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Cite as: Rev. Sci. Instrum. **91**, 063101 (2020); <https://doi.org/10.1063/5.0006721>

Submitted: 11 March 2020 . Accepted: 08 May 2020 . Published Online: 01 June 2020

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Submitted: 11 March 2020 • Accepted: 8 May 2020 •

Published Online: 1 June 2020

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ABSTRACT

Technologically relevant gas phase processes rely on reactants in vapor form for the production of thin films and nanoparticles. An instrument is described which enables the investigation of such vapors by x-ray absorption spectroscopy. Corresponding *in situ* studies provide information about gas phase precursor chemistry and optimized synthesis processes. The setup consists of a sealed vapor container heated by a hot air bath. Inert gas filling and temperature monitoring are implemented. Fluid dynamic simulations reveal a homogeneous temperature distribution without hot or cold spots. Temperature stability better than 1 K for at least 190 min allows time-dependent measurements or improved signal to noise ratios by averaging of datasets. Iron acetylacetonate is studied as a model system. X-ray absorption spectra measured by fluorescence are of high quality, allowing a detailed analysis of X-ray Absorption Near Edge Structure (XANES) and extended x-ray absorption fine structure. A molecular structure transformation is observed in XANES spectra of iron acetylacetonate vapor above 480 K probably due to the loss of one ligand. The setup allows the investigation of low volatility compounds with vapor pressures above 2 kPa at temperatures up to 520 K.

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I. INTRODUCTION

In processes such as chemical vapor deposition (CVD) where films are produced, and chemical vapor synthesis (CVS) where nanoparticles are generated, reactants need to be evaporated before using them as precursor materials. For most metals, only compounds of low volatility are available such as β -diketonates, for example metal acetylacetonates, which are solid under ambient conditions.¹ Therefore, sublimation is an important unit operation in CVD and CVS processes. Understanding film and particle formation in the gas phase requires the study of the initial state of the precursor, i.e., in the form of a vapor. The present study reports the design of a corresponding vapor cell for X-ray Absorption Spectroscopy (XAS) investigations. This system also allows the assessment of *in situ*/in operando studies of the gas phase in CVD and CVS processes itself as the number density of atoms is conserved.

In the present study, we use iron acetylacetonate $[\text{Fe}(\text{acac})_3]$, $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$, tris(acetylacetonato)iron(III)] as the model system. It is a solid precursor used to generate iron containing thin films

in CVD² and nanoparticles in CVS.³ Mass spectrometric studies of precursor pyrolysis⁴ and thermogravimetric analysis (TGA)^{5,6} provide information about the decomposition of the precursor at elevated temperatures. However, little is known about the local and electronic structure of the $\text{Fe}(\text{acac})_3$ vapor.

XAS contains information about the local and electronic structure around the corresponding absorber atom, X-ray Absorption Near Edge Structure (XANES) spectra about electronic structure and site symmetry, and Extended X-ray Absorption Fine Structure (EXAFS) spectra about the local structure as described by partial pair distribution functions, essentially coordination numbers, coordination distances, and displacement factors.⁷

Most XAS experiments are performed in transmission with samples of optimized absorption. For samples of low number density of the absorber atoms such as vapors, the transmission mode provides an insufficient signal-to-noise ratio. For instance, solid $\text{Fe}(\text{acac})_3$ has a number density of iron atoms of $8.9 \times 10^{26} \text{ m}^{-3}$. In the gas phase at 450 K, when $\text{Fe}(\text{acac})_3$ is evaporated in an inert atmosphere at 101 kPa pressure, the number density of absorption

atoms decreases to $4 \times 10^{23} \text{ m}^{-3}$. However, fluorescence detection may be used and offers sufficient data quality.

XAS of gaseous species has been measured previously, for example cadmium metal vapor in a quartz cell.⁸ However, only a few investigations of molecular species in the gas phase with hard x rays exist, among them is the seminal work of Kincaid and Eisenberger on Br_2 and GeCl_4 ,⁹ where Br_2 and GeCl_4 are filled in a low-pressure cell analogously to ionization chambers. The high volatility of these compounds enables measurements of gaseous molecular species in transmission. $\text{Fe}(\text{acac})_3$ has been investigated as a solid under ambient conditions by XANES as a precatalyst¹⁰ and EXAFS as a catalyst.¹¹

Here, we present the design of a cell for *in situ* investigation of vapors of low volatility compounds with x-ray absorption spectroscopy in fluorescence mode at elevated temperatures. The geometry of the vapor container of the cell is comparable to the typical CVS lab-reactors.

