－報　文－

A Novel Iridium Precursor for MOCVD

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A novel liquid iridium precursor (1,3-cyclohexadiene)(ethylcyclopentadienyl)iridium, Ir(EtCp)(CHD), was synthesized and its physical properties examined. Ir (EtCp) (CHD) showed physical properties suitable for metal-organic chemical vapor deposition (MOCVD). It exhibited enough vapor pressure (0.1 Torr/75℃), excellent volatility, and adequate decomposition temperature. The characteristics of Ir films deposited by MOCVD method using Ir(EtCp)(CHD) and a conventional Ir precursor (1,5-cyclooctadiene) (ethylcyclopentadienyl) iridium Ir(EtCp)(COD) were compared. The Ir films grown using Ir(EtCp)(CHD) showed shorter incubation time and higher nucleation density than those from Ir(EtCp)(COD) at initial growth stage of deposition.

1. Introduction

Iridium (Ir), ruthenium (Ru), platinum (Pt) and their oxides have been investigated as the capacitor electrodes of next generation memory devices including ferroelectric random access memories (FeRAMs). Among these noble metals, Ir and IrO_2 are especially attractive as materials for the FeRAMs electrodes, because they are excellent barriers to oxygen diffusion and effective for improvement of the fatigue loss of PZT capacitors. For the realization of three-demensional memory devices, more attentions become to be paid to the MOCVD method.

There have been several reports on the Ir and IrO_2 films by MOCVD using (1,5-cyclooctadiene)(cyclopentadienyl)iridium(I) Ir(Cp)(COD), [1] (1,5-cyclooctadiene) (methylcyclopentadienyl)iridium(I) Ir(MeCp)(COD), [1-3] tris(acetylacetonato)iridium (III) $Ir(acac)_3$, [4-7] (1,5-cyclooctadiene)(2,2,6,6-tetramethyl-3,5-heptanedionate)iridium(I) Ir(thd)(COD), [7,8] and Ir(EtCp)(COD) [9]. Among these, Ir(EtCp)(COD) was intensively investigated because it is a liquid at room temperature, having higher vapor pressure than other solid precursors described above. Liquid precursors are of great advantage in MOCVD from the viewpoint of material delivery. Ir(EtCp)(COD) has a rigid structure and is very stable under MOCVD conditions. When the growth conditions were optimized, the Ir films of good step coverage and/or conformality were deposited. However, it was difficult so far to deposit iridium oxide thin film by MOCVD using Ir(EtCp)(COD).

2. Experimental

Molecular structures of Ir(EtCp)(CHD) and Ir(EtCp)(COD) are shown in **Fig.1** (a) and (b) respectively. Ir(EtCp)(COD) was commercially available. A novel iridium precursor, Ir(EtCp)(CHD),

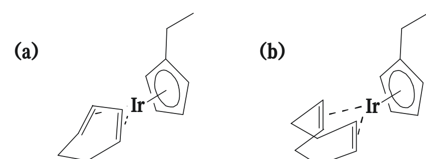

Fig. 1 Molecular structures of (a) Ir(EtCp)(CHD) and (b) Ir(EtCp)(COD).

was prepared by a similar synthetic route (**Fig. 2**) as described in the previous paper [11].

2.1 Preparation

Iridium(III) chloride hydrate was purchased from Furuya metal Co., Ltd. 1,3-Cyclohexadiene and ethylcyclopentadiene dimer were purchased from Aldrich Chemical Co., Inc. *n*-BuLi in hexane was bought from Kanto Kagaku. Tetrahydrofuran was purified by distillation from sodium / benzophenone under argon. All other solvents were deoxidized by bubbling argon before use. Nuclear magnetic resonance (NMR) spectra were measured with a Varian VXR-500s spectrometer. Mass spectra were obtained from gas chromatography/electron impact mass spectrometry (GC/EI-MS), using a Hewlett Packard G1800A GCD System.

