

Thin Film Deposition and Photodissociation Mechanisms for Lanthanide Oxide Production from Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)-Ln(III) in Laser-Assisted MOCVD

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Photoionization mass spectrometry reveals details of the multistep unimolecular mechanism, whereby the 2,2,6,6-tetramethyl-3,5-heptanedionato (thd⁻) anionic ligand decomposes, while still bound in the metal complex, to yield a gas-phase metal oxide product in metal-organic chemical vapor deposition (MOCVD) of lanthanide oxides from Ln(thd)₃ precursors. The decomposition occurs with stepwise elimination of small closed-shell hydrocarbon fragments and carbon monoxide up to a penultimate $Ln(OC_2H)$ ethyneoxide, from which both LnO (dominant) and LnC₂ (minor) products are derived. Formation of the metal oxide and carbide occurs in competition with a previously described mechanism¹⁻³ wherein sequential dissociation of ligand radicals produces the reduced metal Ln⁰. Evidence for gas-phase formation of a Ln₂(thd)₆ dimer as a result of expansioncooling in the precursor source assembly is also given. Laser-assisted MOCVD of Eu(thd)₃ on silica, with subsequent exposure to atmosphere, produces amorphous Eu_2O_3 with small areas of crystallinity attributed to reaction of the oxide with atmospheric carbon dioxide and water.

Introduction

High-quality thin films of metal oxides with useful dielectric,⁴ semiconducting,⁵ insulating,⁶ antiferromagnetic,⁷ catalytic,⁸ and corrosion resistance⁹ properties have been prepared using laser-assisted metal-organic chemical vapor deposition (L-MOCVD or LCVD). Depending on the geometry of the deposition process, photolytic activation of the precursor may occur in the gas-phase, just above the surface of the substrate or, when the laser impinges directly on the substrate, decomposition may proceed from precursor molecules adsorbed at the surface. In the former case, deposition occurs without direct substrate heating and unintended modification of the growing film or underlying substrate. The latter case allows greater spatial control in the deposition but can result

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in elevated temperatures, particularly if the substrate or growing film absorb at the photolysis wavelength.

In general, preparation of oxide films requires the presence of a coprecursor or subsequent exposure to an oxidizing atmosphere.¹⁰ In a recent series of studies on β -diketonate complexes, the gas-phase photolytic mechanisms, which lead to production of reduced metal,^{1-3,11,12} and the mechanisms that lead to carbide³ and fluoride¹³ contamination in deposited films were examined. It was also noted that photolysis of the common lanthanide oxide precursor, tris(2,2,6,6,-tetramethyl-3,5-heptanedionato)-Ln(III), or Ln(thd)₃, resulted in significant formation of gas-phase LnO in addition to the reduced metal, $Ln^{0.1-3}$ Formation of the reduced metal was attributed to three sequential ligand-to-metal charge-transfer (LMCT) steps, wherein the anionic ligand reduced the metal and was itself ejected intact from the complex as a neutral thd radical. Formation of the oxide was hypothesized to result from a competing unimolecular reaction, but the mechanism was unclear.

Parallels exist in the metal-organic chemistry of the transition elements. Unimolecular gas phase formation of vanadium oxide, VO^+ from $O=V(OCH_3)_3^+$ has been reported^{14,15} and aerosolized ZnO nanoparticles have been created with

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gas-phase sintering from $[CH_3Zn(OCH(CH_3)_2)]_4$.¹⁶ In the former case, the methoxyl fragments are thought to be ejected intact or lost as formaldehyde with hydrogen migration. In the latter case, formation of ZnO in inert atmosphere requires breaking the carbon–oxygen bond in the *iso*-propoxide and is thought to proceed through elimination of propene and methane from the central Zn₄O₄ core. It is this latter chemistry that may be expected to show the greatest similarity to formation of LnO from β -diketonates precursors.

In this work, photoionization time-of-flight mass spectrometry (PI-TOF-MS) reveals a detailed map of how fragmentation of the 2,2,6,6,-tetramethyl-3,5-heptanedionate ligand, while still bound to the partially reduced metal, can lead to production of the major LnO and minor LnC₂ products. This work provides an illustration of the power of PI-TOF-MS to reveal mechanistic details in a highly complex decomposition process. It is only through such detailed understanding of the fragmentation mechanisms that it will become possible to eventually engineer precursor molecules with desirable decomposition characteristics.

As an illustration of LCVD results, europium oxide films were prepared on fused silica using 532 nm photolysis and a $Eu(thd)_3$ precursor. The morphology and luminescence properties of the sparse coverage were investigated using atomic force microscopy, transmission electron microscopy, and confocal luminescence.