II. THE XAS EXPERIMENT

As mentioned above, solid samples have to be optimized for the measurement in transmission in order to get an edge step of $\Delta\mu \cdot x < 1.5$.⁷ For solid $\text{Fe}(\text{acac})_3$, the corresponding attenuation length is about $27 \text{ }\mu\text{m}$. For $\text{Fe}(\text{acac})_3$ vapor at 450 K with a partial vapor pressure of 2.5 kPa at 101 kPa, it is about 2 m, a result of the low density of absorber atoms in the gas phase. The vapor pressure is computed according to the Clausius–Clapeyron equation with parameters given by Fahlman and Barron¹² and is shown in Fig. 1 together with the number density of iron atoms in the vapor at corresponding temperatures. An optimized edge step for a vapor sample in the transmission mode can be obtained either by very large vapor containers, which is technically not feasible, or at high temperatures in the case of $\text{Fe}(\text{acac})_3$. However, the decomposition of $\text{Fe}(\text{acac})_3$ starts already at 468 K, and at temperatures higher than

FIG. 1. Vapor pressure of iron acetylacetonate and the resulting number density of iron atoms. The green field marks the parameter window used in the experiments described.

FIG. 2. Experimental beamline setup with *in situ* vapor cell, x-ray beam, ionization chambers, and fluorescence detector with corresponding intensities $I_{0,t,\text{ref},f}$.

505 K, precursor molecules lose one of the acetylacetonate ligands.⁵ As a result, low volatility compounds are not suitable for XAS studies in transmission mode, and XAS using a fluorescence detector is needed.

XAS measurements at the iron K-edge (7112 eV) are performed using two different fluorescence detectors. At the P65 beamline, PETRA III, Deutsches Elektronen Synchrotron (DESY, Germany), a Si-Passivated Implanted Planar Silicon (Si-PIPS) single channel detector is used. At the I20-spectroscopy beamline, the Diamond Light Source (DLS, United Kingdom), a Ge-fluorescence detector¹³ with 64 channels is used. The experimental setup according to Fig. 2 is used at both beamlines. A detailed scheme of the cell is presented in Sec. III.

A series of XAS measurements of the $\text{Fe}(\text{acac})_3$ vapor is simultaneously performed in transmission and fluorescence detection to allow internal energy calibration of the collected data using an iron metal foil as the reference.

The energy resolution at the iron absorption edge of the I20 beamline can be estimated to be 0.92 eV and that of the P65 to be 0.99 eV based on the beamline optics. Figure 3 displays the setup at the I20 beamline at the Diamond Light Source, where the vapor cell is installed between the I_0 and I_1 ionization chambers and the fluorescence detector. The cell is mounted on an aluminum block with gas outlet for a stable installation on a positioning stage for horizontal and vertical movements.

All experiments are performed with $\text{Fe}(\text{acac})_3$ for synthesis (Merck, >99%). Additionally, pellets and dispersions of $\text{Fe}(\text{acac})_3$ in

FIG. 3. Setup at the I20 beamline at the DLS. The *in situ* vapor cell is placed in the center; to the right, the fluorescence detector with its large acceptance angle can be seen.

acetone (5 mg/ml), isopropanol (4.6 mg/ml), and water (4.6 mg/ml) are measured for comparison. In the case of the precursor in the pellet form, starch is used as the diluting agent for optimized transmission and improved mechanical stability during uniaxial pressing and further handling. All dispersions are ultrasonicated and measured in fluorescence, while the pellet is measured in transmission. The ionization chambers are filled with a mixture of argon and helium to optimize the signal-to-noise ratio.

III. THE CELL DESIGN

The aim of the constructed cell is to provide a container for vapors of substances with low vapor pressure under ambient conditions, but sufficient vapor pressure at elevated temperatures suitable for *in situ* XAS measurements. The maximum long-term operating temperature of about 520 K is in a range typical for precursor vapors for CVD and CVS and is limited due to the materials used for construction and sealing, especially polyimide (Kapton®) for x-ray transparent windows and fluoroelastomer (Viton®) O-rings for sealing individual parts. Additionally, the use of any material containing elements with x-ray absorption edges close to the investigated energy region has to be avoided to minimize the disturbing fluorescence radiation by the materials in the housing. Consequently, all solid parts of the cell are made from electrolytic aluminum of high purity. The cell design is based on two concentric cylinders, in the following called the outer and inner chambers (Fig. 4).

