

New Precursors for Chemical Vapor Deposition of Iridium

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Electrically conductive and chemically stable electrode materials are required for use in both high-density dynamic random access memories (DRAMs) and ferroelectric-based memory devices (FeRAMs) that incorporate (Ba,Sr)TiO₃ (BST), Pb(Zr,Ti)O₃ (PZT), or SrBi₂Ta₂O₇ (SBT) thin films as capacitor layers. Since the capacitor layer is deposited at high temperatures in oxygen ambient, the electrodes must be robust; they should not react with the substrate, not be readily oxidized, or oxidized to form electrically conductive oxides. Platinum (Pt) has been widely studied for this purpose.^{1–4} However, it is questionable whether the Pt electrodes can be integrated into a manufacturable process for depositing the capacitor layer. Pt films have been found to react with silicon at temperatures as low as 200 °C, forming PtSi that is easily oxidized to SiO₂ by oxygen diffused through the Pt films.⁵ To circumvent this problem, a diffusion barrier layer, such as TiN, between Pt and polycrystalline silicon plug is commonly employed. Recently, Onishi reported that the Pt/TiN electrode tended to peel at high temperatures (~600 °C) in oxygen ambient.⁶ This can be attributed to the high oxygen diffusivity of platinum, so that the barrier layer underneath the Pt film can be readily oxidized. In addition, it is difficult to etch Pt films, which adds to the difficulty in device fabrication. Therefore, alternate, chemically stable electrode materials are highly desired.

The use of iridium (Ir) and iridium oxide (IrO₂) electrodes is increasingly attractive due to their high conductivity and excellent thermal and chemical stability.^{5,7–9} Bulk Ir metal displays a resistivity of 5.3 μΩ cm at 20 °C, and IrO₂ is highly conductive, with a

reported resistivity of 100 μΩ cm. Iridium films also display excellent adhesion to SiO₂ and are excellent barriers to oxygen diffusion. Dielectric materials, such as BST, grown on Ir bottom electrodes exhibit high capacitance density and low leakage current.⁸ The oxidation of Ir, leading to the formation of IrO₂, occurs only at elevated temperatures (>550 °C) in O₂. During the high-temperature chemical vapor deposition (CVD) process for the growth of the dielectric or ferroelectric thin-film capacitors, the formation of IrO₂ can be advantageous for limiting interdiffusion and, thereby, provide a robust, low-leakage electrode. Unlike RuO₂, IrO₂ is nonvolatile and, thus, stable. Ir and IrO₂ films can be easily “dry” etched by chemical and plasma processes.¹⁰ Ir and IrO₂ films, thus, can function as a high-temperature, stable electrode in a working device.

CVD of Ir and IrO₂ enables low-temperature, conformal coverage and radiation damage-free deposition as preferred for the fabrication of devices. CVD of Ir was reported previously using iridium(III) halides, iridium(III) tris(acetylacetonate) and iridium(III) tris(allyl) precursors.¹¹ For example, Ir films were epitaxially grown onto sapphire, Si and GaAs substrates by CVD from iridium(III) tris(acetylacetonate) at deposition temperatures of 500–600 °C with oxygen as a reactive gas.¹² Ir films were also deposited onto glass and quartz at atmospheric pressure at 370–550 °C in the presence of hydrogen from iridium(III) tris(acetylacetonate).¹³ Ir films were deposited at 100 °C from iridium(III) tris(allyl), but these compounds are extremely air-sensitive.¹⁴ Because the compounds of (β-diketonate)M^IL, M = Ag, Cu, and L = S(C₂H₅)₂ and 1,5-cyclooctadiene (1,5-COD), have proved to be suitable precursors for the low-temperature CVD of Ag and Cu in hydrogen ambient,^{15,16} we believed that Ir compounds of the same empirical formulas of (β-diketonate)Ir^IL, would be suitable source materials for low-temperature CVD of Ir thin films as well. In this work, we report the synthesis and characterization of (β-diketonate)Ir^I Lewis base adducts and the preliminary studies for their use as precursors for CVD of Ir films.

