Development of Novel Silicon Precursors for Low‑Temperature CVD／ALD Processes

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Si-TBES (**2**) and Si-TBAS (**4**), novel CVD/ALD precursors bearing a diazasilacyclopentene framework, were synthesized. Thermal analyses revealed that both of them are highly volatile, and their decomposition temperatures were lower than those of comparable silicon precursors, $Si(OEt)_4$ (TEOS) and $SiH(NMe_2)_3$ (TDMAS). Deposition properties of SiO_2 thin films were investigated by a thermal CVD apparatus. The deposition rates of SiO_2 thin films using these new precursors were higher than that of TDMAS. Deposition rate dependency on oxygen partial pressure indicates the high reactivity of the diazasilacyclopentene framework towards oxygen contributes to the high growth rates. Details of the SiO_2 thin films were evaluated by XPS, AFM, and SIMS. While Si-TBAS can form conformal SiO_2 thin films efficiently, Si-TBES can provide a film with low carbon and nitrogen contamination.

1. Introduction

Silicon is the most commonly-used element in semiconductor industry, and silicon containing materials are used in various parts of semiconductor devices. For these manufacturing processes, chemical vapor deposition (CVD) and atomic layer deposition (ALD) processes have been extensively investigated to form thin films on a three-dimensional surface with a uniform thickness and conformality. As the recent improvement of device integrations and flexible devices, low-temperature deposition processes are required for the damage-free processes to form a thin film on patterned film structures or heat labile substrate such as glasses or plastics. Although SiH_4 or $Si(OEt)_4$ (TEOS) are well-known precursors for CVD/ALD processes [1], they require high deposition temperature [2], plasma assistance [3-4], or highly reactive coreactant such as ozone gas [5] to produce thin films.

We have been designing state-of-art precursors which have high reactivity with coreactant, and recently succeeded in developing a new titanium precursor, Ti-DOT (**1**), which enables to form TiO_2 thin films at high deposition rate by the CVD with oxygen [6]. This compound was also found to react readily with oxygen gas concerted with the dissociation of the bidentate vinylenediamide ligand as the neutral diimine. This

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result indicates that this reaction contributes to the efficient rate of thin film formation. We herein report the syntheses, properties and film depositions of novel silicon precursors bearing the diazasilacyclopentene framework.

2. Experiment

2.1 Preparations

All reactions were performed under argon atmosphere using standard Schlenk tube and vacuum-line techniques. The products were characterized on the basis of ^{1}H and ^{13}C nuclear magnetic resonance spectra. Dehydrated hexane and tetrahydrofuran used in this work were purchased from Kanto Chemical Co., Inc. Benzene-d_6 was distilled from sodium/benzophenone ketyl prior to use. $Si(OEt)_4$, $SiHCl_3$, and NH_3 were purchased from Aldrich, TCI, Japan Fine Products, respectively, and were used as received.

Synthesis of Si[N(^{t}Bu)CH=CHN(^{t}Bu)](OEt)$_2$ (2; Si-TBES).

N,N'-di-$tert$-butyl-1,4-diazabuta-1,3-diene (8.15 g, 48.4 mmol) [7] was dissolved in 80 mL of tetrahydrofuran, and then sodium (2.28 g, 99.2 mmol) was added. The reaction mixture was stirred at room temperature for 16 h. To the resulting deep-red solution, $Si(OEt)_4$ (9.79 g, 47.0 mmol) was added dropwise at room temperature and stirred for 24 h at 50℃. The resulting mixture was filtered and the solvent was removed under reduced pressure. The residue was purified by vacuum distillation (76℃/2.0x10^2 Pa) to obtain 11.33 g of Si-TBES (84% yield) as a colorless oil. ^{1}H NMR (500 MHz, C$_6$D$_6$, 20℃, δ/ppm): 5.78 (s, 2 H, NCH=CHN), 3.76 (q, J = 7 Hz, 4 H, OCH_2CH$_3$), 1.29 (s, 18 H, NC(CH_3)$_3$), 1.18 (t, J = 7 Hz, 6 H, OCH$_2$CH_3). ^{13}C NMR (125 MHz, C$_6$D$_6$, 20℃, δ/ppm): 110.7, 58.9, 50.9, 30.9, 18.4.

Synthesis of Si[N(^{t}Bu)CH=CHN(^{t}Bu)]Cl (3).

