

# Development of a Novel Ru Precursor for Non-Oxidative MOCVD

Advanced Materials Research Laboratory, TOSOH Corporation Sagami Chemical Research Institute Hiroyuki Oike Ken-ichi Tada

# 1. Introduction

Ruthenium thin films have attracted much attention for a wide variety of technological applications, such as metal capping layers<sup>1</sup>, liners of Cu interconnects in integrated circuits,<sup>2</sup> and electrodes in dynamic random access memory.<sup>3-5</sup> In the cases of metal capping layers and liners of Cu interconnects, Ru thin films have to be deposited under non-oxidative conditions to prevent the oxidation of barrier layers or substrates.

However, many of the known Ru precursors, such as bis( $\eta^5$ -ethylcyclopentadienyl) ruthenium,<sup>6</sup> ( $\eta^5$ -2,4dimethylpentadienyl) ( $\eta^5$ -ethylcyclopentadienyl) ruthenium,<sup>6</sup> ( $\eta^5$ -ethylcyclopentadienyl) ( $\eta^5$ - pyrrolyl) ruthenium,<sup>7</sup> and tris(2,2,6,6-tetramethyl-3,5heptanedionato)ruthenium,<sup>8</sup> require oxidative conditions for thin film deposition.

Several precursors have been studied for nonoxidative MOCVD (metal organic chemical vapor deposition). However, they have some weak points. Carbonyl coordinated precursors, such as tricarbonyl( $\eta^4$ -cycloocta-1,3,5,7-tetraene) ruthenium<sup>9</sup> and tricarbonyl( $\eta^4$ -1,3-cyclohexadiene)ruthenium,<sup>10</sup> lack thermal stability and can not provide pure Ru thin films. Amidinate precursor, such as bis(N, N'-di-tertbutylacetamidinato)dicarbonylruthenium,<sup>11</sup> is a solid at room temperature that means it has difficulties in handling for MOCVD processes. Recently, RuO<sub>4</sub> <sup>12</sup> has been investigated as a precursor for thin film deposition with H<sub>2</sub> as reaction gas, however, it is too heat-labile to feed into the CVD reactor. In this study, We developed a novel Ru precursor, ( $\eta^{5}$ -2,4-dimethyl-1-oxa-2,4-pentadienyl) ( $\eta^{5}$ ethylcyclopentadienyl)ruthenium [Rudense<sup>®</sup>], to form pure Ru thin films under non-oxidative conditions and evaluated the deposition characteristics of Rudense<sup>®</sup> by CVD with ammonia (NH<sub>3</sub>) as non-oxidative gas.<sup>13</sup> We also examined the surface flatness and the step coverage of the films from Rudense<sup>®</sup>.

Our development will contribute to improvement in energy efficiency.

# 2. Experiment

# 2.1 Preparations

All manipulations were carried out under argon (Ar) atmosphere with standard Schlenk techniques. Acetonitrile, dichloromethane, diethylether, and hexane were purchased from Kanto Chemical Co. Inc. as dehydrated grade.  $Bis(\eta^5$ -ethylcyclopentadienyl) ruthenium (1), lithium carbonate, mesityl oxide, and tetrafluoroboric acid diethyl ether complex were purchased from Sigma-Aldrich Co. LLC and used without further purification. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a Varian VXR-500S instrument at 293 K.

# Synthesis of $[Ru(\eta^5-C_5H_4Et)(NCMe)_3][BF_4]$ (2)

Tetrafluoroboric acid diethyl ether complex (2.55 g, 15.7 mmol) was slowly added to a solution of bis( $\eta^{5}$ - ethylcyclopentadienyl)ruthenium (1) (4.31 g, 15.0 mmol) in 40 mL of acetonitrile at 0 °C . The reaction



Fig. 1 Synthetic route of Rudense®

mixture was stirred at this temperature for 0.5 h, and then warmed to room temperature and additionally stirred for 20 h. After the removal of solvent under reduced pressure, the residue was washed with CH<sub>2</sub>Cl<sub>2</sub> (5 mL)/Et<sub>2</sub>O (50 mL) to give complex **2** as a yellowish brown solid (5.93 g, 98%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 4.10-4.15 (m, 2 H), 3.89-3.94 (m, 2 H), 2.40 (s, 9 H), 2.03 (q, J = 7.0 Hz, 2 H), 1.07 (t, J = 7.0 Hz, 3 H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 124.9, 96.7, 70.0, 63.4, 20.3, 13.6, 3.7.

