

A Novel Liquid Cobalt Precursor for Area - Selective Deposition

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1. Introduction

Area-selective deposition, in which the thin film is formed only on the surface of selected materials of the substrate, is currently regarded as one of the most important technology for next-generation semiconductor manufacturing. The key to successful area-selective deposition depends on the use of precursors with finely tuned reactivity. There is a strong demand for the development of innovative cobalt precursors for areaselective CVD/ALD, because cobalt is a material of some important parts such as CoSi₂ contacts, capping layers, and liners of copper interconnects.

During the past some decades, multiple cobalt compounds have been investigated as CVD/ALD precursors. For example, carbonyl coordinated precursors, such as [Co₂(CO)₈],⁴ [Co(CO)₃NO],⁵ $[Co(CO)_3(CF_3)]$, $[Co(CO)_3H]$, $[Co(CO)_3(\eta^3-CH_2C)^{t}Bu)$ CH_2],⁸ $[Co_2(CO)_6(\eta^2 - HC \equiv C^t Bu)]$,⁹ $[Co(Me_2Im)_2(CO)$ (NO)] (Me₂Im = 1,3-dimethyl-2-imidazolin-2ylidene),¹⁰ and $[Co({}^{i}Pr_{2}Im)(CO)(NO)(PMe_{3})]$ (${}^{i}Pr_{2}Im$ = 1,3-bis(1-methylethyl)-2-imidazolin-2-ylidene),¹¹ and phosphite coordinated precursor, such as $[Co(P(OMe)_2(OPr))_4H]$,¹² are too heat-labile to feed into the CVD/ALD reactor. Cyclopentadienyl precursors, such as $[Co(\eta^5-C_5H_5)_2]$,⁶ $[Co(\eta^5-C_5H_5)$ $(CO)_{2}]^{6}$, $[Co(\eta^{5}-C_{5}H_{5})(\eta^{4}-CH_{2}C(Me)CHCH_{2})]^{13}$, and $[Co(\eta^5-C_5H_5)(\kappa^2-iPrNCHCHN^iPr)]$,¹⁴ require high deposition temperature to form cobalt thin films due to high thermostability. Divalent precursors, such as $[Co(\kappa^2 - OC(Me)CHC(Me)O)_2]$,¹⁵ $[Co(\kappa^2 - OC(Me)CHC(Me)O)_2]$ -OC(^tBu)CHC(^tBu)O)₂],¹⁶ [Co(κ^2 -OC(CF₃)CHC(CF₃) O)₂(Me₂NCH₂CH₂NMe₂)],¹⁷ [Co(κ^2 -OC(Me)CHC(Me) $N^{i}Pr)_{2}$],¹⁸ [Co(κ^{2} -^tBuNNCHCHN^tBu)₂],¹⁹ [Co(κ^{2} -'BuNNCHC('Bu)O)₂],²⁰ [Co(OC(Me)(^{*i*}Pr)CHN^{*t*}Bu)₂],²¹ $[Co(^{i}PrNC(Me)N^{i}Pr)_{2}]$,²² $[Co(\kappa^{2}-OC(^{t}Bu)CHC(^{t}Bu)$

O) (OCMe₂CH₂NMe₂)]₂,²³ and [Co(N('Bu)₂)₂],²⁴ are solid at room temperature that means it has difficulties in handling for CVD/ALD processes. Recently, it was reported that selective ALD using [Co(κ^2 -'BuNCHCHN'Bu)₂] as a precursor on metallic and non-metallic substrates.²⁵ However, the melting point of the compound is high (174-175 °C), it is therefore hard to vaporize it at a constant rate by keeping it in a liquid state.

Herein, we report the development of a novel liquid Co complex, [(2-dimethylamino-1,1-dimethylethyl) (trimethylsilyl) amino] (2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt [Ts-Co10], as a precursor for area-selective deposition of Co thin films (metal-on-metal). A part of this report includes the content of the poster presentation (Program Number: AS-TuP1) at the AVS 20th International Conference on Atomic Layer Deposition (ALD2020).²⁶

Our development will contribute to improvement in energy efficiency through semiconductor technology innovation.

