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## PAPER

### Ru cyclooctatetraene precursors for MOCVD†

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A series of  $Ru^0$  cyclooctatetraene complexes are presented with optimal properties for MOCVD (metal organic chemical vapour deposition) applications, including combinations of the two lowest melting points and lowest decomposition temperatures yet reported for such materials. The compounds are easy to handle and lead to highly conformal thin films of Ru on SiO<sub>2</sub> features; even within holes with aspect ratios of 40:1. SEM, AFM and XPS studies confirm the near ideal nature of the resulting conformal thin film.

#### Introduction

In order for next-generation devices to become more efficient and complex, engineers must be able to reliably coat thin films onto ever smaller and more closely-packed features. That such films can be made efficiently from Ru is becoming increasingly apparent as a result of its low resistivity and good deposition characteristics. Currently, it is employed as an electrode in dynamic RAM devices<sup>1</sup> and as a diffusion barrier for Cu interconnects in integrated circuits.<sup>2</sup>

Although there are several methods for preparing layers of Ru, MOCVD (metal organic chemical vapour deposition) and ALD (atomic layer deposition) are suitable for forming Ru thin films. Gordon and co-workers achieved the deposition of a Ru film with an aspect ratio of 40:1 using a Ru<sup>II</sup> amidinate complex by ALD.<sup>3</sup> However, the ALD requires a number of reactive cycles to generate thin films and a slow deposition rate.<sup>4</sup> MOCVD provides highly conformal and uniform films, even on challenging threedimensional surfaces such as narrow holes with high aspect ratios. Furthermore, the growth rate of the films is fast enough to support modern and future manufacturing for microelectronics. For these reasons, developing Ru thin film precursor compounds has become an important target for technology industries. Several MOCVD precursors have been developed.<sup>5-16</sup> The ideal MOCVD precursor compound would have a complete set of complementary physical properties. Its melting point would be low, so as to enable easy transition to the liquid state; as a liquid, it would have a high vapour pressure to enable easy transport; and it would have a low decomposition temperature to enable easy removal of the organic ligands. With respect to these properties, Fig. 1 shows some of the previously-reported candidates **A**–**H** of precursors for MOCVD.<sup>5*a*–*c*,7*a*,7*b*,8*b*,12-16</sup> The highest aspect ratio of 6.4 : 1 was published by using **B**,<sup>16</sup> however, a Ru precursor with a higher aspect ratio has yet to be reported.



Fig. 1 Some of the previously-reported candidates A-H of precursors for MOCVD.

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We report herein Ru precursors for MOCVD with the highest aspect ratio of 40:1 by tuning the nature of Ru<sup>0</sup> COT complexes,  $[Ru^0(\eta^4-COT-R)(CO)_3]$  (R = H: 1, R = Me: 2, R = Et: 3, COT-R = R-cycloocta-1,3,5,7-tetraene, Fig. 2).<sup>17</sup> Introduction of alkyl groups such as a methyl and ethyl group into COT makes the nature of a Ru<sup>0</sup> COT complex close to the ideal properties for MOCVD. The resulting Ru thin films have good properties as revealed by scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The films were deposited on a SiO<sub>2</sub> substrate and were conformal even within a hole with an aspect ratio of 40:1. We believe these compounds will be of great benefit in the continuing drive towards greater miniaturisation.



Fig. 2 Structures and melting points of 1–3.

#### **Experimental**

#### Materials and methods

All reactions for the synthesis of **1–3** and COT-R were carried out under an N<sub>2</sub> atmosphere using standard vacuum line techniques or handled in an N<sub>2</sub>-glovebox. Complex **1**, COT-Me and COT-Et were prepared using the previously reported methods.<sup>18–20</sup> [Ru<sup>0</sup><sub>3</sub>(CO)<sub>12</sub>] was supplied by Tanaka kikinzoku kogyo KK and other reagents were purchased from Aldrich, Kanto Chemical Co., Inc. and Wako Pure Chemical Industries. All reagents were used as received without further purification.

