



# ● A Novel Liquid Cobalt Precursor for Low Temperature Deposition

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## 1. Introduction

The design of semiconductor devices is becoming highly miniaturized and three-dimensional year by year. However, the development of new materials is essential to realize the designed device from the imagination. One of the important keys to manufacturing these advanced devices is the introduction of innovative materials to replace conventional materials, i.e. copper (Cu) interconnect and tungsten (W) contact. Cobalt (Co) have attracted much attention as an excellent material that can overcome various problems such as increased resistance and wiring life caused by the decrease of line width.

Similar to research on new materials for next-generation semiconductor, technologies for forming ultra-thin films on 3D substrates are also being developed. Currently, chemical vapor deposition (CVD) and atomic layer deposition (ALD), are promising methods for forming a highly conformal metal thin film even on a deep trench substrate.

Low temperature deposition is quite important for achieving a conformal ultra-thin film with excellent smoothness. Since CVD/ALD precursor for low temperature deposition is required to have high reactivity with a reactant gas, our study focused on amide complexes with Co-N bonds, which are expected to be extremely reactive.

During the past some decades, several Co-amide compounds have been investigated as CVD/ALD precursors, such as  $\text{Co}(\text{N}(\text{tBu})_2)_2$ ,<sup>1</sup>  $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{THF})$ ,  $\text{Co}[\text{N}(\text{SiMe}_2\text{Et})_2]_2(\text{THF})$ ,  $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{pyridine})$ ,  $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{NMe}_2\text{Et})$ ,  $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{NMeEt}_2)$ ,  $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{NEt}_3)$ ,  $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(1\text{-methyl-pyrrolidine})$ , and  $\text{Co}[\text{N}(\text{SiMe}_2\text{Et})_2]_2(\text{NMe}_2\text{Et})$ .<sup>2</sup> However, these complexes

have some drawbacks. First, since most of them are solid at room temperature, it is difficult to vaporize them at a constant rate by keeping them in a liquid state. Second, they are too heat-labile to feed into the CVD/ALD reactor.

In this paper, we report the development of a novel liquid Co-amide complex, [(2-dimethylamino-1,1-dimethylethyl)(trimethylsilyl)amino][bis(trimethylsilyl)amino]cobalt [Ts-Co9], as a precursor for low temperature deposition of Co thin films.<sup>3</sup> In addition, we also show the possibility of Ts-Co9 for area-selective deposition (ASD), which allows a desired thin film to form in one region of a surface. ASD is currently regarded as one of the most important technology for next-generation semiconductor manufacturing, since this process eliminates many steps associated with conventional patterning.<sup>4</sup>

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

## 2. Experimental

### 2.1 Preparations

All manipulations were carried out under argon (Ar) atmosphere with standard Schlenk techniques. Anhydrous  $\text{CoCl}_2$  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), butyllithium in hexane (1.6 mol/L), chlorotrimethylsilane, and chloroform- $d_1$  ( $\text{CDCl}_3$ ) were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. Benzene- $d_6$  ( $\text{C}_6\text{D}_6$ , 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.<sup>5</sup>  $^1\text{H-NMR}$  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  $-78\text{ }^\circ\text{C}$ . 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  $0\text{ }^\circ\text{C}$ , and then stirred at room temperature for 4 h. After the solvents were removed under vacuum, the crude product was distilled under reduced pressure ( $80\text{--}82\text{ }^\circ\text{C}/40\text{ Torr}$ ) to afford **2** as a colorless liquid (7.05 g, 87%).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  /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  $\text{CoCl}_2$  (13.0 g, 100 mmol) in THF (50 mL) at  $-78\text{ }^\circ\text{C}$ . 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<sup>®</sup>-padded G4 glass filter. The filtrate was concentrated, and the residual solid was purified by sublimation under reduced pressure ( $120\text{ }^\circ\text{C}$ , 51 Pa) to give **3** as a deep green solid (40.1 g, 89%).  $^1\text{H-NMR}$  (400 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ /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 ( $103\text{ }^\circ\text{C}/56\text{ Pa}$ ) to afford Ts-Co9 as a dark green liquid (19.7 g, 89%).  $^1\text{H-NMR}$  (400 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$  /ppm): 149.5 (brs, 6H), 118.7 (brs, 2H), 62.0 (brs, 6H), 32.7 (brs, 9H), -12.7 (brs, 18H).