Experimental Section

Precursor Preparation. EuCl₃·6H₂O (99.9%) was purchased from GFS Chemicals. Tb(NO₃)₃·6H₂O (99.9%), Er(NO₃)₃· 6H₂O (99.9%), and Gd(NO₃)₃·6H₂O (99.9%) were purchased from Sigma-Aldrich. The ligand, 2,2,6,6-tetramethyl-3,5-heptanedione (Hthd, 98%) was purchased from Fluka. Resolved-Al Eu [(2,2,6,6-tetramethyl-3,5-heptanedionate) Europium, Eu(thd)₃] was purchased from Sigma-Aldrich. The other Ln(thd)₃ chelates were prepared according to the method of Eisentraut and Sievers.¹⁷ The chelates were purified by recrystallization from *n*-hexane. The crystal structure was found to be comprised of dimers, Ln₂(thd)₆ for Eu³⁺, Gd³⁺, and Tb³⁺ and of monomers, Er(thd)₃ in the case of erbium, consistent with the literature.¹⁸

Time of Flight (TOF) Mass Spectroscopy. The experimental design for the laser photoionization time-of flight mass spectrometer has been described in a previous publication.¹³ Briefly, the molecular source is provided by the metal–organic precursor seeded in He gas. The He and precursor mixture is introduced into the ionization region through a General Valve series 9 high-speed solenoid valve (0.5 mm orifice) with ~200 μ s pulses at 10 Hz and a variable He backing pressure of 30–100 kPa (absolute). The molecular-beam source assembly, which includes a reservoir of solid precursor, is heated to approximately 150 °C. The ionization region for the mass spectrometer is

centered in a six-way stainless steel cross with 8-in. flanges evacuated through the bottom flange by a 6-in. diffusion pump, fitted with a liquid- N_2 baffle to reduce pump oil in the chamber. Repeller, extraction, and accelerator plate voltages in the vertically aligned lens stack are set to 3 kV, 2 kV, and 0 V respectively. Four horizontal steering plates, located just above the ion source and lens stack, are adjusted between 100 V and -100 V to optimize ion signal. The 1-m long flight tube extends vertically from the top of the chamber. At the top of the flight tube is a 40 mm microchannel triple-plate detector assembly. The lens stack, flight-tube, and detector were purchased from Jordan TOF Products, Inc. The detector current is measured using a Tektronix TDS2022 200-MHz dual-channel digital oscilloscope using 50 or 300 Ω termination. The flight tube is additionally pumped using a Varian V300HT 6-in. air-cooled turbomolecular pump. The molecular source, as described above, enters the ionization region in the horizontal plane between the repeller plate and extraction grid at 90° relative to the photoionization laser beam, which also lies in the horizontal plane. The photoionization laser is a Continuum Surelite II Nd:YAG operating at 266 nm, 355 nm, or 532 nm. Alternatively, the YAG laser pumps an optical parametric oscillator (Continuum SLOPO) that operates between 410 and 720 nm, which subsequently serves for photoionization. In both cases, the laser is focused into the center of the ionization region using a 12-in focal length, fused silica lens.

Laser-Induced Thin Film Deposition. Films of lanthanide oxides were grown from the Ln(thd)₃ precursors using laserassisted MOCVD (LCVD). LCVD was carried out at a precursor pressure of ~1 Torr using a Continuum Surelite II Nd: YAG laser as the excitation source, operating at 532 nm, 10 Hz, and 200 mJ/ pulse. The lanthanide precursor was heated in a crucible, located in the center of a 2.5 in. stainless steel tube, whose ends were sealed with quartz windows for optical access. The tube was also provided with a vacuum port to remove atmospheric oxygen and water before the deposition process. This simple apparatus served as the static deposition chamber. The quartz, glass or silicon substrates for deposition were cleaned in Piranha solution for 0.5 h, rinsed in nanopure water, dried, and placed adjacent to the crucible along the optical axis of the tube. The tube was wrapped with heating tape, pre-evacuated down to 10 mTorr at room temperature, and placed in the center of a second vacuum chamber, devised from a 6 in. six-way stainless steel cross. This second chamber was also evacuated to 10 mTorr prior to the deposition, providing thermal insulation and protection of the heating tape from oxygen. The entire deposition (inner) chamber was heated to 150 °C. The precursor was allowed to sublime and photodissociation was accomplished by an unfocused, pulsed laser beam passing through the center of the deposition tube (532 nm and 200 mJ/cm² @ 10 Hz). Typical deposition time was about 2 h, after which the tube was cooled to room temperature. The prepared film was subsequently heat treated (145 °C) under vacuum overnight to remove residual precursor.

