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 area-selective 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(CF₃)]₆, [Co(CO)₃H]₇, [Co₂(CO)₆(η²-HC≡C(tBu))₁₉]₉, [Co(Me₂Im)₂(CO)(NO)]₁₀ (Me₂Im = 1,3-dimethyl-2-imidazolin-2-ylidene), and [Co(iPr₂Im)(CO)(NO)(PMe₃)]₁₁ (iPr₂Im = 1,3-bis(1-methylethyl)-2-imidazolin-2-ylidene), require high deposition temperature to form cobalt thin films due to high thermostability. Divalent precursors, such as [Co(κ²-OC(Me)(CHN)iPr)₂]₁₂, [Co(κ²-OC(Me)CHNtBu)₂]₁₅ and [Co(N(tBu)₂)₂]₁₄ 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(κ²-tBuNCHCN'Bu)₂] as a precursor on metallic and non-metallic substrates. 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). 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 CoCl₂ 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-d₁ (CDCl₃) were purchased from Tokyo Chemical Industry Co.,
Ltd. and used without further purification. Benzene-$d_6$ (C$_6$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$_1$N$_2$-Trimethylpropane-1,2-diamine (1) was prepared according to a literature procedure. $^1$H-NMR spectra were recorded on a Bruker Avance HD 400 MHz spectrometer at 293 K.

Synthesis of N$_1$N$_1$N$_2$-trimethyl-N$_2$-tris(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%). $^1$H-NMR (400 MHz, CDCl$_3$, δ/ppm): 2.32 (s, 6H), 2.11 (s, 2H), 1.09 (s, 6H), 1.05 (br, 1H), 0.06 (s, 9H).

Synthesis of N$_1$N$_1$-trimethyl-2,2-(dimethylsilyl)aminocobalt (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/38 Pa) to give Ts-Co9 as a dark green liquid (19.7 g, 89%). $^1$H-NMR (400 MHz, C$_6$D$_6$, δ/ppm): 149.5 (br, 6H), 118.7 (br, 2H), 62.0 (br, 6H), 32.7 (br, 9H), -12.7 (br, 18H).

Synthesis of [(2-dimethylamino-1,1-dimethylethyl)(trimethylsilyl)amino]bis(trimethylsilyl)amino)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%). $^1$H-NMR (400 MHz, C$_6$D$_6$, δ/ppm): 65.6 (br, 6H), 53.8 (br, 1H), 46.1 (br, 1H), 40.3 (br, 6H), 14.2 (br, 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 high-purity 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 four-point 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>
<thead>
<tr>
<th>Table 1</th>
<th>Experimental conditions of CVD using Ts-Co₁₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depo. temp.</td>
<td>100~400°C</td>
</tr>
<tr>
<td>Depo. press.</td>
<td>1 or 10 Torr</td>
</tr>
<tr>
<td>Depo. time.</td>
<td>15~90 min</td>
</tr>
<tr>
<td>Prec. feed</td>
<td>0.06 sccm</td>
</tr>
<tr>
<td>Reactant gas</td>
<td>0<del>80 vol % (NH₃) / 0</del>1vol % (HCO₂H)</td>
</tr>
<tr>
<td>Total gas flow</td>
<td>200 sccm</td>
</tr>
<tr>
<td>Substrate</td>
<td>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 / SiO₂(100 nm)/Si</td>
</tr>
</tbody>
</table>

Fig. 2 CVD apparatus
synthesized by sequentially reacting Co(hmds)₂(thf) (3), which is an easily available raw material, with N-silyldiamine (2) and dipivaloylmethane. 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 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 μΩ 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
observed. At a deposition temperature of 200 °C, there was the clear difference in the deposition rates between Ru and SiO$_2$ substrates (approximately 20 nm/h). In the case without NH$_3$, 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$_2$H on Ru, Cu, and SiO$_2$ substrates is plotted in Fig. 9. Co thin films were not formed on SiO$_2$ substrates at 150-250 °C, whereas Co thin films were grown smoothly on both Ru and Cu substrates at 150-400 °C. Since the substrate-selective 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$_2$H 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$_2$H (Fig. 11), Co thin film thickness linearly increased on Ru, Cu, and Pt
substances within a deposition time of 90 min, while no Co thin film was formed on SiO₂ substrate. The excellent selectivity between these metal substrates and SiO₂ 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 area-selective deposition.

