



Mechanism of dicarbonyl(2,4-pentanedionato)iridium(I) decomposition on iron surface and in gas phase: Complex experimental and theoretical study

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ABSTRACT

The mechanism of thermal destruction of $\text{Ir}(\text{acac})(\text{CO})_2$ as one of the most important MOCVD precursors for Ir coatings deposition was proposed on the footing of the *in situ* mass spectrometry analysis and quantum chemical modeling. Calculated structural parameters and vibrational spectra of $\text{Ir}(\text{acac})(\text{CO})_2$ molecule were found to be in a fairly good agreement with the experimental data. $\text{Ir}(\text{acac})(\text{CO})_2$ was found to unlikely decompose in the gaseous phase while its adsorption onto the iron surface leads to major structural distortions easing the bond cleavage, molecule decomposition with subsequent formation of iridium films.

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1. Introduction

Iridium-containing film materials have a number of topical applications, e.g. oxidant-resistant refractory coatings for aerospace devices [1], electrochemical biocompatible layers for cardio- and neurosurgery electrodes [2–5]. These materials could be obtained using different techniques, namely, electrodeposition [6,7], magnetron sputtering [8–10], Metal Organic Chemical Vapor Deposition (MOCVD) [11,12], and some others. The latter method is recognized to be one of the most promising ones since it combines the possibility of uniform coverage for complex shape substrates, precious multiparameter monitoring permitting to control characteristics of the deposited coating including variation of its composition and structure, and high ratio of precursor utilization [11,12].

Thermochemical parameters of initial volatile compounds

(precursors) play a key role in the development of processes of deposition from the gaseous phase. To be effectively used in MOCVD process, the precursor must possess sufficient vapor pressure values (volatility), high stability in the evaporation temperature range, complete decomposition at substrate (deposition) temperatures and some other characteristics. Knowledge of a precursor vapor thermolysis mechanism is essential for the evaluation of coating composition and optimization of the MOCVD conditions. Currently, there are only few methods for experimental investigation of thermal destruction processes on the heated surface (substrate), such as *in situ* high temperature mass spectrometry [13–16] and *in situ* infrared absorption spectroscopy [17–19]. However, they are unique and quite inaccessible due to the requirement of special equipment and complexity of data interpretation. Thus, quantum chemical modeling of these processes seems to be more efficient tool for their investigation.

Thus, the present paper describes the first attempt of thermal destruction modeling for iridium precursor vapors. To date, a wide number of iridium complexes with β -diketones and their derivatives, cyclopentadienyls, alkenes, carbonyls, phosphines and other ligands have been proposed as MOCVD precursors [11,12] and

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references therein, [20–23]. Nevertheless, the investigations of vapor thermal destruction on the heated surface have only been carried out for Ir(acac)₃ (acac = acetylacetonato) [24,25], Ir(cod)(acac) (cod = cyclooctadiene-1,5) [26], Ir(cod)(MeCp) (MeCp = methylcyclopentadienyl) [26] and Ir(acac)(CO)₂ [24,27] complexes. Among them, Ir(acac)(CO)₂ is characterized by the highest volatility (temperature dependence of saturated vapor pressure at 306–333 K: $\lg(P, \text{Torr}) = 12.6 - 4910/(T, \text{K})$) [28] along with the lowest carbon content providing the purity of the obtained coatings and relatively low deposition temperatures, even at hydrogen atmosphere (<350 °C) [24,27]. These features make Ir(acac)(CO)₂ promising MOCVD precursor. For this reason, this complex has been chosen as a subject of the present investigation in order to compare theoretical and experimental data.

2. Experimental procedure

Synthesis of Ir(acac)(CO)₂ precursor was carried out according to the procedure described previously in the literature [24] by bubbling carbon monoxide through Ir(cod)(acac) solution in hexane in inert atmosphere. The product was purified by vacuum sublimation (80 °C, 5·10⁻² Torr). Yield is 90%. Anal. Calc. for IrC₇H₇O₄ (mass. %): C, 21.2; H, 2.0. Found (Model CARLO-ERBA-11008 elemental analyzer): C, 21.2; H, 2.1. Synthesis and detailed characterization of Ir(cod)(acac) are described in [29]. IR spectrum of Ir(acac)(CO)₂ as a pellet in KBr was recorded using a Vertex 80 FTIR spectrometer (see Fig. 1b). Raman spectrum of Ir(acac)(CO)₂ powder (see Fig. 1d) were recorded with a Triplemate SPEX spectrometer equipped with CCD detector in a back-scattering geometry. The 488 nm, 10 mW line of an Ar-laser was used for spectral excitation.