The outer chamber provides a scaffold to clamp the inner chamber, a heat bath, and protection against leakage of the vapor. The outer chamber contains and guides the heating gas from the source to the outlet, which is connected to an exhaust at the beamline. The use of a hot gas (air) as heat bath minimizes the absorption of x rays. It may be further reduced using helium.

The outer chamber contains a larger window, which allows the exchange of the inner chamber through the opening. The window of the outer chamber is sealed using a polyimide (Kapton HN) adhesive tape with a thickness of 25 μm . Ambient air is heated and blown into the cell by a heat gun (GHG 660 LCD, Bosch). Temperature and flow profiles are simulated using computational fluid dynamics (CFD) with ANSYS® Fluent 17.0 as shown in Fig. 5 (left). Figure 5 (right) displays the temperature profile along the inner chamber at the dashed line in Fig. 5 (left). A flow of hot air of 375 l/min is chosen for fast, controllable heating rates and stable temperature profiles as observed in experiments and simulations. The temperature of the outer cell is measured during heating as well as the temperature of

FIG. 5. CFD simulation of the temperature distribution of hot air (at ambient pressure and a volume flow of 375 l/min) between the inner and outer chamber (left), temperature profile along the gray dashed line (right). The position of the thermocouple is marked with X at the inlet of the cell.

the heating gas. The results are used as boundary conditions in the CFD simulations. The heating gas temperature of the simulation is adjusted to 473 K corresponding to the measured value. The position of the thermocouple at the inlet for the measurement is marked in Fig. 5.

Hot air flow from the top heats the inner chamber from the outside and leads to a homogeneous temperature profile in the cell. The main heat loss is through the surface of the outer chamber and the hot air outlet. However, these do not affect the temperature profile of the inner chamber. The simulated temperature profile inside the outer chamber indicates the absence of cold or hot spots. The temperature difference between the upper and lower parts and the walls and the center of the inner cell prohibits condensation at the windows and the top since the upper part is steadily hotter than the precursor reservoir at the bottom. This is a major advantage of this heating geometry.

The inner chamber functions as a container for the precursor and as a reservoir for the precursor vapor generated. The position of the inner chamber is fixed relative to the outer chamber by two

FIG. 4. Schematic drawing of the cross section of the cell: side-view (left), front-view (center), and top-view (right). The x rays are marked as violet arrows, the solid precursor to be evaporated as the orange field.

tubes attached to the outer chamber using a sealed tube screw connection. The seals are gas tight. The tubes serve also as the gas inlet and outlet for the inner chamber. They are used to flood the inner chamber with inert gas (nitrogen or helium) prior to each heating procedure and to avoid overpressure caused by evaporation of the precursor species or volume expansion due to heating. Additionally, a thermocouple is inserted into the lower part of the tube for *in situ* temperature measurements of the $\text{Fe}(\text{acac})_3$ vapor during the experiments directly above the surface of the solid precursor powder (Fig. 4).

The inner chamber has an O-ring sealed detachable cup as the reservoir for the solid precursor powder. The $\text{Fe}(\text{acac})_3$ powder is placed in the cup at the bottom of the cell. Batches can be exchanged fast by replacing the cup and flushing the inner chamber with inert gas, making an efficient use of the beam time.

Analogous to the outer chamber, the inner chamber also has three windows for incoming, transmitted, and fluorescent x rays. It is sealed gas tight in order to avoid the contamination of the outer chamber and the environment with precursor vapor. The window material of the inner chamber is polyimide-foil (Kapton HN) with a thickness of 25 μm . Sealing of polyimide is ensured by an epoxy resin (DURALCO® 4480) or by using an adhesive tape. For all windows, polyimide is the material of choice due to its high x-ray transmittance and sufficient temperature resistance up to 680 K.

Connections between single parts (exhaust and inlet tubes, precursor cup, inner chamber) are sealed with fluoroelastomer (Viton) O-rings. Therefore, the maximum temperature limit of the cell is about 520 K. This limitation can be lifted using seal materials of higher thermal stability such as Kalrez® or metal gaskets.