## 2.2 Measurement of physical properties

Thermogravimetric analysis (TG) was carried out under an Ar flow (400 mL/min) at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  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  $10\text{ }^\circ\text{C}/\text{min}$  with a sealed container in a high-purity Ar gas atmosphere. The sample weights used for TG and DSC were 18.9 and 7.5 mg, respectively.

## 2.3 Deposition of Co thin films and the film quality improvement

Co thin films were deposited on  $\text{SiO}_2$  and ruthenium (Ru) substrates at the deposition temperature range from  $100$  to  $300\text{ }^\circ\text{C}$  by CVD of Ts-Co9 using CVD apparatus we assembled (**Fig. 1**). The Co precursor was supplied by a bubbling method with the vapor pressure of 6.67 Pa at  $70\text{ }^\circ\text{C}$ . This vapor was transferred to a cold wall type CVD reactor chamber using Ar as a carrier gas. Ammonia ( $\text{NH}_3$ ) or a mixed gas [ $\text{NH}_3$ ,  $\text{H}_2$ , and dipivaloylmethane (DPM)] was used as a reactant gas. In the case with DPM, it was supplied by a bubbling method with the vapor pressure of 800 Pa at  $73\text{ }^\circ\text{C}$ . The detailed deposition conditions for Co thin films by CVD are summarized in **Table 1**.

$\text{H}_2$  annealing treatment conditions to improve the film quality are shown in **Table2**.

## 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 four-point probe method at room temperature. The atomic composition of the films was analyzed by means of X-ray photoelectron spectroscopy (XPS) after  $\text{Ar}^+$  sputtering. Atomic force microscope (AFM) was used to characterize surface roughness.

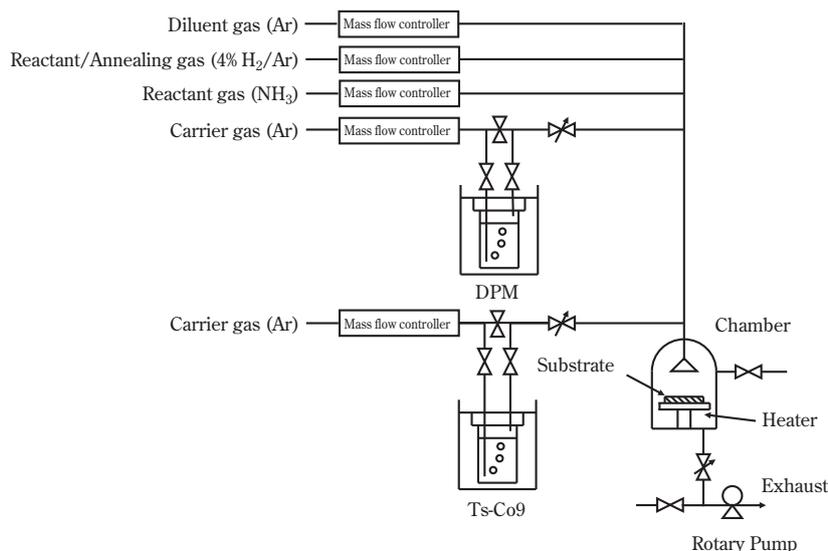


Fig. 1 CVD apparatus

Table 1 Experimental conditions of CVD using Ts-Co9

Depo. temp.	100-300°C
Depo. press.	5 or 10 Torr
Depo. time.	15-120 min
Prec. feed	0.06 sccm
Reactant gas	NH <sub>3</sub> (0-80 vol%) A mixture of NH <sub>3</sub> (50 vol%), H <sub>2</sub> (1.31 vol%), and DPM (0.03 vol%)
Total gas flow	200 sccm
Substrate	Ru (20 nm)/Ti (10 nm)/SiO <sub>2</sub> (100 nm)/Si SiO <sub>2</sub> (100 nm)/Si