Two Ir complexes, namely (hfac)Ir^I(1,5-COD) and (thd)Ir^I(1,5-COD), where hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate, thd = 2,2,6,6-tetramethyl-3,5-heptanedionate, were synthesized through a salt-elimination reaction by mixing corresponding (β-diketonate)Na

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and chloro-1,5-cyclooctadiene iridium(I) dimer in diethyl ether at room temperature.¹⁷ The ether was evaporated under vacuum after completion of the reaction, and the solid residue was extracted with dry pentane. After filtration, removal of pentane in vacuo gave solid products that gave satisfactory elemental analysis results without further purification. The (hfac)Ir^I(1,5-COD) is a dark brown solid while the (thd)Ir^I(1,5-COD) is a bright yellow solid. Both complexes were characterized by solution ¹H and ¹³C NMR and solid-state Fourier transform (FT) IR. The spectroscopic data were consistent with their molecular formulas. The complexes are air-stable,¹⁸ which further simplifies the handling and operation of a CVD process.

The solid-state molecular structure of (hfac)Ir^I(1,5-COD) was determined by single-crystal X-ray diffraction.¹⁹ Single crystals of (hfac)Ir^I(1,5-COD) were grown from a hexane solution by slow evaporation of the solvent at room temperature. A suitably sized crystal was selected for single crystal X-ray diffraction studies. A summary of the crystal data and experimental details is presented in Table 1. There are two identical, but crystallographically independent, molecules in the structure. Shown in Figure 1 is an ORTEP plot of the molecular structure of (hfac)Ir^I(1,5-COD). The fluorine atoms in one of the trifluoromethyl groups of the molecule were disordered. It is monomeric with a nearly perfectly square planar geometry around iridium metal (based on the C=C centroids). The maximum deviation from the planarity is ca. 0.02 Å and the angles are within 2° of 90° or 180°.

The volatility and thermal stability of (hfac)Ir^I(1,5-COD) and (thd)Ir^I(1,5-COD) were qualitatively examined by thermal analysis and vacuum sublimation. Both compounds were analyzed by simultaneous ther-

(17) **Preparation of (hfac)Ir^I(1,5-COD)**: The general reaction was carried out under a steady flow of nitrogen using standard Schlenk techniques. Chloro-1,5-cyclooctadieneiridium(I) dimer (1.0 g, 1.5 mmol) and (hfac)Na (0.70 g, 3.0 mmol) were suspended in 10 mL of diethyl ether in a Schlenk flask. The mixture was stirred magnetically at room temperature. The solution became dark and white precipitation was observed. The mixture was stirred for 4 h at room temperature. Then the ether was evaporated under vacuum and a black solid residue was obtained; 20 mL of dry pentane was used to extract the product from the residue. After filtration, removal of the pentane filtrate in vacuo gave 1.3 g (~85%) of dark brown solid, which can be further purified by sublimation at ~60 °C under 50 mTorr. Characterization data: Anal. Calcd for C₁₃H₁₃O₂F₆Ir: C, 30.77; H, 2.58. Found: C, 30.91; H, 2.58. FT-IR (KBr pellet, cm⁻¹): 2954 (m), 2843 (m), 1595 (s), 1555 (m), 1444 (s), 1350 (m), 1260 (s), 1200 (s), 1154 (s), 1102 (m), 982 (m), 817 (m), 689 (m). ¹H NMR (C₆D₆): δ 1.39 (m, 4H, 2 × -CH₂-), 1.96 (m, 4H, 2 × -CH₂-), 4.21 (m, 4H, 2 × -CH=CH-), 6.02 (s, 1H, -CH- of hfac). ¹³C NMR (C₆D₆): δ 30.9 (s, -CH₂- of 1,5-COD), 62.0 (s, -CH=CH- of 1,5-COD), 93.0 (s, -CH- of hfac), 118.8 (q, CF₃), 174.1 (q, C=O). **(thd)Ir^I(1,5-COD)** was prepared similarly from (thd)Na and [ClIr^I(1,5-COD)]₂. Characterization data: Anal. Calcd for C₁₉H₃₁O₂Ir: C, 47.18; H, 6.46. Found: C, 47.55; H, 6.58. FT-IR (KBr pellet, cm⁻¹): 2965 (m), 2874 (m), 1538 (s), 1499 (s), 1447 (m), 1375 (s), 1356 (s), 1219 (m), 1134 (m), 977 (m), 877 (m), 800 (m), 644 (m); ¹H NMR (C₆D₆): δ 1.11 (s, 18H, 6 × CH₃), 1.60 (m, 4H, 2 × -CH₂-), 2.19 (m, 4H, 2 × -CH₂-), 4.25 (m, 4H, 2 × -CH=CH-), 5.92 (s, 1H, -CH- of thd); ¹³C NMR (C₆D₆): δ 28.9 (s, CH₃), 31.9 (s, -CH- of 1,5-COD), 41.6 [s, C(CH₃)₃], 59.2 (s, -CH=CH- of 1,5-COD), 92.2 (s, -CH- of thd), 196.8 (s, C=O).