IV. EXPERIMENTAL RESULTS

With the setup described above, vapors in a temperature range between 450 K and 490 K are studied. The lower temperature limit is a result of the low vapor pressure of $\text{Fe}(\text{acac})_3$ (compare Fig. 1) at which even the fluorescent signal is too low to obtain data of a sufficient signal-to-noise ratio. The upper limit is due to the decomposition of $\text{Fe}(\text{acac})_3$. XAS data reduction and analysis is performed using empirical line shape functions implemented in the XAFS X code.¹⁴ The edge energies (E_0) are determined by first analyzing the reference spectrum and calibrating the energy scale according to tabulated values for the Fe–K-edge.¹⁵ The edge energies of the sample spectra are determined by fitting the edge and XANES data with an empirical step function, a linear combination of arctangent- and error-function (fit parameters: edge energy E_0 , edge width, and fraction of arctangent) to describe the absorption edge for the Fe–K spectra, and, additionally, with a pseudo-Voigt function (fit parameters: energy position E , width, and fraction of Lorentzian) for the white line.

XANES spectra of the $\text{Fe}(\text{acac})_3$ vapor, as a solid and in isopropanol and acetone, are quite similar in contrast to $\text{Fe}(\text{acac})_3$ in water, where the absorption is clearly shifted and other spectral features change dramatically, especially visible at the prominent white line at about 7125 eV. This is probably due to a decomposition reaction upon dissolving $\text{Fe}(\text{acac})_3$ in water.¹⁶ The Fe–K-edge spectra of $\text{Fe}(\text{acac})_3$ as vapor, in liquid solution, and as pellets between 7100 eV and 7250 eV are displayed in Fig. 6 together

FIG. 6. XANES spectra of $\text{Fe}(\text{acac})_3$ from XAS obtained using a single Si-detector (SC), a 64 multichannel Ge-detector (MC), dispersions in acetone, isopropanol, and water (all measured in fluorescent mode with the MC detector), and a solid $\text{Fe}(\text{acac})_3$ sample diluted in starch together with iron oxide (maghemite) and iron metal in transmission mode.

with the spectra of iron oxide (maghemite) and iron metal foil as standard.

The precursor vapor is measured at 450 K, and all other samples are measured under ambient conditions. One individual measurement takes about 20 min. A comparison of vapor measured using a single channel Si-detector and a multiple channel Ge-detector shows a clear difference in the quality of the data. By using the Si-detector, no data of sufficient quality could be obtained. In the following, we will limit the discussion of fluorescent measurements to data obtained using the Ge-detector.

The magnitude of the XAS fluorescence signal depends on temperature through the increasing density of the absorbing element with increasing vapor pressure of the precursor. Therefore, only those measurements where the measured deviation from the desired temperature is less than 1 K are included in the analysis within a series of measurements. For this reason, the high temperature stability of the cell is of great advantage. Figure 7 represents *in situ* measurements of the temperature obtained by a thermocouple with a read-out accuracy of 0.1 K inside the inner chamber. This temperature stability enables measuring times of more than 190 min. Therefore, the heating (equilibration) time of the cell before the measurement is adjusted to 15–40 min. Thus, the time needed to perform an experiment with loading the cell, setting up, heating up, and recording the data with sufficient quality can be estimated to 150 min.

Within one measurement series, all positions of the spectral features (pre-edge peak, white line, etc.) do not change as demonstrated in Fig. 8 for the case of 450 K. This high reproducibility of the spectra allows the averaging of data obtained during a series of experiments at constant temperature. Additionally, the signal-to-noise

FIG. 7. Cell temperatures during the experiment measured with an inserted thermocouple.

FIG. 9. XANES spectra of $\text{Fe}(\text{acac})_3$ vapor at different temperatures.

ratio can be further improved by inspecting and merging of only the best signals of the 64 individual channels of the Ge-fluorescence detector.

On an average, six measurements with signals from 55 individual channels are used to create a merged spectrum. Merged XANES spectra for the whole temperature range can be seen in Fig. 9. Conspicuous is that the white line at about 7132 eV becomes broader and the shoulder at about 7145 eV becomes less developed with increasing temperature. Results of the analysis of the E_0 are shown

FIG. 8. XANES spectra from individual measurements at a desired temperature of 450 K. Spectra are marked corresponding to the points in Fig. 7.

in Fig. 10, where the edge energy of the corresponding vapor sample is plotted against temperature. For comparison, the edge energies of solid $\text{Fe}(\text{acac})_3$ and solutions in isopropanol, acetone, and water (dashed lines in Fig. 10), as well as the edge energy of $\text{Fe}(\text{acac})_2$ as published by Gregori *et al.*¹⁷ (dotted line in Fig. 10) are added. The edge energy of the $\text{Fe}(\text{acac})_3$ vapor when measured at the lowest temperature at 450 K is about 7125 eV closer to the energies of $\text{Fe}(\text{acac})_3$ in acetone and isopropanol with 7125.5 eV than to the solid precursor with 7126.8 eV, respectively. With rising temperature of the cell, the energy shifts toward smaller values. The shift is not large, but at

FIG. 10. The edge energies, E_0 , of analyzed samples: solid $\text{Fe}(\text{acac})_3$ —long dashed line, in fluids—short dashed lines, vapor—full line, and solid $\text{Fe}(\text{acac})_2$ from the data of Gregori *et al.*¹⁷—dotted line.