# Synthesis of Ru( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>Et)( $\eta^{5}$ -CH<sub>2</sub>C(Me)CHC(Me) O) (Rudense<sup>®</sup>)

Lithium carbonate (1.36 g, 18.4 mmol) was added to a solution of complex 2 (1.49 g, 3.68 mmol) in 15 mL of mesityl oxide at room temperature. After the stirring for 0.5 h at room temperature, the reaction mixture was stirred at 80 °C for 8 h. After the removal of solvent under reduced pressure, the residue was extracted with hexane (60 mL) and filtered through a Celite-padded G4 glass filter. The filtrate was concentrated, and the residual oil was purified by distillation under reduced pressure (88°C, 5 Pa) to give Rudense<sup>®</sup> as a deep red liquid (0.93 g, 86%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 5.44 (s, 1 H), 4.59-4.63 (m, 1 H), 4.51-4.55 (m, 1 H), 4.48-4.51 (m, 1 H), 4.37-4.40 (m, 1 H), 3.80 (s, 1 H), 2.24 (s, 3 H), 2.13 (q, J = 7.5 Hz, 2 H), 1.70 (s, 3 H), 1.53 (s, 1 H), 1.12 (t, J = 7.5 Hz, 3 H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 134.2, 101.1, 100.3, 84.2, 75.7, 74.5, 74.4, 73.9, 52.3, 26.7, 24.1, 21.2, 14.8.

## 2.2 Measurement of physical properties

Thermogravimetric analysis (TG) was carried out under an argon flow (400 mL/min) at a heating rate of 2  $^{\circ}$ C/min with an instrument 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 at a heating rate of 10  $^{\circ}$ C/min with a sealed container in a high-purity argon gas atmosphere. Vapor pressures were estimated with a diaphragm gauge (Baratron<sup>®</sup>) placed in a thermostatic oven.

# 2.3 Deposition of Ru thin films

Ru thin films were deposited on Pt, Ru, Si, and  $SiO_2$  substrates at the deposition temperature range from 300

to 500 °C by CVD using Rudense<sup>®</sup>. The Rudense<sup>®</sup> was supplied by a bubbling method with the vapor pressure of 5.3 Pa at 64 °C . This vapor was transferred to a cold wall type CVD reactor chamber using Ar as a carrier gas.  $NH_3$  was used as a reaction gas. The concentration of  $NH_3$  was kept at 70% in the total reactor chamber pressure. The typical deposition conditions are summarized in **Table 1**.

### 2.4 Evaluation of Ru thin films

Deposition amount of the films was measured by the X-ray fluorescence (XRF) calibrated by standard samples. The crystallinity, depth profiles of contaminations, and surface roughness were determined by X-ray diffraction (XRD), secondary ion mass spectroscopy (SIMS), and atomic force microscopy (AFM), respectively. The resistivity of the films was measured by a four-point probe method at room temperature. Transmission electron microscopy (TEM) was used to characterize film morphology and conformality.

#### 3. Results and discussion

# 3.1 Physical properties of Rudense®

Rudense<sup>®</sup> is a deep red liquid around room temperature. The vaporization property and the selfdecomposition temperature of Rudense<sup>®</sup> were measured with the help of TG and DSC, respectively (**Fig. 2**). As shown in the TG curve, Rudense<sup>®</sup> exhibited single-step weight loss and had almost no residues. The exothermic peak due to thermal decomposition was observed around 230 °C by DSC. The Clausius-Clapeyron plots of Rudense<sup>®</sup> are presented in **Fig. 3**, and the vapor pressure was determined to be 13 Pa at 76°C. These results indicate that Rudense<sup>®</sup> has sufficient vapor