N,N'-di-$tert$-butyl-1,4-diazabuta-1,3-diene (32.00 g, 190.2 mmol) was dissolved in the mixture of 50 mL of tetrahydrofuran and 150 mL of hexane, and then lithium (2.66 g, 383 mmol) was added. The reaction mixture was stirred at room temperature for 16 h. The resulting deep-red solution was added dropwise to a solution of $SiHCl_3$ (25.20 g, 186 mmol) in 50 mL of hexane at 0℃. The resulting mixture was allowed to warm to room temperature and stirred for 3 h. The resulting mixture

was filtered and the solvent was removed by distillation. The residue was purified by vacuum distillation (80℃/3.8x10^2 Pa) to obtain 35.58 g of Si[N(^{t}Bu)CH=CHN(^{t}Bu)]Cl (83% yield) as a colorless oil. ^{1}H NMR (500 MHz, C$_6$D$_6$, 20 ℃, δ/ppm): 6.40 (s, 1 H, SiH), 5.77 (s, 2 H, NCH=CHN), 1.21 (s, 18 H, NC(CH_3)$_3$). ^{13}C NMR (125 MHz, C$_6$D$_6$, 20℃, δ/ppm): 113.1, 51.9, 30.8.

Synthesis of Si[N(^{t}Bu)CH=CHN(^{t}Bu)] (H)NH$_2$ (4; Si-TBAS).

Si[N(^{t}Bu)CH=CHN(^{t}Bu)]Cl (6.44 g, 27.7 mmol) was dissolved in 20 mL of hexane. The solution was degassed by freeze-pump-thaw cycles, and NH$_3$ was introduced from 5 L baloon. After starring at room temperature for 3 h, precipitate was filtered out and the solvent was removed by distillation. The residue was purified by vacuum distillation (78℃/3.7x10^2 Pa) to obtain 5.45 g of Si-TBAS (92%) as a pale-yellow oil. ^{1}H NMR (500 MHz, C$_6$D$_6$, 20 ℃, δ/ppm): 5.81 (s, 2 H, NCH=CHN), 5.68 (s, 1H, SiH), 1.29 (s, 18 H, NC(CH_3)$_3$), 0.83 (br, 2 H, NH_2). ^{13}C NMR (125 MHz, C$_6$D$_6$, 20℃, δ/ppm): 111.9, 51.4, 31.4.

2.2 Measurement of physical properties

Thermal gravimetric analysis (TG) was performed under an argon flow (400 ml/min) at a heating rate of 10℃/min. Differential scanning calorimetry (DSC) was measured at same heating rate in a stainless steel closed container sealed under an argon atmosphere. Vapor pressures were measured with a diaphragm gauge (Baratron®) placed in a thermostatic oven.

2.3 Deposition of SiO$_2$ thin films

SiO$_2$ thin films were deposited on sapphire (C-plane) substrates at the deposition temperature range from 350 to 500℃ by CVD using Si-TBES, Si-TBAS, and TDMAS. The vapor of the precursors was generated by bubbling method. This vaporized precursor was transferred to the cold wall type CVD reaction chamber with argon carrier gas. The reactant gas was O$_2$, and its concentration was constantly controlled at 0 to 50% of the total reaction chamber pressure. The typical deposition conditions of SiO$_2$ thin films are summarized in **Table 1**.

2.4 Evaluation of the thin films

Deposition amount of the films was measured by the X-ray fluorescence (XRF) calibrated by standard

Table 1　Typical film deposition conditions for SiO₂ thin films by CVD

Precursors	Si-TBES (**2**)	Si-TBAS (**4**)	TDMAS
Bath temperature	51℃	40℃	1℃
Vapor pressure*	31.4 Pa	31.4 Pa	126 Pa
Carrier gas（Ar）flow rate	20 sccm	20 sccm	10 sccm
Diluent gas（Ar）flow rate	220 sccm	220 sccm	230 sccm
Internal pressure of bubbler	13.3 kPa	13.3 kPa	26.7 kPa
Feeding rate**	1.2×10^{-4} mol/h	1.2×10^{-4} mol/h	1.2×10^{-4} mol/h
Reaction gas（O₂）flow rate	60 sccm（20%）		
Total gas flow rate	300 sccm		
Deposition temperature	350-500℃		
Deposition time	60 min		
Chamber pressure	1.3 kPa		

*　Vapor pressures of the precursors were estimated on Clausius-Clapeyron plots in Fig.3
** The feeding rates of precursors were calculated assuming that the precursors were
　　vaporizing as monomer

samples. The film composition and surface roughness were measured by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), respectively. The depth profiles of the thin film were measured by secondary ion mass spectroscopy (SIMS).