Chlorobis(1,3-cyclopentadiene) iridium(I) IrCl $(CHD)_2$—A mixture of iridium (III) chloride hydrate (48 g, 132 mmol), 1,3-cyclohexadiene (100 ml, 1056 mmol), 2-propanol (900 ml) and H_2O (600 ml) was heated with stirring at 73°C (reflux) for 6 h under argon (Ar) atmosphere. The mixture was cooled to 0°C and a resulting white precipitate was filtered under Ar, washed with methanol and hexane and dried under high vacuum to yield a white powder (42.5 g, 83%). ^{1}H-NMR (500 MHz, C_6D_6, δ /ppm) : 4.30-4.15 (m, 2H, -CH=C<u>H</u>-C<u>H</u>=CH-),3.35-3.20 (m, 2H, -C<u>H</u>=CH-CH=C<u>H</u>-), 2.60-2.45 (m, 2H, =CH-C<u>H</u>$_2$-C<u>H</u>$_2$-CH=), 1.70-1.50 (m, 2H, =CH-C<u>H</u>$_2$-C<u>H</u>$_2$-CH=).

(1,3-cyclohexadiene)(ethylcyclopentadienyl) iridium(I) Ir(EtCp)(CHD)—*n*-BuLi solution (1.58 M 73.2 ml, 114 mmol) in *n*-hexane was added dropwise to a freshly prepared ethylcyclopentadiene (EtCpH) monomer (13.2 ml, 114 mmol) in tetrahydrofuran (THF, 600 ml) at −78°C during the course of 45min. After the addition was complete, the reaction mixture was allowed to warm to room temperature (r.t.). The resulting EtCpLi solution in THF was added slowly to a mixture of chlorobis(1,3-cyclohexadiene) iridium (42.3 g, 109 mmol) and THF (300 ml) at −78 °C during 2 h. After addition, the solution was allowed to warm to r.t. and stirred for additional 1 h. *n*-Hexane (1.8 L) was added to the mixture and precipitated inorganic salt was filtered off. The filtrate was concentrated *in vacuo* and the residue distilled yield yellow oil (36.9 g, 93%). ^{1}H-NMR (500 MHz, C_6D_6, δ /ppm) : 4.97 (t, *J*=2.0 Hz, 2H, Cp-<u>H</u>), 4.97-4.95 (m, 2H, -CH=C<u>H</u>-C<u>H</u>=CH-), 4.89 (t, *J*=2.0 Hz, 2H, Cp-<u>H</u>), 3.54-3.49 (m, 2H, -C<u>H</u>=CH-CH=C<u>H</u>-), 2.24 (q, *J*=7.5 Hz, 2H, C<u>H</u>$_2$-CH$_3$), 1.74-1.68 (m, 2H, =CH-C<u>H</u>$_2$-C<u>H</u>$_2$-CH-), 1.54-1.48 (m, 2H, =CH-C<u>H</u>$_2$-C<u>H</u>$_2$-CH=), 1.01 (t, *J*=7.5 Hz, 3H, -CH$_2$-C<u>H</u>$_3$). ^{13}C-NMR (C_6D_6, δ /ppm) : 100.46 (s, -CH$_2$-<u>C</u>H$_3$), 75.59 (s, -<u>C</u>H$_2$-CH$_3$), 75.08 (s, =CH-<u>C</u>H$_2$-<u>C</u>H$_2$-CH=), 65.94 (s, -<u>C</u>H=CH-CH=<u>C</u>H-), 44.11 (s, -CH=<u>C</u>H-<u>C</u>H=CH-), 28.45 (s, <u>Cp</u>-H), 21.47 (s, <u>Cp</u>-H), 15.62 (s, <u>Cp</u>-Et). EI/MS (50 eV, 25 °C) : m/z (^{193}Ir) 362 M$^+$.

2.2 Measurement of physical properties

Viscosity was measured by use of a rotational viscosimeter. Vapor pressure was determined with our original handmade equipment. Volatility of Ir precursors was estimated by thermal gravimetry analysis (TG) and decomposition temperature was measured using a differential scanning calorimeter (DSC).