(18) No NMR spectral changes were noted in the Ir precursors after 7 days (168 h) of ambient air exposure.

(19) The diffraction data were collected on a Siemens P4 diffractometer equipped with a SMART CCD detector. Semiempirical corrections for absorption were applied to the data. The structure was solved using direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix, least-squares procedures. All software and sources of the scattering factors are contained in the SHELXTL (version 5.03) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Table 1. Crystal, Data Collection, and Refinement Parameters for (hfac)Ir^I(1,5-COD)

empirical formula	C ₁₃ H ₁₃ F ₆ IrO ₄
FW	507.43
cryst syst	orthorhombic
space group	Pbca
a, Å	17.6226(2)
b, Å	16.3050(3)
c, Å	20.3016(2)
V, Å ³	5833.4(2)
Z	16
ρ _{calc} , g/cm ³	2.311
cryst color and habit	dark red block
abs coeff, mm ⁻¹	9.225
temp, K	198(2)
2θ scan range, deg	4.0–56.7
no. of rflns collected	22300
no. of indep rflns	6824
transmission (min, max)	0.745, 0.888
N _o /N _v	15.0
GOF	1.074
R(F), %	2.79
R _w (F ²), %	7.35
diff peak (min, max) e/Å ³	0.914, -0.878

$$^a \text{Quantity minimized} = R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; R_w(F^2) = \frac{\sum [w(F_o^2 - F_c^2)^2 / \sum (wF_o^2)^2]^{1/2}}$$

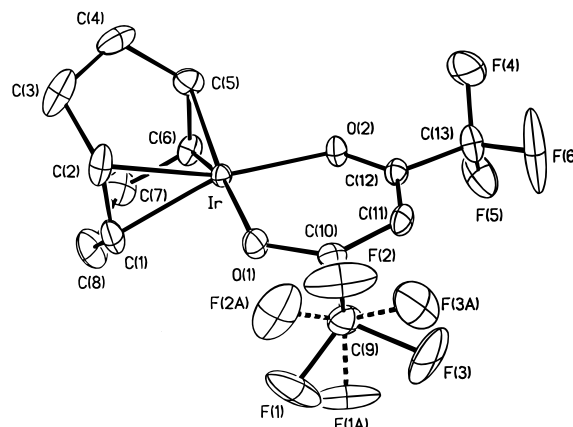


Figure 1. Molecular structure of (hfac)Ir^I(1,5-COD) showing disordered fluorine atoms. Selected bond lengths (Å) and angles (deg) are given as follows: Ir–O(1) = 2.064(3), Ir–O(2) = 2.067(3), Ir–C(5) = 2.090(5), Ir–C(6) = 2.108(5), Ir–C(1) = 2.100(5), Ir–C(2) = 2.102(5); O(1)–Ir–O(2) = 90.58(13), O(1)–Ir–C(2) = 91.0(2), O(1)–Ir–C(1) = 88.7(2), O(2)–Ir–C(5) = 89.8(2), and O(2)–Ir–C(6) = 92.3(2).

mogravimetric analysis (TGA) and differential scanning calorimetry (DSC) with a heating rate of 10 °C/min using Ar as a purge gas (25 mL/min). (hfac)Ir^I(1,5-COD) melted at 120 °C and was completely transported by vaporization below 230 °C at atmospheric pressure.²⁰ In the case of (thd)Ir^I(1,5-COD), a melting endotherm was observed at 179 °C and a 6.3% residual weight was observed at temperatures >294 °C, which is far below that calculated for the molecular iridium content of 39.8%. This discrepancy is due to weight loss from vaporization prior to pyrolytic decomposition at the elevated temperatures. The vaporization of each complex under vacuum was also studied. All of these complexes sublimed intact at 60–70 °C at 50 mTorr.