Table 2 H<sub>2</sub> annealing conditions of the deposited films

Annealing temp.	200°C
Pressure	10 Torr
Annealing time	120 min
Annealing gas	4% H <sub>2</sub> /Ar
Total gas flow	200 sccm (H <sub>2</sub> : 8 sccm, Ar : 192 sccm)

### 3. Results and discussion

#### 3.1 Molecule Design, Synthesis, Physical and Chemical properties of Ts-Co9

Essential properties of an excellent CVD/ALD precursor generally include sufficient volatility and adequate thermal stability. In order to obtain a high vapor pressure, it is important to reduce intermolecular interactions and, especially in the case of metal complexes, to prevent dinuclearization due to bridging coordination of the ligand. Improvement of the thermal stability of metal complexes can be achieved by selecting appropriate ligands that can bind tightly

to the metal center, but in the case of precursors for low temperature deposition, high reactivity with the reactant gas is also required. Controlling the balance of these requirements is the decisive factor in determining the performance of the precursor. In the development of Ts-Co9, the requirements were successfully met by the placement of trimethylsilyl and methyl groups at specific positions and the effective introduction of specially designed chelating ligands.

The new cobalt compound Ts-Co9 can be obtained by treatment of Co(hmds)<sub>2</sub>(thf) (3) with N-silyldiamine (2) (Fig. 2). The Co precursor, which is a dark green liquid at room temperature (Fig. 3), can be purified by distillation. The vaporization property and the self-decomposition temperature of this complex were measured with the help of TG and DSC, respectively (Fig. 4 and 5). Ts-Co9 represented single-step weight loss on the TG curve, and approximately 10% residue remained. The DSC measurement confirmed that the thermal decomposition temperature was 183 °C or