FIG. 11. k^3 weighted EXAFS of the Fe-K-edge of solid $\text{Fe}(\text{acac})_3$ (in pellet form and in isopropanol) and vapor at temperatures indicated.

higher temperatures, the tendency becomes significant with the edge energy shifting toward the value of $\text{Fe}(\text{acac})_2$ at 7123.1 eV. This may be explained by the decomposition of the $\text{Fe}(\text{acac})_3$ species, especially by taking into account that a partial decomposition becomes more probable with increasing temperature. The shift of the edge energy toward lower values with decreasing oxidation state of the metal is already observed in metal organics by Kirby *et al.*¹⁸ This

FIG. 12. Magnitude of the phase corrected Fourier transform of the spectra displayed in Fig. 11.

suggests that due to the decomposition of $\text{Fe}(\text{acac})_3$, iron is reduced from an oxidation state of 3+ to 2+ as in $\text{Fe}(\text{acac})_2$ due to the loss of one acetylacetonate ligand.

In order to verify the suitability of the EXAFS data obtained using the fluorescence detector for further analysis, the data are displayed in Fig. 11. The data obtained from the vapor in the range above $k = 8 \text{ \AA}^{-1}$ becomes increasingly noisy in comparison to the data from the pellet and dispersion, especially above k of $12 \text{ \AA}^{-1}$. The corresponding phase corrected Fourier transforms of the obtained EXAFS spectra are shown in Fig. 12. The first peak between 1.96 Å and 2.04 Å corresponds to the iron oxygen bond in $\text{Fe}(\text{acac})_3$ close to 1.99 Å observed by Schoch *et al.*¹⁰ The second peak between 2.86 Å and 3.03 Å corresponds to the iron carbon correlation as also found by Schoch *et al.*¹⁰ in solid $\text{Fe}(\text{acac})_3$ at 2.93 Å. This peak differs in shape and position for vapor samples in comparison to the solid compound. The second peak changes little in the case of vapors at 450 K and 470 K in contrast to vapor at 490 K. This indicates that the molecule undergoes local structural changes with increasing temperature and shows that these can be detected with the help of the setup presented. A further detailed analysis of the EXAFS region and the local structure of iron in $\text{Fe}(\text{acac})_3$ will be the subject of another study.

V. CONCLUSION

We present an enabling tool for x-ray absorption spectroscopy of low volatility compound vapors in transmission and fluorescence mode. Correspondingly, CVD and CVS precursors and other materials of similar evaporation behavior can be sublimed and studied *in situ* in a temperature range from the ambient 300 K to elevated temperatures of up to 520 K or even higher, with modifications proposed in Sec. III. This opens a new window for the investigation of decomposition and reaction mechanisms in related processes. The sealed chambers of the cell also enable the study of vapors in desired atmospheres (reducing, inert, or oxidizing) beneficial for the investigation of the precursor chemistry. The long-term pressure and temperature stability of the setup allows the superpositioning of multiple datasets. The quality of the XANES and EXAFS data makes it possible to reveal changes in the local and electronic structure of the molecule investigated as a function of temperature. The observed shift in the energy of the absorption edge can be explained by a partial decomposition of $\text{Fe}(\text{acac})_3$ at elevated temperatures.

ACKNOWLEDGMENTS

We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities under Proposal No. I-20170647. Parts of this research were carried out at PETRA III, and we would like to thank E. Welter and M. Herrmann for assistance at the P65 beamline. We acknowledge the Diamond Light Source for time at beamline I20 under Proposal No. 19229 and the support of F. Mosselmans and S. Hayama. We acknowledge the German Research Foundation (DFG) for funding through research unit FOR 2284 “Model-based scalable gas-phase synthesis of complex nanoparticles” (Project No. WI-981/14).

DATA AVAILABILITY

Raw data for the article were generated at previously mentioned synchrotron radiation facilities. Derived data supporting the findings of this study are available from the corresponding author upon reasonable request.

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