<sup>1</sup>H NMR spectra were recorded on a JEOL JNM-AL300 at 25 °C. IR spectra were recorded on a Thermo Nicolet NEXUS 870 FT-IR instrument using 2 cm<sup>-1</sup> standard resolution in a range of 4000 to 400 cm<sup>-1</sup> at 25 °C. Thermal properties of **1–3** were analysed under an N<sub>2</sub> atmosphere by thermogravimetry-differential thermal analysis (TG-DTA) using a Seiko TG-DTA320 instrument. N<sub>2</sub> flow rate is 100 mL min<sup>-1</sup>. Precursors **1–3** (5 mg) were loaded in open type aluminium crucibles. The measurements were done with a heating temperature rate of 5 °C min<sup>-1</sup>.

Ru thin films were analysed by scanning electron microscopy (SEM) using Hitachi S-5000. The film purities were determined by X-ray photoelectron spectroscopy (XPS) using a Nissan Arc PHI 5800 system with an Al/Mg dual anode X-ray source. Binding energies were calibrated by the Si 2p peak of SiO<sub>2</sub> substrates at 103.3 eV.<sup>21</sup> Atomic force microscopy (AFM) was carried out to observe the surface morphology and estimate the root mean square (RMS) roughness value. Electrical resistivity of Ru thin films was measured by a four-point probe method at 25 °C, using a Mitsubishi Chemical MCP-T610. The crystal orientation of the deposited Ru films was evaluated by X-ray diffraction (XRD) patterns using an X-ray diffractometer (Rigaku Ultramax IV) with Cu-K $\alpha$  radiation generated at 40 kV and 40 mA {scan speed:  $20^{\circ} \text{ min}^{-1} (2\theta = 25-55^{\circ}), 1^{\circ} \text{ min}^{-1} (2\theta = 37-45^{\circ})$ }.

#### [Ru<sup>0</sup>(η<sup>4</sup>-COT-Me)(CO)<sub>3</sub>] (2)

A suspension of  $[Ru^{0}_{3}(CO)_{12}]$  (0.750 g, 1.17 mmol) in COT-Me (3.00 g, 25.4 mmol) and cyclohexane (25 mL) was stirred for 72 h with irradiation by UV light. Some unreacted  $[Ru^{0}_{3}(CO)_{12}]$ was removed by filtration, and the solvent was removed in vacuo. The residue was purified by sublimation (23 °C, 40 Pa) followed by recrystallisation from a hexane solution at -40 °C. **2** was obtained as orange crystals (yield: 46% based on the metal atoms in  $[Ru^{0}_{3}(CO)_{12}]$ ). <sup>1</sup>H NMR (300 MHz, in CDCl<sub>3</sub>, reference to TMS):  $\delta$  5.85 (t, 2H, C<sub>8</sub>H<sub>7</sub>CH<sub>3</sub>), 5.55 (t, 1H, C<sub>8</sub>H<sub>7</sub>CH<sub>3</sub>), 5.12 (t, 2H, C<sub>8</sub>H<sub>7</sub>CH<sub>3</sub>), 4.70 (d, 2H, C<sub>8</sub>H<sub>7</sub>CH<sub>3</sub>), 1.99 (s, 3H, C<sub>8</sub>H<sub>7</sub>CH<sub>3</sub>). FT-IR (cm<sup>-1</sup>, KBr disk): 2065 (CO), 1997 (CO). Anal. Calcd for **2**: C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>Ru: C, 47.52; H, 3.32. Found: C, 47.38; H, 3.22.