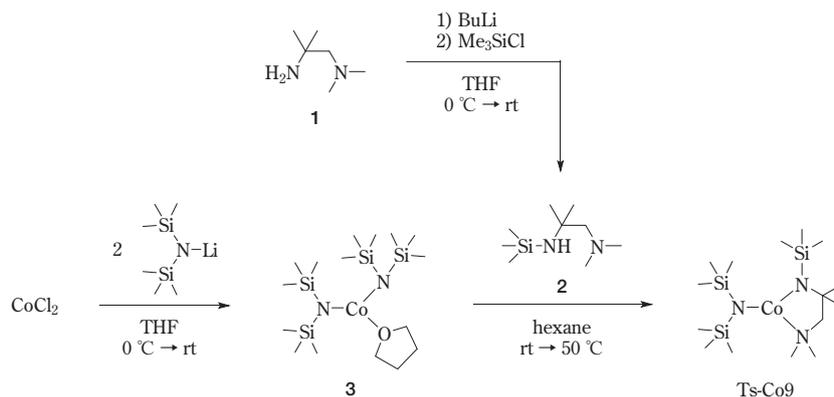


Fig. 2 Synthetic route of Ts-Co9



Fig. 3 Appearance of Ts-Co9

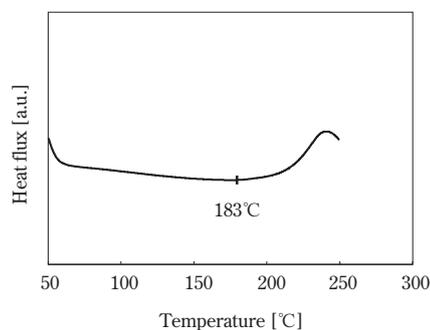


Fig. 5 DSC curve of Ts-Co9

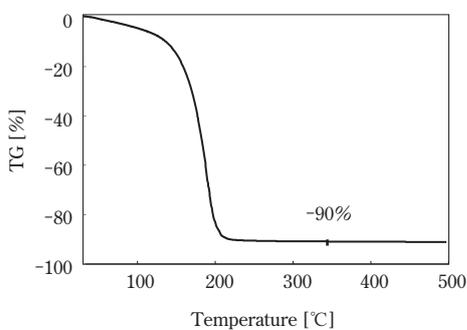
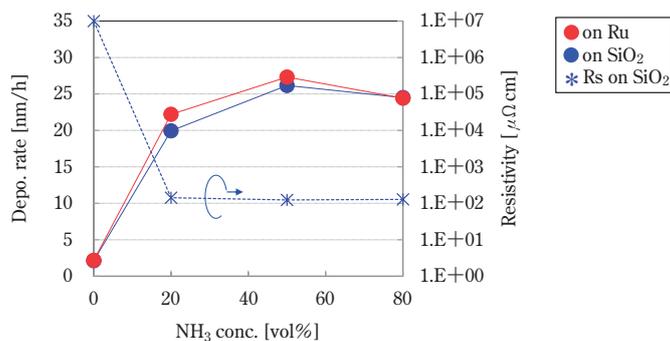


Fig. 4 TG curve of Ts-Co9

higher. This compound has good volatility and favorable thermal stability for use as a material for the CVD/ALD processes.

### 3.2 Reactant gas concentration dependency

$\text{NH}_3$  concentration dependency of Co thin film deposition rate on Ru and  $\text{SiO}_2$  substrates at 200 °C under 10 Torr was examined to determine the optimal concentration in the total reactor chamber pressure (Fig. 6). The concentration of  $\text{NH}_3$  were varied 0-80

Fig. 6  $\text{NH}_3$  concentration dependency of deposition rate on Ru and  $\text{SiO}_2$  substrates and electric resistivity of Co thin film on  $\text{SiO}_2$  substrate at 200 °C

vol%. The deposition rates on Ru and SiO<sub>2</sub> substrates were increased with increasing NH<sub>3</sub> concentration and saturated near about 50 vol%, which reveals that Ts-Co9 has favorable reactivity with NH<sub>3</sub>. Also, the resistivity values of the films deposited on SiO<sub>2</sub> substrate in the presence of 20 vol% or more of NH<sub>3</sub> concentration were as low as 123 to 142  $\mu\Omega\text{cm}$ , while the film prepared without NH<sub>3</sub> exhibited much higher resistivity.

### 3.3 Deposition temperature dependency

The temperature dependency of Co thin film deposition rate from Ts-Co9 with and without NH<sub>3</sub> (50 vol%) on Ru and SiO<sub>2</sub> substrates under 10 Torr is presented in Fig. 7. The figures indicate that there is a significant effect of NH<sub>3</sub> as a reactant gas on the deposition rate at various deposition temperature. Co thin films were deposited with NH<sub>3</sub> on Ru and SiO<sub>2</sub> substrates at 150-300 °C. At a deposition temperature range from 200-275 °C, the deposition rate was saturated on both of Ru and SiO<sub>2</sub> substrates and the

resistivity of the films on SiO<sub>2</sub> substrate was almost constant in the temperature range of 175-250 °C. At the deposition temperatures of 200 and 250 °C, there appears to be a slight difference in deposition rates between Ru and SiO<sub>2</sub> substrates (approximately 4 nm/h). In the case without NH<sub>3</sub>, almost no Co thin film was formed at 100-200 °C, except for film deposition at 300 °C. This suggests that film formation due to thermal decomposition of the complex is unlikely to occur. From these findings, 200-250 °C seems to be the optimum temperature for CVD using the Co precursor and NH<sub>3</sub>.