2. Experiment

2.1 Preparations

All manipulations were carried out under argon (Ar) atmosphere with standard Schlenk techniques. Anhydrous $CoCl_2$ was obtained from FUJIFILM Wako Pure Chemical Corporation and were used as received. Tetrahydrofuran (THF) and hexane were purchased from Kanto Chemical Co. Inc. as dehydrated grade. Lithium bis(trimethylsilyl)amide in THF (1.3 mol/L), 2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane), butyllithium in hexane (1.6 mol/ L), chlorotrimethylsilane, and chloroform- d_1 (CDCl₃) were purchased from Tokyo Chemical Industry Co.,



Fig. 1 Synthetic route of Ts-Co10

Ltd. and used without further purification. Benzene- d_6 (C₆D₆, purchased from FUJIFILM Wako Pure Chemical Corporation) was purified by distillation from Na/ benzophenone ketyl, and then stored under Ar. $N^1,N^1,2$ -Trimethylpropane-1,2-diamine (1) was prepared according to a literature procedure.²⁷ ¹H-NMR spectra were recorded on a Bruker Avance HD 400 MHz spectrometer at 293 K.

Synthesis of N^1 , N^1 ,2-trimethyl- N^2 -(trimethylsilyl) propane-1,2-diamine (**2**)

A solution of butyllithium in hexane (2.65 mol/L, 16 mL, 42.4 mmol) was added dropwise to a solution of **1** (4.95 g, 42.6 mmol) in THF (20 mL) at -78 °C. The reaction mixture was warmed to room temperature and additionally stirred for 15 min. To this stirred solution chlorotrimethylsilane (4.61 g, 42.4 mmol) was slowly added at 0 °C, and then stirred at room temperature for 4 h. After the solvents were removed under vacuum, the crude product was distilled under reduced pressure (80-82 °C/40 Torr) to afford **2** as a colorless liquid (7.05 g, 87%). ¹H-NMR (400 MHz, CDCl₃, δ /ppm): 2.32 (s, 6H), 2.11 (s, 2H), 1.09 (s, 6H), 1.05 (br, 1H), 0.06 (s, 9H).

Synthesis of bis[bis(trimethylsilyl)amino]cobalt (3)

A solution of lithium bis(trimethylsilyl)amide in THF (1.3mol/L, 154 mL, 200 mmol) was added dropwise to a solution of $CoCl_2$ (13.0 g, 100 mmol) in THF (50 mL) at -78 °C. The reaction mixture was warmed to room temperature and additionally stirred for 17 h. After the solvent was removed under vacuum, the residue was extracted with hexane (90 mL) and filtered through a Celite[®]-padded G4 glass filter. The filtrate was

concentrated, and the residual solid was purified by sublimation under reduced pressure (120 °C, 51 Pa) to give **3** as a deep green solid (40.1 g, 89%). ¹H-NMR (400 MHz, C_6D_6 , δ /ppm): 168.2 (br, 4H), 100.2 (br, 4H), -15.9 (br, 36H).

Synthesis of [(2-dimethylamino-1,1-dimethylethyl) (trimethylsilyl)amino][bis(trimethylsilyl)-amino]cobalt (Ts-Co9)

2 (10.2 g, 54.3 mmol) was added to a solution of **3** (24.5 g, 54.3 mmol) in hexane (50 mL) at room temperature. After stirring for 1 h at this temperature, the mixture was refluxed for 18 h. The solvent was removed under vacuum, and then the crude product was distilled under reduced pressure (103 °C/56 Pa) to afford Ts-Co9 as a dark green liquid (19.7 g, 89%). ¹H-NMR (400 MHz, C₆D₆, δ /ppm): 149.5 (brs, 6H), 118.7 (brs, 2H), 62.0 (brs, 6H), 32.7 (brs, 9H), -12.7 (brs, 18H).

