlorosilane modifiers, which give them distinct advantage for use as electronic device materials. The higher stability of aminosilanes towards moisture leads to easier-handling of aminosilanes than the chlorosilane congeners.

The silicon-containing compounds are promising materials for the improvement of organic electronic devices and will contribute greatly to these developments.

List of Publications

Chapter 1.

Preparation of polymers containing Fe(0)-coordinated 2,5-diethynylsilole units

Joji Ohshita, Hidekazu Arase, Tomohisa Sumida, Nobuhisa Mimura, Kazuhiro Yoshimoto, Yosuke Tada, Yoshihito Kunugi, Yutaka Harima, Atsutaka Kunai

Inorganica Chimica Acta, Vol. 358, Issue 14, (2005), 4156

Chapter 2.

Hydrophobic modification of SiO_2 surface with disilanobiphenyl and disilanobithiophene and the application to pentacene-based organic transistors

Hidekazu Arase, Takashi Kai, Seiichi Taniguchi, Yohei Adachi, Yousuke Ooyama, Takuya Mori, Maki Yanase, Shinjiro Hayakawa, Yoshihito Kunugi, Joji Ohshita

Composite Interfaces, in Press

Chapter 3.

Hydrophobic modification of SiO_2 surface by aminosilane derivatives

Hidekazu Arase, Keiichi Taniguchi, Takashi Kai, Kazuya Murakami, Yohei Adachi, Yousuke Ooyama, Yoshihito Kunugi, Joji Ohshita

Composite Interfaces, in Press

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Hidekazu Arase