The change in Co thin film deposition rate at different deposition temperatures using Ts-Co9, NH<sub>3</sub>, H<sub>2</sub>, and DPM on Ru and SiO<sub>2</sub> substrates under 5 Torr is plotted in Fig. 8. Co thin films were not formed on SiO<sub>2</sub> substrates at 150-225 °C, whereas Co thin films were grown smoothly on Ru substrate at 200-300 °C. Since the substrate-selective window was observed at 200-225 °C, this compound has a possibility to achieve ASD around 200 °C.

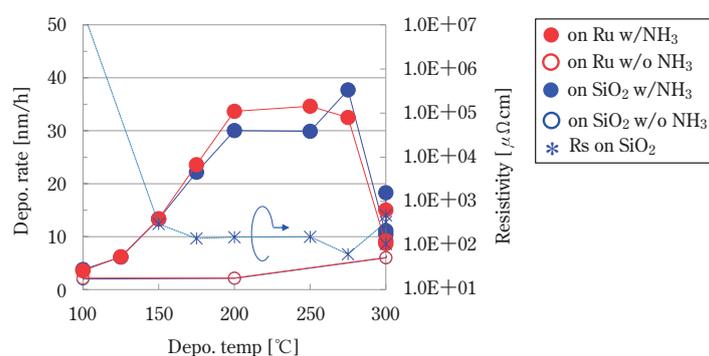


Fig. 7 Temperature dependency of deposition rate and electric resistivity of Co thin films from Ts-Co9 with/without NH<sub>3</sub> on Ru and SiO<sub>2</sub> substrates

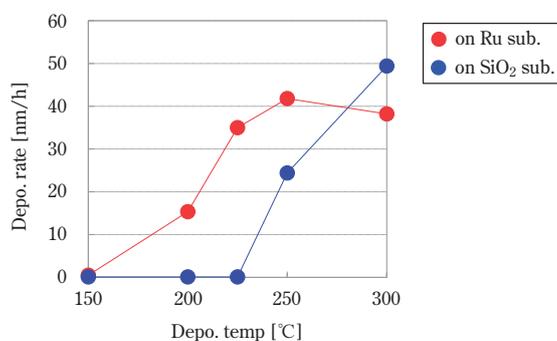


Fig. 8 Temperature dependency of Co thin film deposition rate using Ts-Co9, NH<sub>3</sub>, H<sub>2</sub>, and DPM on Ru and SiO<sub>2</sub> substrates

### 3.4 Deposition time dependency

Substrate-selective behavior was investigated by CVD of Ts-Co9 with  $\text{NH}_3$  or a mixed gas ( $\text{NH}_3$ ,  $\text{H}_2$ , and DPM) as the reactant gas at 200 °C under 10 or 5 Torr on Ru and  $\text{SiO}_2$  substrates.

For the deposition test using  $\text{NH}_3$  (50 vol%) at 10 Torr (Fig. 9), the overall linear Co thin film growth without no incubation time was observed on Ru and  $\text{SiO}_2$  substrates. There was almost no difference in film thickness between the Ru substrate and the  $\text{SiO}_2$  substrate at each deposition time. At 200 °C, ASD using  $\text{NH}_3$  as a single reactant gas seems difficult.

In the case employing the mixed gas at 5 Torr (Fig. 10), Co thin film thickness linearly increased on Ru substrate after an incubation time of about 15 minutes, while no Co thin film was formed on  $\text{SiO}_2$  substrate. The excellent selectivity between Ru and  $\text{SiO}_2$  substrates was clearly observed. However, it should be noted that an island-like pattern without Co film deposition can be seen on the surface of  $\text{SiO}_2$ . The selectivity on both substrates and its pattern on the  $\text{SiO}_2$  substrate

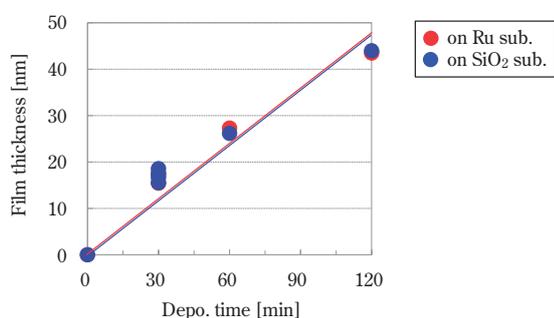


Fig. 9 Deposition time dependency of Co thin film thickness using Ts-Co9 and  $\text{NH}_3$  on Ru and  $\text{SiO}_2$  substrates at 200°C

are unclear at this moment. The use of the mixed gas as a reactant gas is thought to be a better choice in achieving ASD.