Synthesis of [(2-dimethylamino-1,1dimethylethyl)(trimethylsilyl)amino] (2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt (Ts-Co10)

2,2,6,6-Tetramethyl-3,5-heptanedione (6.93 g, 37.6 mmol) was added dropwise to a solution of Ts-Co9 (15.5 g, 38.1 mmol) in THF (80 mL) at 0 °C. The reaction mixture was warmed to room temperature and additionally stirred for 16 h. After the solvent was removed under vacuum, the residue was distilled under reduced pressure (130 °C/38 Pa) to give Ts-Co10 as a dark green liquid (7.3 g, 45%). ¹H-NMR (400 MHz, C₆D₆, ∂ /ppm): 65.6 (br, 6H), 53.8 (br, 1H), 46.1 (br, 1H), 40.3 (br, 6H), 14.2 (brs, 18H), 3.99 (br, 9H), -30.3 (br, 1H).

2.2 Measurement of physical properties

Thermogravimetric analysis (TG) was carried out under an Ar flow (400 mL/min) at a heating rate of 10 °C/min with a SII Technology TG/DTA7200 that was contained in a high-purity nitrogen-filled glovebox to prevent decomposition arising from exposure to air. Differential scanning calorimetry analysis (DSC) was performed using a SII Technology DSC7020 at a heating rate of 10 °C/min with a sealed container in a highpurity Ar gas atmosphere. The sample weights used for TG and DSC were 21.3 and 4.1 mg, respectively. Vapor pressures were estimated with a diaphragm gauge (Baratron[®]) placed in a thermostatic oven.

2.3 Deposition of Co thin films

Co thin films were deposited on ruthenium (Ru), copper (Cu), platinum (Pt), and SiO₂ substrates at the deposition temperature range from 100 to 400 °C by CVD of Ts-Co10 using CVD apparatus we assembled (**Fig. 2**). Ts-Co10 was supplied by a bubbling method with the vapor pressure of 13.3 Pa at 85 °C. This vapor was transferred to a cold wall type CVD reactor chamber using Ar as a carrier gas. Ammonia (NH₃) or formic acid (HCO₂H) was used as a reactant gas. In the case with HCO₂H, it was supplied by a bubbling method with the vapor pressure of 3694 Pa at 15 °C. The detailed deposition conditions for Co thin films by CVD are summarized in **Table 1**.

2.4 Evaluation of Co thin films

Film thickness was estimated by the X-ray fluorescence (XRF) calibrated by standard samples. The resistivity of the films was measured by a fourpoint probe method at room temperature. The atomic composition of the films was analyzed by means of X-ray photoelectron spectroscopy (XPS) after Ar⁺ sputtering. Field emission scanning electron microscope (FE-SEM) and atomic force microscope (AFM) were used to characterize film morphology and surface roughness, respectively.

3. Results and discussion

3.1 Synthesis, Physical and Chemical properties of Ts-Co10

The new cobalt compound Ts-Co10 can be readily

Table 1 Experimental conditions of CVD using Ts-Co10

Depo. temp.	100-400°C
Depo. press.	1 or 10 Torr
Depo. time.	15-90 min
Prec. feed	0.06 sccm
Reactant gas	0-80 vol % (NH ₃)
	0-1vol % (HCO ₂ H)
Total gas flow	200 sccm
Substrate	Ru(20 nm)/Ti(10 nm)/SiO2(100 nm)/Si
	Cu(20 nm),Ti(5 nm)/Si
	Pt(20 nm)/Ti(10 nm)/SiO2(100 nm)/Si
	SiO ₂ (100 nm)/Si