2.3 MOCVD

Ir thin films were deposited on SiO_2/Si substrates by MOCVD at temperatures 250 and 350 °C using Ir(EtCp)(CHD) and Ir(EtCp)(COD). These precursors

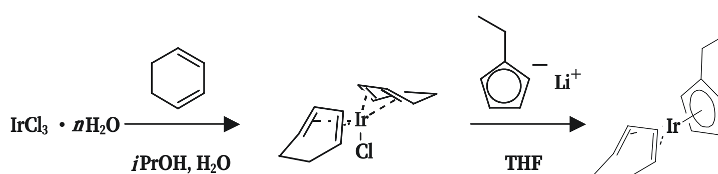

Fig. 2 Sythesis of Ir(EtCp)(CHD).

were supplied by bubbling method using Ar as a carrier gas. During the deposition, Ir(EtCp)(CHD) and Ir(EtCp)(COD) were kept at 70 and 100 ℃, respectively, where the vapor pressures of precursors were around 0.1 Torr. Oxygen was used as a co-reactant gas. The precursor was transferred to a cold wall type MOCVD reactor chamber by Ar carrier gas. The deposition conditions of Ir thin films are summarized in **Table 1**. The nucleation and surface roughness of deposited films were observed by atomic force microscopy (AFM). Thickness of deposited films was measured with a Dektak profilometer.

Table 1 Experimental conditions for Ir film deposition by MOCVD

Conditions	Ir(EtCp)(CHD)	Ir(EtCp)(COD)
Deposition temperature	250 ℃, 350 ℃	250 ℃, 350 ℃
Reactor pressure	4 Torr	4 Torr
Carrier gas flow rate (Ar)	100 cm^3/min	200 cm^3/min
Reacting gas flow rate (O_2)	25 cm^3/min	50 cm^3/min
Purge gas flow rate (Ar)	50 cm^3/min	30 cm^3/min
Precursor temperature	70 ℃	100 ℃
Substrate	SiO_2/Si(100)	SiO_2/Si(100)
Deposition time	5-40 min	1-60 min

3. Results and Discussion

A novel iridium precursor, Ir(EtCp)(CHD) was synthesized successfully from iridium chloride *via* $IrCl(CHD)_2$ and characterized by ^{1}H-NMR, ^{13}C-NMR and GC/EI-MS. Without the ethyl group on cyclopentadienyl ligand, the main product from the second stage was $Ir(Cp)(CHD)_2$ (data not shown). The bulkiness of ethyl group prevented coordinaton by two CHD ligands. Ir(EtCp)(COD) has a rigid structure and is too stable to deposit Ir films by MOCVD. Ir(EtCp)(CHD) has some extent of strain in the molecule in agreement with our strategy in designing the complexes. We expected the descrease of decomposition temperatures due to molecular strain.

Table 2 Physical properties of two precursors

Property	Ir(EtCp)(CHD)	Ir(EtCp)(COD)
Molecular weight	365.5	393.5
Melting point (℃)	15	14
Viscosity (cP)	35	20
Vapor pressure	0.1 Torr/75 ℃	0.1 Torr/105 ℃

Physical properties of two precursors are summarized in **Table 2**.

Ir(EtCp)(CHD) melts at 15℃ and is a pale yellow liquid of low viscosity (*ca.*35 cP) at room temperature. Furthermore, it has higher vapor pressure (0.1 Torr/75 ℃) than Ir(EtCp)(COD) (0.1 Torr/105 ℃). From the view point of precursor delivery liquid phase at room temperature provides great advantage as the MOCVD precursor.

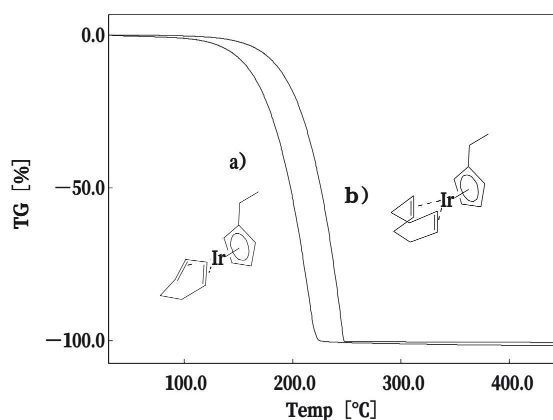

Fig. 3 TG curves of a)Ir(EtCp)(CHD) and b) Ir(EtCP)(COD) under Ar atmosphere (heating rate, 10℃/min).

Fig.3 shows the TG curves as a function of temperature. Ir(EtCp)(CHD) is more volatile than Ir(EtCp)(COD). Molecular weight of Ir(EtCp)(CHD) (Mw 365.5) is about 28 a.m.u. smaller than that of Ir(EtCp)(COD) (Mw 393.5). These precursors have no polar group in molecule, which means that the volatility of these compounds simply depends on their molecular weight.