#### $[Ru^{0}(\eta^{4}-COT-Et)(CO)_{3}]$ (3)

Complex 3 was synthesised by the same method as 2 using  $[Ru^{0}_{3}(CO)_{12}]$  (0.750 g, 1.17 mmol) and COT-Et (3.36 g, 25.4 mmol). After removal of the solvent, distillation (23 °C, 39 Pa) of the residue afforded 3 as an orange liquid (yield: 21% based on the metal atoms in  $[Ru^{0}_{3}(CO)_{12}]$ ). <sup>1</sup>H NMR (300 MHz, in CDCl<sub>3</sub>, reference to TMS):  $\delta$  5.90 (t, 2H, C<sub>8</sub>H<sub>7</sub>CH<sub>2</sub>CH<sub>3</sub>), 5.61 (t, 1H, C<sub>8</sub>H<sub>7</sub>CH<sub>2</sub>CH<sub>3</sub>), 5.13 (t, 2H, C<sub>8</sub>H<sub>7</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.62 (d, 2H, C<sub>8</sub>H<sub>7</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.12 (q, 2H, C<sub>8</sub>H<sub>7</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.07 (t, 3H, C<sub>8</sub>H<sub>7</sub>CH<sub>2</sub>CH<sub>3</sub>). FT-IR (cm<sup>-1</sup>, KBr disk): 2062 (CO), 1987 (CO). Anal. Calcd for 3: C<sub>13</sub>H<sub>12</sub>O<sub>3</sub>Ru: C, 49.21; H, 3.81. Found: C, 48.98; H, 3.65.

#### X-Ray crystallographic analysis

An X-ray quality crystal of **2** was prepared by recrystallisation of a hexane solution at -40 °C for a few days. Measurements were made on a Rigaku/MSC Saturn CCD diffractometer with confocal monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.7107$  Å). Data were collected and processed using the teXsan crystallographic software package of Molecular Structure Corporation.

#### Deposition of ruthenium thin films

Depositions of Ru thin films were conducted using a cold wall MOCVD reactor, with the substrates maintained at 155–175 °C. For each MOCVD experiment, precursors 1–3 were vaporized at 70–75 °C under a pressure of 330 Pa under a flow of N<sub>2</sub> {10 standard cc min<sup>-1</sup> (sccm)} and H<sub>2</sub> (1 sccm). N<sub>2</sub> and H<sub>2</sub> are the carrier gas and the reactant gas, respectively. The deposition time was set to a period of 60–70 min. Deposited Ru films were annealed at 450 °C for 30 s under a flow of H<sub>2</sub> (10 sccm).

The substrates had an 80 nm layer of  $SiO_2$  on Si and were used as received from the supplier (Ites). Patterned  $SiO_2$  substrates (Tei solutions) containing holes with a diameter of 200 nm and an aspect ratio of 40:1 were used to determine the conformal deposition of Ru thin films.

#### **Results and discussion**

#### Synthesis and characterisation of zero-valent Ru precursors

Ru<sup>0</sup> precursors 1–3 were prepared by the photochemical reaction of  $[Ru^0_3(CO)_{12}]$  with COT-R (R = H, Me and Et) in cyclohexane,

Precursor	Melting point (°C)	Decomposition temperature (°C)	Vapour pressure (Pa/°C)	Reference
1	78ª	97ª	20/23 <sup>b</sup>	this work
2	24ª	95ª	$40/23^{b}$	this work
3	<-20 <sup>a</sup>	100 <sup>a</sup>	39/23 <sup>b</sup>	this work
Α	20–25	110–150	27/56	12 <i>a</i> – <i>c</i>
В	17	270	5.3/60	13
С	71.5	160-200	0.036-20/45	14
D	150	150	0.4/40	5 <i>a</i> ,15

<sup>*a*</sup> The melting points and decomposition temperatures were determined by TG-DTA (Fig. S5–S7 in ESI<sup>†</sup>). <sup>*b*</sup> The values of the vapour pressures were determined by sublimation of **1** and **2** or distillation of **3**.



Fig. 3 Synthesis of 1-3

respectively (Fig. 3). Molecular structures of **2** and **3** were characterised by FT-IR (Fig. S1 and S2 in ESI†) and <sup>1</sup>H NMR spectroscopy (Fig. S3 and S4 in ESI†), but also the structure of **2** was determined by X-ray analysis.

Recrystallisation of **2** from a hexane solution at -40 °C yielded orange crystals of **2**, which were available for X-ray analysis (Fig. 4). Fig. 4 reveals that the Ru atom is surrounded by one COT-Me and three CO ligands. Two C=C bonds of COT-Me are coordinated to the Ru centre in an  $\eta^4$ -fashion. The bond distances between Ru and the C atoms of CO ligands {1.927(2), 1.936(2), and 1.933(2) Å for Ru1–C1, Ru1–C2 and Ru1–C3, respectively} are much shorter than those between Ru and the C atoms of COT-Me {2.205(2), 2.189(2), 2.262(2) and 2.238(2) Å for Ru1– C4, Ru1–C11, Ru1–C5 and Ru1–C10, respectively}.