Fig. 2 CVD apparatus

synthesized by sequentially reacting Co(hmds)₂(thf) (3), which is an easily available raw material, with N-silvldiamine (2) and dipivalovlmethane. Ts-Co10, which is a green liquid at room temperature (Fig. 3), can be readily purified by distillation, and has good storage stability. Also, this compound has excellent volatility and favorable thermal stability as a CVD/ALD precursor. As shown in Fig. 4, Ts-Co10 vaporized in single-step on TG measurement, and almost no residue remained. The DSC measurement confirmed that the thermal decomposition temperature was 210 °C or higher. Fig. 5 shows the Clausius-Clapeyron plot of Ts-Co10 in relation to temperature and measured vapor pressure in the range of 90 °C to 120 °C. From this plot, it was clarified that the vapor pressures of Ts-Co10 were 0.1 Torr at 88 °C and 1.0 Torr at 133 °C, respectively, which are sufficient for use as a material for the CVD/ ALD process.

3.2 Reactant gas concentration dependency

Reactant gas (NH₃ and HCO₂H) concentration dependency of Co thin film deposition rate on Ru and SiO₂ substrates at 200 °C under 10 Torr was



Fig. 3 Appearance of Ts-Co10



Fig. 4 TG and DSC curves of Ts-Co10



Fig. 5 Clausius-Clapeyron plot of Ts-Co10

examined to determine these optimal concentration in the total reactor chamber pressure (Fig. 6 and 7). The concentrations of NH₃ and HCO₂H were varied 0-80% and 0-1%, respectively. For CVD of Ts-Co10 using NH₃, the deposition rates on Ru and SiO₂ substrates were increased with increasing NH₃ concentration and saturated at 50%, which reveals that Ts-Co10 has favorable reactivity with NH₃. Additionally, the difference in the deposition rate of about 20 nm/h between Ru and SiO₂ substrates was observed in the NH₃ concentration range from 20 to 80%. Also, the resistivity values of the films deposited on SiO₂ substrate in the presence of 50% or more of NH₃ concentration were as low as 200 to 300 μ Ω cm, while the film prepared with lower NH₃ concentration exhibited much higher resistivity. For CVD with HCO₂H, Ts-Co10 showed specific reactivity in a very narrow range around 0.075% selectively on Ru substrate. From the above results, the concentrations of NH₃ and HCO₂H for use in the following CVD experiments were determined to be 50% and 0.075%, respectively.

3.3 Deposition temperature dependency

The temperature dependency of Co thin film deposition rate from Ts-Co10 with and without NH₃ on Ru and SiO₂ substrates under 10 Torr is presented in **Fig. 8**. The figures indicate that there is a significant effect of NH₃ as a reactant gas on the deposition rate at various deposition temperature. Co thin films were deposited with NH₃ on Ru and SiO₂ substrates at 200-400 °C. At a deposition temperature of 300 °C, the highest deposition rate on both of Ru and SiO₂ substrates and the lowest resistivity of the films on SiO₂ substrate were



Fig. 6 NH₃ concentration dependency of deposition rate on Ru and SiO₂ substrates and electric resistivity of Co thin film on SiO₂ substrate at 200°C



Fig. 7 HCO₂H concentration dependency of Co thin film deposition rate on Ru and SiO₂ substrate at 200°C

observed. At a deposition temperature of 200 °C, there was the clear difference in the deposition rates between Ru and SiO₂ substrates (approximately 20 nm/h). In the case without NH₃, almost no Co thin film was formed at 100-300 °C, except for slight film deposition at 400 °C. This suggests that film deposition due to thermal decomposition of Ts-Co10 is unlikely to occur.

The change in Co thin film deposition rate at different deposition temperatures using Ts-Co10 and HCO_2H on Ru, Cu, and SiO_2 substrates is plotted in **Fig. 9**. Co thin

films were not formed on SiO₂ substrates at 150-250 °C, whereas Co thin films were grown smoothly on both Ru and Cu substrates at 150-400 °C. Since the substrateselective window was observed at 150-250 °C, Ts-Co10 has a possibility to achieve area-selective deposition around 200 °C.