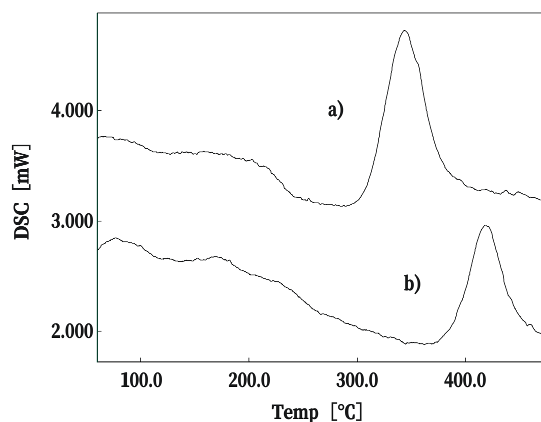

Fig. 4 DSC curves of a)Ir(EtCp)(CHD) and b)Ir(EtCp)(COD) under N_2 atmosphere (heating rate, 10℃/min).

Fig. 4 displays the DSC curves as a function of temperature. The exothermic peaks indicate the decomposition temperatures of the precursors. The result shows that the starting temperature of decomposition of Ir(EtCp)(CHD) (*ca.*300 ℃) is 70 ℃ lower than that of Ir(EtCp)(COD) (*ca.*370 ℃) as expected. In our previous study [10], a novel Ru precursor (2,4-dimethylpentadienyl) (ethylcyclopentadienyl) ruthenium Ru(DMPD)(EtCp) began to decompose at 270 ℃, while the conventional precursor bis(ethylcyclopentadienyl) ruthenium $Ru(EtCp)_2$ started to decompose at 350 ℃. The decomposition temperature of Ru(DMPD)(EtCp) was 70 ℃ lower than that of $Ru(EtCp)_2$. Because of such difference in decomposition temperature, films deposited from Ru(DMPD)(EtCp) showed excellent step coverage and high nucleation density at initial growth stage of deposition. Thus, we expected that Ir(EtCp)(CHD) would show excellent depositing characteristics similar to the Ru precursor.

Fig. 5 illustrates the nucleation density at initial growth stage. Using Ir(EtCp)(CHD), there formed many nuclei on the substrate even after 5min deposition as expected. Using Ir(EtCp)(COD), however, there were scarcely observed nuclei formation even after 20min deposition. Ir films of smaller grain and smoother surface were obtained from Ir(EtCp)(CHD) as compared with Ir(EtCp)(COD). The film thicknesses for c) and f) in **Fig.5** were 32 nm and 25 nm, respectively. The RMS values for c) and f) in **Fig.5** were estimated 1.2 nm and 6.6 nm, respectively. The roughness is better in c) than that in f), though the film in c) is thicker than in f). Fine morphology could be realized by carefully controlling the decomposition temperature of precursors.

Fig. 6 shows the deposition time dependence of film thickness. When Ir(EtCp)(CHD) was used as the precursor, the Ir films showed little incubation time even at low temperature (250 ℃) and the film thickness increased in proportion to the deposition time. In contrast, with obvious incubation time was observed