Characterization of Deposits. Morphology of the lanthanide oxide deposits was measured on a Nano-R² atomic force microscope (Pacific Nanotechnology Inc. Santa Clara, CA) using noncontact mode under ambient conditions. Transmission electron microscopy (TEM) studies of deposits on a copper grid were made with a TF20 S-Twin from FEI (200 kV). Spatially resolved luminescence was obtained using an Aramis confocal microscope (Horiba Jobin Yvon, Edison, NJ) equipped with a diodepumped solid-state (DPSS) laser for 532 nm excitation. Spatially resolved images were created using emission intensity collected

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Figure 1. PI-TOF mass spectrum of $Eu(thd)_3$ with photolysis at 410 nm and 30 mJ/pulse (500 MW/cm²), sublimation at 150 °C, and He backing pressure of 40 kPa. The spectrum shows evidence of dimer, $Eu_2(thd)_6$, formation and provides evidence for the mechanisms for formation of the Eu and EuO photolysis products.

at 610 ± 10 nm, derived from the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺. However, the full emission spectrum was recorded at every point. Accompanying white-light optical micrographs were also recorded.

Results and Discussion

Gas Phase Ln₂(thd)₆ Dimer Formation. The photoionization mass spectrum of Eu(thd)₃, which is known to sublime predominantly as the monomer at high temperatures, ¹⁹ shows significant signal for the dimer $Eu_2(thd)_6^+$ under the moderate-pressure expansion conditions of our experiment. Figure 1 shows the PI-TOF mass spectrum using 410 nm photoionization and low fluence. Also observed are $Eu_2(thd)_5^+$ and $Eu(thd)_4H^+$ fragments, which are thought to arise from fragmentation of the parent dimer. The observed $Eu(thd)_3^+$ species likely arises from a combination of as-sublimed gas-phase Eu(thd)₃ and $Eu_2(thd)_6$ fragmentation. $Tb_2(thd)_6^+$ and $Tb_2(thd)_5^+$ had been previously reported under similar experimental conditions³ and were confirmed in this work as illustrated in Figure 2. New features, $Tb(thd)_4H^+$ and $[Tb(thd)_3 (CH_3)_3CC(O)CH_3]^+$, are also seen in Figure 2.

Under conditions of higher laser fluence and over a wide range of wavelengths, the dominant photoionization products are Ln⁺ and LnO⁺ which are also observed with moderate intensity in the low mass range of Figure 1. It should be noted that the experimental conditions that allow optimal and simultaneous observation of both the high-mass, $Ln_2(thd)_6^+$ dimer and the low-mass, Ln^+ are difficult to achieve with the current experimental design. The molecular source, seeded in He carrier gas, enters the vacuum chamber in the horizontal plane, perpendicular to the vertical flight tube of the mass spectrometer. Expansion of the gas through the small-orifice nozzle induces a narrow distribution of speeds, with a high linear velocity approaching that of the carrier gas. Thus the massive dimer has considerable forward momentum and requires a 100-200 V "stopping voltage" on the horizontal steering plates to prevent its missing the 40 mm detector after its relatively



Figure 2. PI-TOF mass spectrum of $Tb(thd)_3$ with photolysis at 410 nm and 30 mJ/pulse (500 MW/cm²), sublimation at 150 °C, and He backing pressure of 40 kPa. Dimer $[Tb_2(thd)_6]$ formation is evident in the spectrum.



Figure 3. PI-TOF mass spectrum of Gd(thd)₃ with photolysis at 266 nm and 20 mJ/pulse (300 MW/cm²), sublimation at 150 °C, and a He backing pressure of 40 kPa (left panel) and He-backing-pressure dependence of the intensity ratio of Gd(thd)₄H⁺ and Gd(thd)₃⁺ features (right panel). The pressure dependence suggests that the dinuclear complex, from which Gd(thd)₄H⁺ derives, is formed as the gas cools in the expansion into the vacuum chamber.

slow (55 μ s) vertical assent through the time-of-flight tube. A voltage of this magnitude not only decelerates and stops the lighter Ln⁺ ion but, can also impart a velocity in the reverse horizontal direction, causing the Ln⁺ ions to miss the detector. Thus, in some spectra, where either the highmass or low-mass fragment are not observed, their absence may be attributed to selective optimization of steering plate conditions rather than to the absence of those species.