3.4 Deposition time dependency

Substrate-selective behavior was examined by CVD of Ts-Co10 with NH_3 or HCO_2H as a reactant gas at 200 °C under 10 Torr on Ru, Cu, Pt, and SiO_2 substrates.

For the deposition test using NH_3 (Fig. 10), the overall linear Co thin film growth after short incubation time (about 6 min) was observed on Ru substrate. Alternatively, Co film growth was hindered on SiO_2 substrate for approximately 26 min, followed by Co film deposition at the same deposition rate as that on Ru substrate. This indicates that normal CVD growth was performed once the surface of the SiO_2 substrate was covered with an ultrathin Co layer.

In the case employing HCO_2H (Fig. 11), Co thin film thickness linearly increased on Ru, Cu, and Pt



Fig. 8 Temperature dependency of deposition rate and electric resistivity of Co thin films from Ts-Co10 with/without NH₃ on Ru and SiO₂ substrates



Fig. 9 Temperature dependency of Co thin film deposition rate using Ts-Co10 and HCO₂H on Ru, Cu, and SiO₂ substrates

substrates within a deposition time of 90 min, while no Co thin film was formed on SiO_2 substrate. The excellent selectivity between these metal substrates and SiO_2 substrate was clearly observed. The reason why cobalt thin films grow selectively only on metallic substrates is not clear at this moment. The incubation times on Ru, Cu, and Pt substrates were 4, < 1, and 3 min, respectively. The use of HCO₂H as a reactant gas is thought to be a better choice in achieving an ideal areaselective deposition.

3.5 Visible substrate-selectivity

The observation of substrate-selective Co thin film deposition from Ts-Co10 with NH_3 or HCO_2H on Ru and SiO_2 substrates at 200 °C under 10 Torr was conducted by FE-SEM and AFM analysis.

For the deposition test with NH_3 (Fig. 12), it could be seen that Co thin film started to deposit on Ru substrate in a deposition time of 15 min, and then the film thickness and surface roughness increased with



Fig.10 Deposition time dependency of Co thin film thickness using Ts-Co10 and NH₃ on Ru and SiO₂ substrates



Fig.11 Deposition time dependency of Co thin film thickness using Ts-Co10 and HCO₂H on Ru, Cu, Pt, and SiO₂ substrates

increasing the deposition time within 60 min. Good surface flatness was demonstrated for the films during the deposition time range. On the other hand, there was a short nucleation delay (~ 15 min) on SiO₂ substrate. After Co thin film growth on SiO₂ substrate commenced, the film thickness and surface roughness remarkably increased with increasing the deposition time compared with the deposition on Ru substrate. These results suggest that it is possible to selectively form a Co thin film using the difference in the incubation time between Ru and SiO₂ substrates.

In the case with HCO_2H (Fig. 13), the initial Co thin film growth on Ru substrate was observed in a deposition time of 15 min, and then the film thickness and surface roughness increased with increasing the deposition time. At a deposition time of 90 min, it was confirmed that the Co thin film on Ru substrate has a thickness of 33 nm and RMS value of 2.45 nm. Good surface flatness was showed for the film deposited on Ru substrate at 200 °C. In contrast, there was no detectable Co film growth on SiO₂ substrate during a deposition time of 90 min. These results clearly demonstrate substrate-selectivity between Ru and SiO₂ substrates.

3.6 Film composition

Table 2 shows chemical composition (estimated by XPS) of the film prepared by CVD of Ts-Co10 with NH₃ and HCO₂H at deposition temperatures of 150-300 °C under pressures of 1-10 Torr on Ru and SiO₂ substrates.