The chemical vapor deposition of Ir films was studied using (hfac)Ir^I(1,5-COD) as the precursor. Blanket

(20) The thermal analysis data of (hfac)Ir^I(1,5-COD) and scanning electron micrograph of the deposited Ir film from this precursor are available as Supporting Information from the journal.

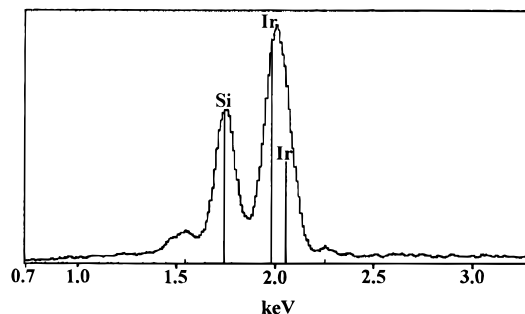


Figure 2. EDS data of an iridium film grown from (hfac)Ir^I(1,5-COD) on a SiO₂ substrate at 350 °C.

silicon (SiO₂/Si), Pt-coated silicon (Pt/Si), and Cu-coated silicon (Cu/Si) wafers were used as substrates. Deposition experiments were conducted at substrate temperatures over a range from 250 to 400 °C and at precursor bubbler temperatures from 60 to 65 °C in a warm-wall bell jar CVD reactor. N₂ was used as carrier gas and 5% H₂ in N₂ as a reactive gas. The reactor pressure was maintained between 1 and 4 Torr during the experiments. Under these conditions, reflective Ir films were deposited on SiO₂/Si, Pt/Si, and Cu/Si substrates. The films were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), and energy dispersive spectroscopy (EDS). The XRD data revealed that the film was composed of iridium metal. XRF and EDS (see Figure 2) data further confirmed the presence of the Ir in the film. The morphology of a film grown on SiO₂/Si at a substrate temperature of 350 °C was investigated by SEM, which shows a rough texture with grain size ranging from 0.1 to 0.3 μm.²⁰ A typical deposition rate was calculated to be 150 Å/min at a substrate temperature of 350 °C and a precursor bubbler temperature of

65 °C. The film resistivity was measured using a four-point probe and found to be 45 μΩ cm at 20 °C. For comparison, a sputtered Ir film²¹ was deposited and found to be 22 μΩ cm at 20 °C using the same equipment. Therefore, the relative film resistivity is 2 times that of sputtered bulk films.

In summary, the synthesis and characterization of (hfac)Ir^I(1,5-COD) and (thd)Ir^I(1,5-COD) were described. The (hfac)Ir^I(1,5-COD) was structurally characterized for the first time by single crystal X-ray diffraction. Using these new precursors, Ir films were deposited by CVD at substrate temperatures between 250 and 350 °C in the presence of hydrogen. The advantages of these compounds are the ease of synthesis and handling, excellent volatility and thermal stability, and the formation of Ir films at relatively low temperatures. Detailed studies related to the CVD of both Ir and IrO₂ films, via both a conventional precursor delivery and a liquid-source delivery using these new precursors, are in progress.

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Supporting Information Available: The thermal analysis data of (hfac)Ir^I(1,5-COD), scanning electron micrograph of the deposited Ir film, X-ray structure determination summaries and tables of bond lengths and angles, anisotropic displacement coefficients, and H atom coordinates (19 pages). See any current masthead page for ordering information.

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(21) A sputtered thin-film of iridium was deposited using a Varian M2I deposition system and used to calibrate the four-point probe electrical test equipment.