### 3.5 Film composition

Table 3 shows chemical composition (estimated by XPS) of the film prepared by CVD of Ts-Co9 with  $\text{NH}_3$  and ( $\text{NH}_3$ + $\text{H}_2$ +DPM) mixture at deposition temperatures of 150-200 °C under pressures of 5 and 10 Torr on  $\text{SiO}_2$  and Ru substrates.

Co-based film formed using  $\text{NH}_3$  at 200 °C under 5 and 10 Torr had a large resistivity value ( $159 \mu\Omega \text{ cm}$  on  $\text{SiO}_2$ ) and a significant amount of nitrogen (14-15 atom%). Some studies reported that cobalt nitride ( $\text{Co}_x\text{N}$ ,  $x = 3-6$ ) films have been deposited by CVD of several Co precursors with  $\text{NH}_3$  at 200 °C and are stable at this temperature.<sup>1,6</sup> According to these previous studies, the N impurity in the film is thought to be derived from  $\text{NH}_3$  rather than the N atoms in Ts-Co9. Even at 150 °C or using the mixed gas ( $\text{NH}_3$ ,  $\text{H}_2$ ,

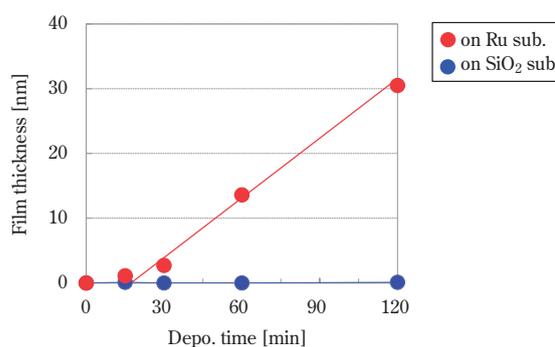
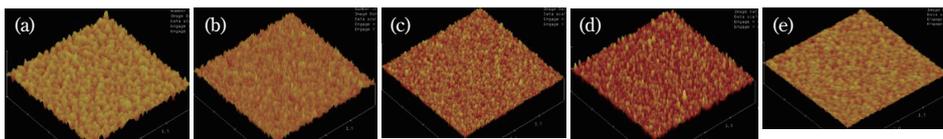


Fig.10 Deposition time dependency of Co thin film thickness using Ts-Co9,  $\text{NH}_3$ ,  $\text{H}_2$ , and DPM on Ru and  $\text{SiO}_2$  substrates at 200°C

Table 3 Chemical composition of Co thin films deposited on  $\text{SiO}_2$  and Ru substrates at 150 and 200°C

Reactant gas (vol%)	Depo. press. (Torr)	Depo. temp. (°C)	Sub.	$\text{H}_2$ annealing time (min)	Film thickness (nm)	Composition by XPS (atom%)					Resistivity ( $\mu\Omega \cdot \text{cm}$ )	AFM	
						Co	O	C	N	Si		RMS value (nm)	Image (Fig.11)
$\text{NH}_3$ (20)	10	200	$\text{SiO}_2$	0	23	77	5	2	14	3	159	3.64	a
				120	21	80	16	1	1	2	98	3.08	b
	5		$\text{SiO}_2$	0	18	82	2	1	15	ND	159	1.52	—
				120	17	85	10	1	ND	3	121	—	—
$\text{NH}_3$ (50)	10	150	$\text{SiO}_2$	0	14	81	2	1	16	ND	229	2.11	d
				120	18	90	8	2	ND	ND	72	—	—
	5		Ru	0	20	—	—	—	—	—	—	1.82	—
				0	12	—	—	—	—	—	—	1.25	c
$\text{NH}_3/\text{H}_2/\text{DPM}$ (50/1.31/0.03)	10	200	Ru	0	45	84	ND	ND	16	ND	—	—	—
	5			31	84	1	ND	15	ND	—	2.25	e	