Thermal decomposition of Ir(acac)(CO)₂ complex was studied by the analysis of gas phase mass spectra temperature dependence (see Fig. 2). The data regarding the ions presence in the reaction chamber give the important information about the chemical process. However, there are still some issues couldn't be explained since the experimental conditions of mass spectra detection themselves influence on the nature of the observed ions, namely, on the presence of radical particle C₂H₃O⁺ etc. In addition, some of the reaction products cannot be seen in the spectra if they are adsorbed on the reactor's wall. These drawbacks of the experimental technique do not allow us to propose an unambiguous scheme of the reaction. Moreover, one can expect that the act of

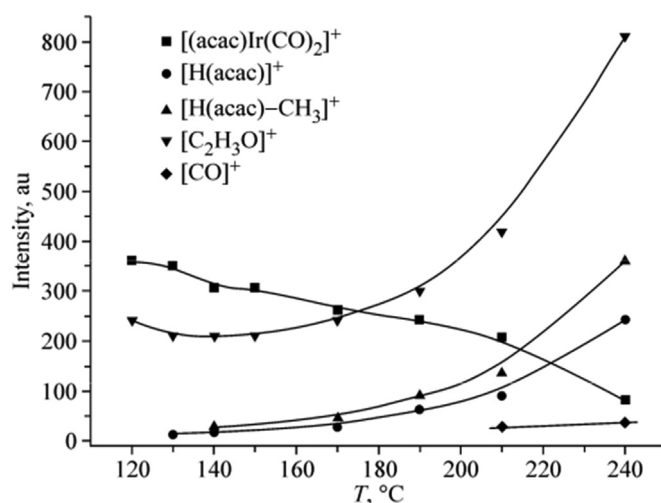


Fig. 2. Intensities of ion peaks in mass spectra versus temperature during the Ir(acac)(CO)₂ vacuum decomposition [24].

decomposition would take place rather on the reactor walls than in the gas phase. Seeking for the elucidation of these issues, we then performed density functional theory (DFT) simulation of the Ir(acac)(CO)₂ decomposition in the gas phase and on the iron surface.

3. Modeling and discussion

3.1. Ir(acac)(CO)₂ single molecule decomposition

Geometry optimization of Ir(acac)(CO)₂ was carried out by means of density functional theory using BLYP exchange-correlation functional, def2-SVP and def2-SVP/J (auxiliary) basis sets and effective core potentials for Ir atom using an ORCA quantum chemistry program package [30]. Optimization was performed until the energy difference between two steps was less than 10⁻⁴ eV, and root-mean squared energy gradient was less than 5·10⁻³ eV/Å. A good agreement with crystallographic data [31] was reached (see Table S1, inset of Fig. 1). Then IR and Raman spectra were calculated for the equilibrium geometry (Fig. 1a and c) and compared with the experimentally measured spectra. Due to the symmetry of the molecule, all vibrational frequencies present both

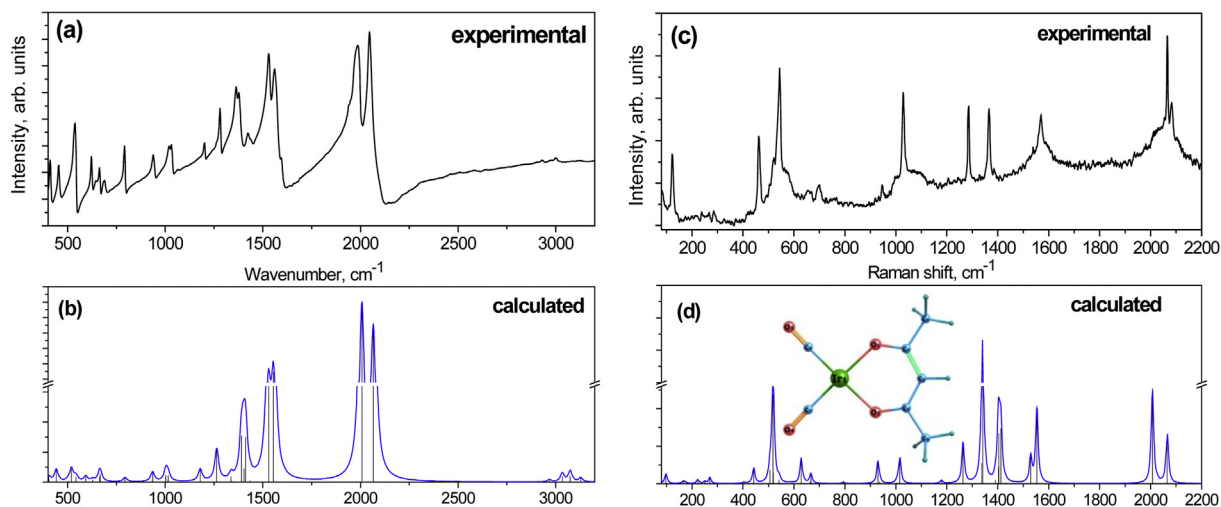


Fig. 1. Calculated (a,c) and experimental (b,d) IR (a,b) and Raman (c,d) spectra for Ir(acac)(CO)₂. The inset shows the structure of Ir(acac)(CO)₂ molecule.

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