**Fig. 4** An ORTEP drawing of **2** with ellipsoids at 50% probability. Selected interatomic distances (l/Å) and angles ( $\phi/^{\circ}$ ): Ru1–C1 = 1.927(2), Ru1–C2 = 1.936(2), Ru1–C3 = 1.933(2), Ru1–C4 = 2.205(2), Ru1–C5 = 2.262(2), Ru1–C10 = 2.238(2), Ru1–C11 = 2.189(2), Ru1–C1–O1 = 175.3(2), Ru1–C2–O2 = 178.0(2), Ru1–C3–O3 = 179.1(2).

IR spectra of 2 and 3 in the solid state indicate strong vibration bands at 1997 and 2065 cm<sup>-1</sup> for 2 and 1987 and 2062 cm<sup>-1</sup> for

**3** typical of v(CO) (Fig. S1 and S2<sup>†</sup>). The carbonyl stretches are red-shifted with respect to the free CO vibration (2143 cm<sup>-1</sup>) due to the back-donation of electron density from the  $d\pi$  orbital of Ru<sup>0</sup> to the  $\pi^*$  anti-bonding orbital of the CO ligands.

Fig. S3 and S4<sup> $\dagger$ </sup> show <sup>1</sup>H NMR spectra of **2** and **3** in CDCl<sub>3</sub>, respectively. The signal at 1.99 ppm observed in **2** is assigned to the methyl protons and the signals at 2.12 and 1.07 ppm in **3** are responsible for the ethyl protons. The protons of the cyclooctatetraene rings in **2** and **3** are observed at 4.6–6.0 ppm.

#### Physical properties of zero-valent Ru complexes 1-3

The physical properties of 1–3 and the previously-reported precursors A–D are summarised in Table 1 and a three-dimensional plot of the physical properties is shown in Fig. 5. Thermal properties of 1–3 were analysed by TG-DTA under a flow of N<sub>2</sub> gas (Fig. S5–S7 in ESI†). The DTA curves of 1 and 2 show endothermic peaks at 78 and 24 °C, respectively, without weight loss in the TG analysis, indicative of melting without decomposition. Complex 3 solidified below –20 °C, indicating the melting point is <–20 °C. The melting point depends on the bulkiness of the ligand substituent. The order of the melting points is 3 < 2 < 1. This result is probably attributed to the lowering of the symmetry of the molecular structures of Ru<sup>0</sup> complexes 2 and 3 by introduction of the methyl and ethyl groups into COT.



**Fig. 5** A three-dimensional plot of physical properties of the Ru precursors for MOCVD. These data are obtained from Table 1.

At 95–100 °C, weight losses were observed in the TG analyses of 1-3 with endothermic peaks in the DT analyses (Fig. S5–S7 in ESI†), indicative of decompositions (Table 1).

Sufficient volatility is a very important requirement for MOCVD precursors and quantitatively estimated by determining

the vapour pressure. The vapour pressures of 1-3 were determined as 20, 40 and 39 Pa, respectively, by sublimation of 1 and 2 or distillation of 3 at 23 °C without decomposition (Table 1).

As mentioned above, an ideal precursor has a high vapour pressure, low melting point and low decomposition point, which corresponds to the top of the front-left corner of the diagram in Fig. 5. Fig. 5 demonstrates that **2** and **3** are almost exactly in this sweet spot, relative to the best previously-reported candidates **A–D** of precursors for MOCVD.