3.　Results and discussions

3.1　Syntheses and properties of Si-TBES (2) and Si-TBAS (4)

Si-TBES (**2**) was readily synthesized by the reaction of TEOS with disodium vinylenediaminide (**5**) (**Fig. 1**). By the reaction of lithium vinylenediaminide **6** with trichlorosilane, corresponding chlorohydrosilane **3** was obtained in good yield. Si-TBAS (**4**) was obtained by the reaction of excess NH₃ with **3** in high yield (**Fig. 2**).

Both of Si-TBES (**2**) and Si-TBAS (**4**) are liquid at room temperature. **Fig. 3** shows the Clausius-Clapeyron

plots of these precursors, and the vapor pressures estimated from the plot were summarized in **Table 2**. Their volatilities are sufficient to apply to CVD and ALD processes.

Their thermal stabilities were compared with well-known precursors, TEOS and TDMAS [8] by DSC (**Fig. 4**). Exothermic peaks due to thermal decomposition were observed for Si-TBES (**2**) and Si-TBAS (**4**) at 378℃ and 320℃, respectively. In contrast, TEOS and TDMAS were not decomposed below 450℃. Although these precursors showed slight exothermic baseline shifts around 320℃, the same behavior was observed by cooling and reheating the samples. It means these exotherms do not come from decompositions, but from the reversible change of heat capacity, possibly by phase
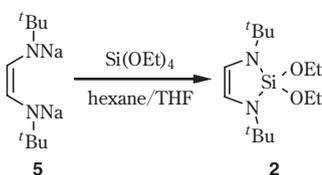
Fig. 1　Synthetic route of Si-TBES（**2**）
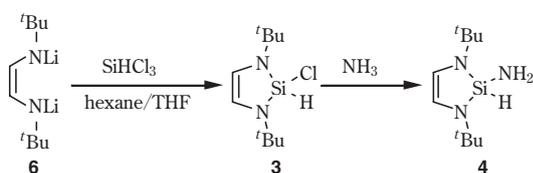
Fig. 2　Synthetic route of Si-TBAS（**4**）
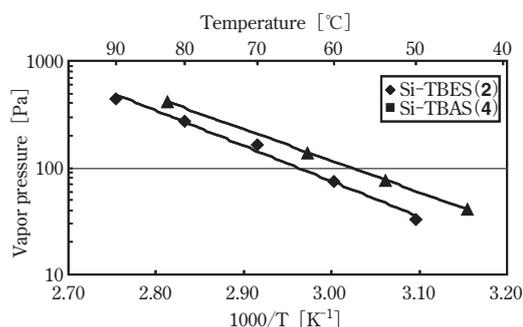
Fig. 3　Clausius-Clapeyron plots of Si-TBES（**2**）and Si-TBAS（**4**）

Table 2　Vapor pressures of **2** and **4** calculated from Clausius-Clapeyron plots

Precursors	0.1 Torr	1.0 Torr
Si-TBES（**2**）	37℃	69℃
Si-TBAS（**4**）	28℃	62℃

transitions. These results indicate that Si-TBES (**2**) and Si-TBAS (**4**) will be suitable to form silicon containing thin films at lower temperature than comparable precursors. Although Si-TBES (**2**) and Si-TBAS (**4**) have low decomposition temperature, TG curves revealed that they still have the sufficient volatilities to vaporize without any undesirable residue (**Fig. 5**).

3.2 SiO$_2$ thin film deposition by a CVD apparatus

Deposition properties of SiO$_2$ thin films using Si-TBES (**2**), Si-TBAS (**4**) and TDMAS were investigated by a thermal CVD apparatus. SiO$_2$ thin films were produced on sapphire (C-plane) substrates and oxygen was used as the reaction gas. **Fig. 6** shows the deposition rate of SiO$_2$ plotted against the deposition temperature ranging from 350℃ to 500℃. The deposition rates using these new precursors were higher than that using TDMAS. Especially, Si-TBAS (**4**) enables to form the thin film with about twice to 20 times higher deposition rate than TDMAS at the deposition temperature of 350 to 500℃.