Evidence of dimer formation is also seen for Gd(thd)₃ with photoionization at 266 nm. In Figure 3, the fragments Gd₂(thd)₅⁺ and Gd(thd)₄H⁺, thought to arise from fragmentation of Gd₂(thd)₆, are clearly represented. The intensity of these, Gd₂(thd)₅⁺ and Gd(thd)₄H⁺ fragments, relative to Gd(thd)₃⁺, varies with He backing pressure, the former species being strongly represented at high backing pressures and absent at low backing pressures. This is illustrated in the right panel of Figure 3, where the ratio of Gd(thd)₄H⁺ to Gd(thd)₃⁺ signal intensity as a function of pressure is plotted. The results are consistent with the hypothesis that Gd(thd)₄H⁺ derives from Gd₂(thd)₆

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Scheme 1. Crystal Structure of the Eu₂(thd)₆ Dimer^a



^{*a*} Thermally stable in the absence of oxygen and water, the $Ln(thd)_3$ precursors sublime as a monomers with vapor pressures on the order of 0.1 Torr at 150 °C. Expansion cooling of the vapor results in formation of gas-phase dimers. In this scheme, the *t*-butyl groups are omitted to better illustrate the metal coordination.

which forms from condensation of $Gd(thd)_3$ as the gas cools in expansion. Increasing the He backing pressure does not increase the number of monomer-monomer collisions in the expansion, but instead, lowers the temperature of the gas and makes it more likely that monomer collisions will result in formation of a dimer. This is the same expansion-cooling strategy that is employed to form weakly bound van der Waals complexes like OH-Ar.²⁰ However in the present case, the [Ln(thd)₃]₂ collision complex can easily rearrange to a bridged dimer $Ln_2(thd)_6$. The dimer structure, as shown in Scheme 1, involves two shared bridging oxygens. No bonds are broken in rearrangement to the dimer so the activation energy is expected to be quite low. Nevertheless, the stabilization achieved by the two newly formed Ln-O bonds can be quite significant. The hypothesis that the bridged structure is formed in the gas phase is supported by the robust nature of the metal pairing which is retained in the fragmentation to form $Ln_2(thd)_5$. As illustrated in Figure 4, evidence of dimer formation is also observed for $Er(thd)_3$ despite the fact that in the crystal structure, Er(thd)₃ exists as a monomer, unlike the bridged-dimer structures reported for the larger cations, Eu^{3+} , Gd^{3+} , and Tb^{3+} .^{21,22} Whether the dimer formation and subsequent fragmentation has any significant impact on the final photoproducts, predominantly Ln, LnO, and trace LnC_2 , is unclear (vide infra), but the mechanism for fragmentation from molecular beam sources should acknowledge the dimer as a potential starting point.

Postionization Fragmentation and Post-dissociation Ionization. We had previously hypothesized that Ln^+ was formed in the photofragmentation of $Ln(thd)_3$, (using the monomer as a starting point) in three sequential steps, in each of which the metal was reduced and the intact ligand



Figure 4. PI-TOF mass spectra of Gd(thd)₃, Tb(thd)₃, and Er(thd)₃ with photolysis at 266 nm and 20 mJ/pulse (300 MW/cm²), sublimation at 150 °C, and He backing pressure of 40 kPa. For these three species, extensive cracking of the ligand is seen to begin after dissociation of the first ligand, forming Ln(thd)₂, near m/z = 525. This stands in contrast to Eu(thd)₃ fragmentation, for which Eu(thd)₂ dissociates cleanly to Eu(thd), only after which the ligand begins to crack.

ejected. Each step was mediated via photoexcitation to a ligand-to-metal charge-transfer state. The observed $Ln(thd)_2^+$ and $Ln(thd)^+$ were hypothesized to arise from postdissociation photoionization of the neutral $Ln(thd)_2$ and Ln(thd) dissociation products. Likewise Ln^+ was hypothesized to arise from postdissociation photoionization of Ln^0 . This latter hypothesis was supported by the presence of a strong $Eu^{0.8}S_{7/2} \rightarrow {}^{8}P_{J}$ signature in the Eu^+ REMPI spectrum. This model is not contradicted by the current observation of the dimer except in recognition that some of the fragmentation clearly begins with $Ln_2(thd)_6$.