**Fig.11** AFM ( $2\ \mu\text{m} \times 2\ \mu\text{m}$ ) micrographs for films deposited (a) with  $\text{NH}_3$  under 10 Torr on  $\text{SiO}_2$  at  $200^\circ\text{C}$ ; (b) with  $\text{NH}_3$  under 10 Torr on  $\text{SiO}_2$  at  $200^\circ\text{C}$ , followed by  $\text{H}_2$  annealing; (c) with  $\text{NH}_3$  under 5 Torr on Ru at  $200^\circ\text{C}$ ; (d) with  $\text{NH}_3$  under 10 Torr on  $\text{SiO}_2$  at  $150^\circ\text{C}$ ; (e) with  $\text{NH}_3$ ,  $\text{H}_2$ , and DPM under 5 Torr on Ru at  $200^\circ\text{C}$

and DPM), the film composition was similar to that using  $\text{NH}_3$  at  $200^\circ\text{C}$ . On the other hand, the surface smoothness of the film seems to be ameliorated under low pressure or low temperature conditions, as indicated by RMS values in **Table 3**. In addition, it was found that the growth film on Ru substrate had a smaller surface roughness than that on  $\text{SiO}_2$  substrate, as shown in RMS values in **Table 3** and diagrams in **Fig. 11**. Furthermore, 4 vol%  $\text{H}_2$  annealing treatment at  $200^\circ\text{C}$  for 2 h of the film grown on  $\text{SiO}_2$  at  $200^\circ\text{C}$  led to an increase in the Co content, a significant decrease in the N content, and improvement in the surface flatness of the film. However, the origin of the increased O content is not well understood at this time. Compared to before the annealing, an order of magnitude lower resistivity value ( $72\ \mu\Omega\text{cm}$ ) approached that for bulk Co ( $5.6\ \mu\Omega\text{cm}$  at  $0^\circ\text{C}$ ).<sup>7</sup> These results of experiments clearly explain the effectiveness of the  $\text{H}_2$  annealing for improving film quality.

#### 4. Conclusions

A novel liquid Co precursor Ts-Co9 was synthesized, and its thermal properties, deposition and film characteristics were evaluated. This precursor has sufficient vapor pressure and thermal stability for CVD/ALD processes. The CVD of Co-based film using the Co precursor under non-oxidative conditions was demonstrated. The differences in Co thin film formation and the film properties between  $\text{NH}_3$  and ( $\text{NH}_3+\text{H}_2+\text{DPM}$ ) mixture as a reactant gas were also revealed by the deposition test of this complex on  $\text{SiO}_2$  and Ru substrates. For CVD with  $\text{NH}_3$ , Co thin films were deposited on Ru and  $\text{SiO}_2$  substrates at  $150\text{--}300^\circ\text{C}$ . There was no large difference in the deposition rate between  $\text{SiO}_2$  and Ru substrates, and the obtained films deposited under these condition had a significant amount of nitrogen. It was suggested that  $\text{H}_2$  annealing

treatment is effective in reducing N contamination, lowering the resistivity and smoothing the surface. In the case of using the mixed gas, Co thin films were grown on Ru substrate between  $200$  and  $300^\circ\text{C}$ , whereas Co thin films were not formed on  $\text{SiO}_2$  substrate at  $200\text{--}225^\circ\text{C}$ . Owing to the excellent substrate selectivity, the use of the mixture as a reactant gas is thought to be a better choice for ASD. It is hoped that Ts-Co9 will contribute to the achievement of low temperature deposition.

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