Fig. 7 illustrates the deposition rates plotted against the concentration of oxygen. The total flow rate was fixed at 300 sccm, and the oxygen flow rate was
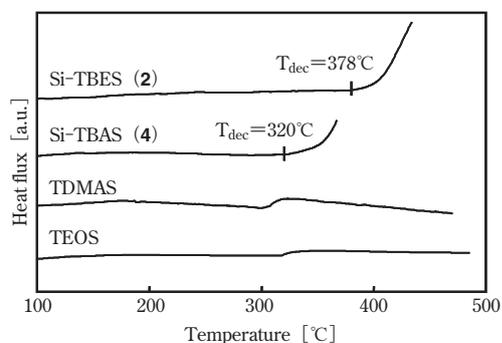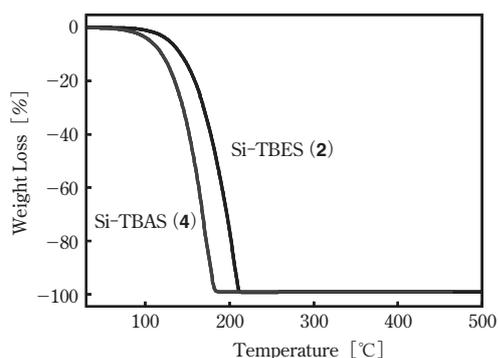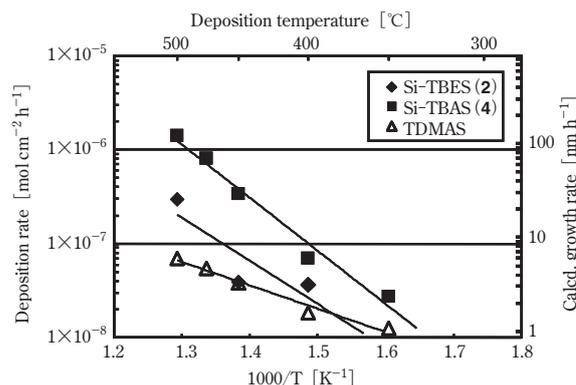

Fig. 6   Temperature dependency of the deposition rate of the SiO$_2$ films from **2,4** and TDMAS
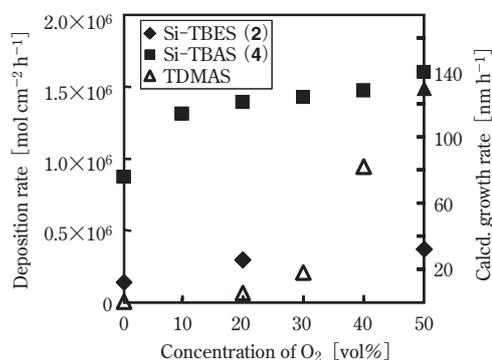
Fig. 7   Oxygen concentration dependency of the deposition rates of the SiO$_2$ films from **2,4** and TDMAS at 500℃

Fig. 4   DSC curves of silicon precursors

Fig. 5   TG curves of Si-TBES (**2**) and Si-TBAS (**4**)

varied from 0 to 150 sccm, corresponding to from 0% to 50% of the oxygen concentration. Interestingly, the growth rates using Si-TBES (**2**) and Si-TBAS (**4**) are less influenced by the concentration of oxygen, while TDMAS requires higher concentration of oxygen to produce thin films. These results indicate that Si-TBES (**2**) and Si-TBAS (**4**) react readily with oxygen to form SiO$_2$ thin film. Although the whole reaction mechanism is unclear, it presumably starts with the dissociation of the bidentate vinylenediamide ligand in the same manner as Ti-DOT (**1**), followed by the decomposition of the reactive silicon containing species to form SiO$_2$ (**Fig. 8**).

3.3 Characterization of the deposited thin films

The atomic compositions of the films deposited at 500℃ were observed by XPS (**Table 3**). All of the films contain oxygen and silicon at the ratio of approximately 2:1, concluding the formation of SiO$_2$ thin films. Carbon and nitrogen concentrations were below the detection limit for Si-TBES (**2**) and TDMAS, while Si-TBAS (**4**)
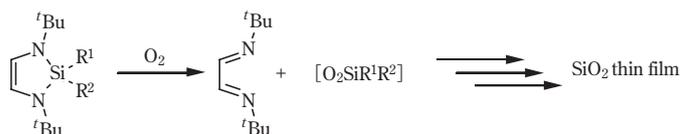
Fig. 8　Plausible decomposition pathway of the silicon precursors

Table 3　Atom concentration of the films estimated by XPS

Precursors	Concentration [atom%]			
	C	N	O	Si
Si-TBES (**2**)	<1	<1	67	31
Si-TBAS (**4**)	<1	2	69	29
TDMAS	<1	<1	69	31

＊Deposition Temperature：500℃

produced SiO_2 film containing 2% of nitrogen, which may derived from $SiNH_2$ moiety.