Co-based film deposited using NH₃ at 200 °C under 10 Torr had a large resistivity value (260 μ Ω cm on



Fig.12 FE-SEM and AFM images after 15 min, 30 min, and 60 min Co thin film deposition using NH³ on Ru and SiO² substrates, with film thickness and RMS values



Fig.13 FE-SEM and AFM images after 15 min, 30 min, 60 min, and 90 min Co thin film deposition using HCO₂H on Ru and SiO₂ substrates, with film thickness and RMS values

SiO₂) and a significant amount of nitrogen (13-17 atom %). It was already reported that cobalt nitride (Co_xN, x = 3-6) films have been deposited by CVD of several Co precursors with NH₃ at 200 °C and are stable at this temperature.^{24,28} Based on these previous studies, we believe that nitrogen impurity in the film is derived from NH₃, not nitrogen atoms in Ts-Co10. The measured oxygen and silicon impurities in the film on SiO₂ substrate may come from SiO₂ and be due to a non-continuous film, as indicated by FE-SEM and AFM data. On the other hand, the film deposited at 300 °C contained only 1 atom % of nitrogen, and the improved resistivity value of 65 μ Ω cm approached that for bulk Co (5.6 μ Ω cm at 0 °C).²⁹

The film grown with HCO_2H at 150 and 200 °C under 10 Torr exhibited a high-purity Co content (\geq 91 atom %) with some oxygen and carbon contaminations, which may be derived from either HCO_2H or the ligand in the complex. Also, lower pressure condition (1 Torr) seems to show slightly higher Co content. Nitrogen and silicon concentrations were below the detection limit. At lower temperature around 200 °C, the films obtained using HCO_2H have a higher purity Co content than those formed using NH₃.

4. Conclusions

A novel liquid Co precursor Ts-Co10 was synthesized,

Reactant gas	Depo. press.	Depo. temp. (°C)	Sub.	Film thickness (nm)	Composition by XPS (atom %)					Resistivity on SiO2
(vol%) (7	(Torr)				Co	0	С	Ν	Si	$(\mu \Omega \cdot cm)$
NH3 (50%)	10	200	SiO ₂	40	71	10	1	13	5	260
			Ru	59	82	ND	1	17	ND	—
		300	SiO ₂	105	89	7	2	1	1	65
HCO ₂ H (0.075%)	10	200	Ru	33	91	2	7	ND	ND	—
	1			34	93	2	5	ND	ND	—
	10	150		42	93	2	5	ND	ND	_
	1			51	95	1	4	ND	ND	_

Table 2Chemical composition of Co thin fims deposited on Ru and SiO2
substrates between 150 and 300°C

and its thermal properties, deposition and film characteristics were evaluated. This precursor has sufficient vapor pressure and thermal stability for CVD/ALD processes. The differences in Co thin film formation and the film properties between NH3 and HCO₂H as a reactant gas were revealed by CVD of this complex on Ru, Cu, Pt, and SiO₂ substrates. In addition, visible substrate-selective behaviour on Ru and SiO₂ substrates was confirmed by means of FE-SEM and AFM. For CVD with NH₃, Co thin films were deposited on Ru and SiO₂ substrates at 200-400 °C. The highest deposition rate on both of Ru and SiO2 substrates and the lowest resistivity of the films on SiO₂ substrate were both observed at 300 °C. There was the difference in the incubation time between Ru and SiO₂ substrates at 200 °C, and the obtained films deposited under these condition had a significant amount of nitrogen. It is possible to substrate-selectively form a Co-based film using the difference in the incubation time between metal and non-metal substrates. In the case of using HCO₂H, Co thin films were grown on both Ru and Cu substrates between 150 and 400 °C, whereas Co thin films were not formed on SiO₂ substrates at 150-250 °C. The Co content was up to 95% when the films were formed on Ru substrate. Owing to the excellent substrate selectivity and high purity of obtained films, the use of HCO₂H as a reactant gas is thought to be a better choice in achieving an ideal area-selective deposition. We propose that Ts-Co10 is a promising precursor for selective Co thin film deposition processes.

5. References

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