Table 1	Typical deposition conditions of Ru thin
	films by CVD

Depo. pressure	1.3 kPa
Precursor feed	0.024 sccm
Carrier gas	30 sccm (Ar)
Reaction gas	70 sccm (NH <sub>3</sub> )
Total gas flow	100 sccm
Substrate	Pt (150 nm)/Ta <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub> /Si
	Ru (100 nm)/Ti/Si
	Si
	SiO <sub>2</sub> (100 nm)/Si



Fig. 2 TG and DSC curves of Rudense®



Fig. 3 Clausius-Clapeyron plots of Rudense®

pressure and thermal stability for CVD processes.

#### 3.2 Reactivity with ammonia

NH<sub>3</sub> concentration dependency of deposition rate of Ru thin films on SiO<sub>2</sub> substrate at 450 °C is shown in **Fig. 4**. The deposition rate is increased with increase in the concentration of NH<sub>3</sub>, which emphasizes that Rudense<sup>®</sup> has favorable reactivity with NH<sub>3</sub>. In addition, the resistivity of the films prepared in the presence of 20% or more of NH<sub>3</sub> concentration is as low as 10 to 20  $\mu\Omega$  cm, while the films deposited with lower NH<sub>3</sub>



Fig. 4  $NH_3$  concentration dependency of deposition rate and electric resistivity of Ru thin films on SiO<sub>2</sub> substrate at 450 °C

exhibits much higher resistivity.

#### 3.3 Deposition time dependency

The deposition time dependency of Ru film thickness on Pt, Ru, Si, and SiO<sub>2</sub> substrates at 400 °C is presented in **Fig. 5**. The incubation time on Pt and Ru substrates was shorter than that on Si and SiO<sub>2</sub> substrates. Although the deposition rates on Si and SiO<sub>2</sub> substrates were much smaller than Pt and Ru at the initial stage, the deposition rate gradually became almost the same as that on Pt and Ru substrates, because the surfaces of Si and SiO<sub>2</sub> substrates were covered with Ru thin films. From these results, it is suggested that the nucleation rate on Si and SiO<sub>2</sub> substrates is lower than the rate on Pt and Ru substrates.

#### 3.4 Deposition temperature dependency

The deposition temperature dependency of Ru film deposition rate on Pt, Ru, Si, and SiO<sub>2</sub> substrates is



Fig. 5 Deposition time dependency of Ru film thickness on Pt, Ru, Si, and  $SiO_2$  substrates at  $400^{\circ}C$ 



Fig. 6 Deposition temperature dependency of Ru film deposition rate on Pt, Ru, Si, and SiO<sub>2</sub> substrates

shown in **Fig. 6**. Ru thin films were not deposited on Si and SiO<sub>2</sub> substrates at 350 °C or lower. In contrast, smooth film growth were observed on Pt and Ru substrates. Since the substrate selective deposition was observed at 350 °C, Rudense<sup>®</sup> has a possibility to achieve area-selective CVD under non-oxidative conditions.

# 3.5 Crystallinity

The Ru thin films deposited on Pt, Si, and SiO<sub>2</sub> substrates at 400 °C were analyzed by XRD to ascertain their crystallographic orientation (**Fig. 7**). All deposited Ru thin films were crystallized and showed the most intense (002) reflection, corresponding to c-axis oriented Ru metal. In addition, low intense (100) and (101) reflections were observed from the deposited films on Si and SiO<sub>2</sub> substrates. The other reflections were associated with the substrates.

#### 3.6 Depth profile

SIMS was performed to investigate the depth profiles of the carbon, nitrogen, and oxygen concentration in Ru thin films deposited on Pt, Ru, Si, and SiO<sub>2</sub> substrates at 400 °C (**Fig. 8**). Each impurity on the surfaces of Ru films on Pt, Ru, Si, and SiO<sub>2</sub> substrates was higher than  $10^{22}$  atoms/cc. In contrast, each impurity inside of Ru film was less than  $10^{21}$  atoms/cc. Hence, the high-purity Ru film can be formed from Rudense<sup>®</sup>.