### 3.5 Visible substrate-selectivity

The observation of substrate-selective Co thin film deposition from Ts-Co₁₀ with NH₃ or HCO₂H on Ru and SiO₂ substrates at 200 °C under 10 Torr was conducted by FE-SEM and AFM analysis.

For the deposition test with NH₃ (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 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 HCO₂H (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 μΩ cm on...
SiO$_2$) and a significant amount of nitrogen (13-17 atom %). It was already reported that cobalt nitride (Co$_x$N, $x = 3$-6) films have been deposited by CVD of several Co precursors with NH$_3$ 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 NH$_3$, not nitrogen atoms in Ts-Co10. The measured oxygen and silicon impurities in the film on SiO$_2$ substrate may come from SiO$_2$ 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 $\mu$Ω cm approached that for bulk Co (5.6 $\mu$Ω cm at 0 °C).$^{29}$

The film grown with HCO$_2$H at 150 and 200 °C under 10 Torr exhibited a high-purity Co content (≥ 91 atom %) with some oxygen and carbon contaminations, which may be derived from either HCO$_2$H 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$_2$H have a higher purity Co content than those formed using NH$_3$.

4. Conclusions

A novel liquid Co precursor Ts-Co10 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 differences in Co thin film formation and the film properties between \(\text{NH}_3\) and \(\text{HCO}_2\text{H}\) as a reactant gas were revealed by CVD of this complex on Ru, Cu, Pt, and SiO\(_2\) substrates. In addition, visible substrate-selective behaviour on Ru and SiO\(_2\) substrates was confirmed by means of FE-SEM and AFM. For CVD with \(\text{NH}_3\), Co thin films were deposited on Ru and SiO\(_2\) substrates at 200-400 \(^\circ\text{C}\). The highest deposition rate on both of Ru and SiO\(_2\) substrates and the lowest resistivity of the films on SiO\(_2\) substrate were both observed at 300 \(^\circ\text{C}\). There was the difference in the incubation time between Ru and SiO\(_2\) substrates at 200 \(^\circ\text{C}\), 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 \(\text{HCO}_2\text{H}\), Co thin films were grown on both Ru and Cu substrates between 150 and 400 \(^\circ\text{C}\), whereas Co thin films were not formed on SiO\(_2\) substrates at 150-250 \(^\circ\text{C}\). 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 \(\text{HCO}_2\text{H}\) 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.

Table 2  Chemical composition of Co thin films deposited on Ru and SiO\(_2\) substrates between 150 and 300\(^\circ\text{C}\)

<table>
<thead>
<tr>
<th>Reactant gas (vol%)</th>
<th>Depo. press. (Torr)</th>
<th>Depo. temp. ((^\circ\text{C}))</th>
<th>Sub.</th>
<th>Film thickness (nm)</th>
<th>Composition by XPS (atom %)</th>
<th>Resistivity on SiO(_2) ((\mu\Omega \cdot \text{cm}))</th>
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<tbody>
<tr>
<td>(\text{NH}_3) (50%)</td>
<td>10</td>
<td>200</td>
<td>SiO(_2)</td>
<td>40</td>
<td>Co 71 O 10 C 1 N 13 Si 5</td>
<td>260</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ru</td>
<td>59</td>
<td>ND 82 ND 1 ND 17 ND</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td></td>
<td>SiO(_2)</td>
<td>105</td>
<td>89 7 2 1 1</td>
<td>65</td>
</tr>
<tr>
<td>(\text{HCO}_2\text{H}) (0.075%)</td>
<td>10</td>
<td>200</td>
<td>Ru</td>
<td>33</td>
<td>ND 91 2 7 ND ND</td>
<td></td>
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<td>51</td>
<td>95 1 4 ND ND</td>
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5. References