　SIMS was performed in order to investigate the depth profiles of the carbon and nitrogen contamination (**Fig. 9** and **Table 4**). Compared with the film deposited from TDMAS, that from Si-TBES (**2**) obviously had lower concentration of carbon and nitrogen. In contrast, Si-TBAS (**4**) tended to form thin films with slightly higher

concentration of carbon and nitrogen than Si-TBES (**2**) and TDMAS. This tendency possibly come from the rapid film growth using Si-TBAS (**4**), which prevents carbon and nitrogen from the desorption.

　Root-mean-square (Rms) surface roughness values were evaluated with AFM images (**Fig. 10** and **Table 5**). SiO_2 thin films were deposited on amorphous SiO_2/ Si substrates using oxygen as the reaction gas. Since Si-TBAS (**4**) can produce SiO_2 thin films more efficiently than TDMAS, the deposition time using Si-TBAS (**4**) is 1/15 of that using TDMAS. Nevertheless, the film using Si-TBAS (**4**) was fairly smooth, and its Rms value was comparable to the film from TDMAS of approximately the same thickness. These results indicate that the Si-TBAS (**4**) can provide SiO_2 thin films of the same roughness in shorter deposition time than TDMAS.

4.　Conclusions

　Novel precursors Si-TBES (**2**) and Si-TBAS (**4**) bearing a diazasilacyclopentene framework were synthesized, and their volatilities, thermal properties, and deposition characteristics were evaluated. They
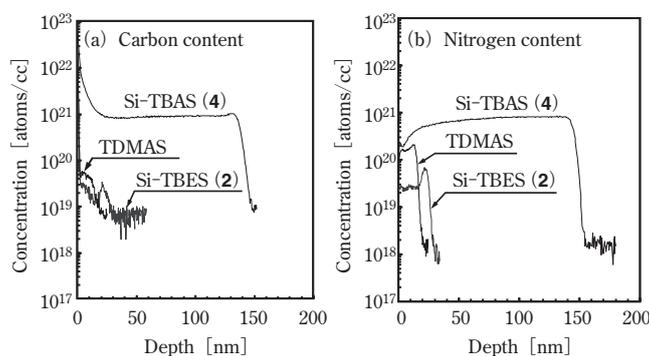
Table 4　Carbon and nitrogen concentration calculated from SIMS

Precursors	Concentration [atm%]	
	C	N
Si-TBES (**2**)	0.03	0.03
Si-TBAS (**4**)	1.5	1.0
TDMAS	0.06	0.30

Fig. 9　Depth profiles of (a) carbon and (b) nitrogen concentration in SiO_2 thin films

Table 5　Surface roughness of as-deposited films

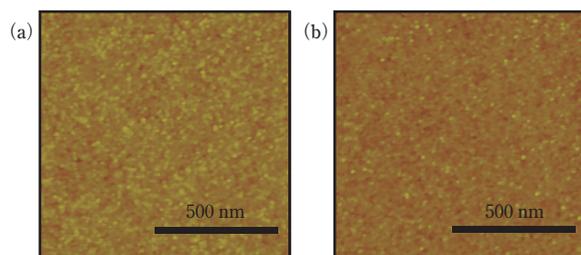| Precursors	Deposition Temp. [℃]	Deposition Time [min]	Film Thickness [nm]	Rms [nm]
Si-TBAS (**4**)	500	10	18	0.26
TDMAS	500	150	15	0.30

Fig.10　AFM images of SiO$_2$ thin films on amorphous SiO$_2$/Si substrates deposited from (a) Si–TBAS (**4**) and (b) TDMAS

are volatile enough for CVD/ALD precursors, and their decomposition temperatures were significantly lower than those of TEOS and TDMAS. CVD processes with these precursors provided SiO$_2$ thin films efficiently, and the oxygen concentration dependency of the deposition rates indicated the high reactivity of Si-TBES (**2**) and Si-TBAS (**4**) towards oxygen caused the efficient thin film formation. Characterizations of the deposited films revealed that Si-TBAS (**4**) can produce smooth thin film efficiently, while the film deposited from Si-TBES (**2**) contains less carbon and nitrogen contamination than that from Si-TBAS (**4**) and TDMAS. Syntheses of other diazasilacyclopentene derivatives and their deposition properties are under investigation.

5.　References

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