#### Preparation of Ru films by MOCVD

The deposition of Ru thin films from 1–3 was carried out by using a cold wall type CVD apparatus. The deposited films were analysed by SEM (Fig. 6 and Fig. S8 and S9 in ESI<sup>†</sup>), AFM (Fig. 7 and Fig. S10 and S11 in ESI<sup>†</sup>), XRD (Fig. S12 in ESI<sup>†</sup>) and XPS (Fig. 8 and Fig. S13 and S14 in ESI<sup>†</sup>). The deposition conditions were as follows; deposition temperature: 155-175 °C, Ru source temperature: 70-75 °C, a flow rate of carrier N<sub>2</sub> gas: 10 sccm, a flow rate of reactant H<sub>2</sub> gas: 1 sccm, pressure: 330 Pa, deposition time: 60-70 min. Deposited Ru films were annealed at 450 °C for 30 s under a flow of H<sub>2</sub> (10 sccm). Fig. 6 shows a SEM image of a Ru film deposited on a SiO<sub>2</sub> substrate from **2** and its film thickness deposited at 155 °C was about 12 nm. The SEM image reveals that



Fig. 6 SEM image of a Ru film deposited from 2 at 155 °C under a flow of  $N_2$  (10 sccm) and  $H_2$  (1 sccm).



Fig. 7 AFM image of a 12 nm Ru film deposited from 2 at 155  $^{\circ}$ C under a flow of N<sub>2</sub> (10 sccm) and H<sub>2</sub> (1 sccm). (a) Two- and (b) three-dimensional views.



**Fig. 8** (a) XPS spectrum of a Ru film deposited from 2 at 155 °C under a flow of  $N_2$  (10 sccm) and  $H_2$  (1 sccm). Peaks for O 1s and Si 2p originate from a SiO<sub>2</sub> substrate. (b) Magnification of Ru  $3d_{3/2}$  and  $3d_{5/2}$  peaks in (a).

a continuous Ru film is deposited and the film is planar. The same is true for 1 and 3 (Fig. S8 and S9 in ESI<sup>†</sup>).

AFM was employed to study the surface roughness of the deposited Ru thin films from 1–3 (Fig. 7 and Fig. S10 and S11 in ESI<sup>†</sup>). RMS roughness values are 1.1 nm for a 13 nm thick film deposited from 1 at 165 °C, 1.1 nm for a 12 nm thick film deposited from 2 at 155 °C and 1.5 nm for a 49 nm thick film deposited from 3 at 175 °C, which correspond to fairly smooth films. XRD analysis shows the diffraction peaks typical of a Ru crystalline film (Fig. S12 in ESI<sup>†</sup>).

Ru films from 1–3 were analysed by XPS after being cleaned by sputtering with Ar ions (Fig. 8 and Fig. S13 and S14 in ESI†). These experiments indicate that the binding energies of Ru  $3d_{3/2}$ and  $3d_{5/2}$  correspond to Ru<sup>0,21</sup> No peaks derived from Ru oxide or ligands were observed,<sup>8a</sup> meaning the Ru<sup>0</sup> centres in 1–3 were not oxidised and the supporting ligands were completely removed during the deposition process.

For Ru films deposited from 1–3, resistivity measurements gave values of 93, 152 and 125  $\mu\Omega$  cm, respectively. Although these values are higher than that of bulk Ru (7  $\mu\Omega$  cm),<sup>5a</sup> they are comparable to previously-reported values for Ru thin films.<sup>22,23</sup>

The excellent properties of 1–3 allowed even coverage of Ru films within features with very high aspect ratios. Ru films were deposited on the surface of a high aspect ratio hole (40:1). SEM images of the cross section of Ru films show that very conformal Ru films with about 70% step coverage were formed on the substrates using precursors 1–3 (Fig. 9 and Fig. S15 and S16 in ESI†). Although the values of step coverage were a little lower than that of the Ru<sup>II</sup> amidinate complex (80%),<sup>3</sup> it shows that suitable tuning of the nature of the precursors enables us to deposit Ru films with a very high aspect ratio which is comparable to ALD.



Fig. 9 (a) SEM image of holes with aspect ratios of 40:1. A Ru film was deposited from 2 at 165 °C under a flow of  $N_2$  (10 sccm) and  $H_2$  (1 sccm). Magnified images of (b) top, (c) middle and (d) bottom of the hole.

#### Conclusions

We conclude that zero-valent Ru complexes 1–3 are outstanding MOCVD precursors because they have both a high volatility and a low decomposition point. Pure Ru films with small RMS roughness can be deposited. We achieved the deposition of Ru films on holes with aspect ratios of 40:1. We believe these compounds will be promising materials as MOCVD precursors for miniaturised devices.

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