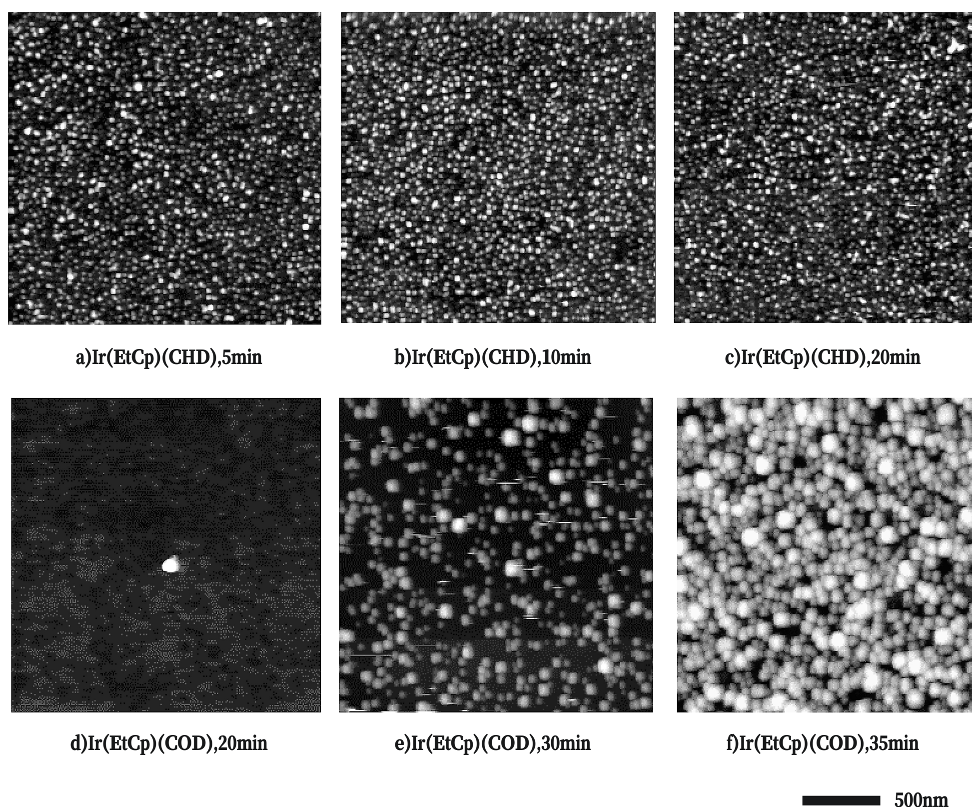

Fig. 5 AFM images of the surface of Ir films deposited from Ir(EtCp)(CHD) (a~c) and Ir(EtCp)(COD) (d~f) at 250℃ within the time indicated.

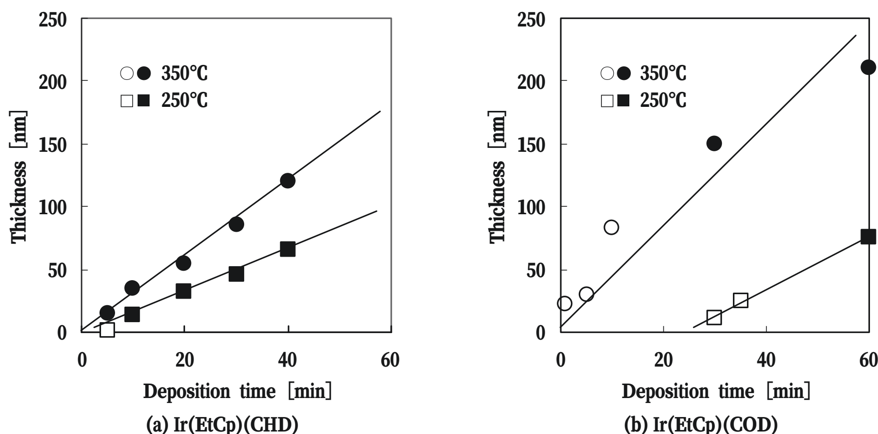

Fig. 6 Deposition time dependence of film thickness for (a) Ir(EtCp)(CHD) and (b) Ir(EtCp)(COD). Films were deposited on SiO2 at 250 ℃(□ and ■) and 350 ℃ (● and ○). Denotations □ / ○ and ■ / ● indicate non-continuous films and continuous films, respectively.

Ir(EtCp)(COD) as shown in **Fig.5** (b). For both precursors, no incubarion time was observed at high temperature (350 ℃), but the films deposited from Ir(EtCp)(COD) were not continuous.

4. Conclusion

In this work, we have synthesized a novel Ir precursor Ir(EtCp)(CHD) for MOCVD and its physical properties examined. This compound showed excellent volatility and adequate decomposition temperature. The Ir thin films deposited by MOCVD using Ir(EtCp)(CHD) did not show remarkable incubation time, while the Ir films from Ir(EtCp)(COD) showed long incubation time at 250 ℃. At initial growth stage, higher nucleation density was observed with Ir(EtCp)(CHD) as compared with Ir(EtCp)(COD). Fine morphology of deposited films could be achieved using Ir(EtCp)(CHD). The phenomena observed with the Ir precursors were the same as those of the Ru precursors reported before. Thus, we have successfully controlled the deposition characteristics of Ir films by modifying the chemical structure of the precursor.

5. References

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