# 3.7 Resistivity

For a 50 nm-thick Ru film on Si substrate and a 51 nm-thick Ru film on SiO<sub>2</sub> substrate deposited in the 70% NH<sub>3</sub> concentration at 400 °C , the resistivity measurements gave values of 16 and 17  $\mu\Omega$  cm, respectively. These values were close to that of bulk Ru (7  $\mu\Omega$  cm).<sup>14</sup>



Fig. 7 XRD patterns of Ru thin films deposited on Pt, Si, and SiO\_2 substrates at 400  $^\circ \rm C$ 



**Fig. 8** Depth profiles of (a) carbon, (b) nitrogen, and (c) oxygen concentration in Ru thin films deposited on Pt, Ru, Si, and SiO<sub>2</sub> substrates at 400 °C

#### 3.8 Surface roughness

AFM micrographs of Ru thin films deposited on SiO<sub>2</sub> substrate at 350, 400, and 500 °C are shown in **Fig. 9**. AFM analysis shows the film morphology and surface roughness to be dependent on deposition temperature (**Table 2**), and particle sizes were found to increase with increasing deposition temperature. The film deposited at 500 °C exhibits a high degree of crystallinity. Good surface flatness was demonstrated for the films deposited at 350 and 400 °C .

#### 3.9 Step coverage

Ru thin film was deposited on SiO<sub>2</sub> holes prepared on Si substrate with an aspect ratio of 5.0 at 350 °C by pulsed CVD. The pulsing sequence was Rudense<sup>®</sup> (5.0 s), Ar purge (5.0 s), NH<sub>3</sub> (10.0 s), and Ar purge (10.0 s) for 600 cycles. The detailed deposition conditions are summarized in **Table 3**. Cross-sectional TEM-EDX image of the film is presented in **Fig. 10**. The deposited film was continuous, and film conformality was good within the tested aspect ratio. The step coverage (the film thickness on groove wall divided by the film thickness on flat surface) was over 90%.

# 4. Conclusions

A synthetic procedure was presented for a novel liquid precursor, Rudense<sup>®</sup>. By using Rudense<sup>®</sup>, Ru thin films were deposited on various substrates such as Pt, Ru, Si, and SiO<sub>2</sub> under non-oxidative conditions.



Fig. 9 AFM (2 μm × 2 μm) micrographs for Ru thin films deposited on SiO<sub>2</sub> substrate at a deposition temperature (a) 500 °C (b) 400 °C (c) 350 °C

Depo. temp.[℃]	Film thickness[nm]	Rms[nm]
500	53	4.5
400	25	1.2
350	4	0.5

Table 3	Detailed deposition conditions of Ru thin
	films by pulsed CVD

Depo. temperature	350 °C
Depo. pressure	1.3 kPa
Pulsing soquence	5.0-5.0-10.0-10.0 s
ruising sequence	(Rudense <sup>®</sup> -Ar-NH <sub>3</sub> -Ar)
Cas flow rate	20/30/15 sccm
Gas now rate	(Carrier/purge/NH <sub>3</sub> )
Cycle number	600
Substrate	SiO <sub>2</sub> /Si
Hole diameter	200 nm
Aspect ratio	5.0



Fig.10 Cross-sectional TEM-EDX images of Ru thin film on SiO\_2 holes prepared on Si substrate at 350  $^\circ C$ 

The characteristics of the film was low-impurity, lowresistivity and good surface flatness. In addition, the film deposited at 350 °C by pulsed CVD showed a good step coverage on a substrate with holes. Furthermore, the incubation time of the Ru thin film depositions on Pt and Ru substrates was shorter than that on Si and SiO<sub>2</sub> substrates. Although Ru thin films were not deposited on Si and SiO<sub>2</sub> substrates at 350 °C , Ru thin films were deposited on Pt and Ru substrates. Therefore, Rudense<sup>®</sup> is a promising precursor for area-selective CVD processes under non-oxidative conditions.

#### 5. References

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