The feature located 57 mass units lower than $Ln(thd)_3^+$ was previously assigned to $[Ln(thd)_3-(tert-butyl)]^+$ or equivalently to $[Ln(thd)_2 (CH_3)_3C(O)CH=C=O]^+$. Note that this satellite does not appear on the low mass side of either Ln(thd)₂ or Ln(thd). It is likely that the satellite results from postionization fragmentation of the thd

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radical in $Ln(thd)_3^+$, which may be represented in more detail by $Ln^{3+}(thd^-)_2(thd)$. A thd radical, easily decomposes as in

$$(CH_3)_3CC(O)CHC(O)C(CH_3)_3$$

$$\rightarrow (CH_3)_3CC(O)CH=C=O+C(CH_3)_3$$

ejecting the relatively stable *tert*-butyl radical from the complex and leaving the closed-shell ketene bound to the metal. In contrast, for photoionization of $Ln(thd)_2$ and Ln(thd), the electron is most favorably removed from the metal, forming $Ln^{3+}(thd^{-})_2$ and $Ln^{2+}(thd^{-})$, respectively, the ionized species lacking the thd radical and not being subject to *tert*-butyl elimination.

The arguments for removal of the electron from the metal vs removal from the β -diketonate ligand are based on the relatively accessible second and third ionization energies (IE) for the lanthanides and the prohibitively large fourth IE as compared to the electron affinity of the β -diketone radical, thd. Also to be considered in the energy balance is the fact that removal of an electron from the metal increases the strength of the ionic metalligand bond, stabilizing the product, whereas removal of an electron from the β -diketonate anion creates a neutral ligand, weakens the metal-ligand bond, and destabilizes the product. In fact, in all cases, the IE favors removal of the electron from the ligand and the complex binding energy favors removal of the electron from the metal. Balancing these two factors provides a rule of thumb; the electron is likely to be removed from the metal up to a maximum oxidation state of +3, whereafter, it is more likely removed from the β -diketonate anion, initially forming a bound thd radical.

Using a similar analysis, the observed $Ln_2(thd)_5^+$ species would be best represented with the two metal ions in the +3 oxidation state and all five ligands as anions. However, $Ln_2(thd)_6^+$ and $Ln(thd)_4H^+$ would be expected to each contain one thd radical and might thus be subject to further radical chemistry. A feature representing loss of *tert*-butyl from the $Ln_2(thd)_6^+$ is not observed in Figure 1 or 2, but may be too weak to discern from the noise. Weak fragments do appear on the low mass side of $Ln(thd)_4H^+$, but neither of the features correspond to a 57 amu shift, consistent with loss of tert-butyl. There does appear a feature shifted to lower mass by 110 amu, consistently present for Eu, Tb, and Gd and this is tentatively assigned to $[Ln(thd)_3(CH_2(OH)CH_2CHO)]^+$. A second feature, consistently shifted by 84 amu to lower mass of $Ln(thd)_4H^+$, is tentatively assigned to $[Ln(thd)_3((CH_3)_3CC(O)CH_3)]^+$ or alternatively to [Ln(thd)₃((CH₃)₃CC(OH)CH₂)]⁺. It is not surprising perhaps that the chemistry for the more sterically crowded Ln(thd)₄H⁺ is different than the radical chemistry for $Ln(thd)_3^+$. In fact, Jiang et al.²³ invoked a similar steric factor as preventing tert-butyl elimination in the EI mass spectrum of products of the thermal decomposition of $Cr(thd)_3$, $Co(thd)_3$, and $Fe(thd)_3$ where the

small ionic radii of the metals causes crowding of the ligands. One might speculate that if t-butyl elimination from a ligand radical is sterically hindered in $Ln(thd)_4H^+$ (because the fragment that remains attached must straighten out in forming the ketene) an alternative chemistry, that releases the excess energy in the complex, could come from one of the anionic ligands along the lines of the path illustrated in Scheme 2 (vide infra), wherein small neutral fragments of ligand are ejected and the fragment that remains attached retains its compact steric profile.

Formation of the LnO⁺ Product. The postionization radical-rearrangement chemistry described in the previous section is quite important in interpreting the mass spectrum, but that fragmentation chemistry is most likely a result of the measurement technique (ionization for mass spectral detection) and is perhaps not a direct contributor to either the thermal or photochemistry that leads from Ln(thd)₃ or Ln₂(thd)₆ to the major Ln and LnO products. However, these latter processes, identified as leading to Ln and LnO, as well as to minor LnC₂, also leave their signature in the mass spectrum.

In the earlier work¹⁻³ it was proposed that the LnO⁺ was formed in a reaction which competes with Ln⁰ production, which latter reaction occurs through LMCT-mediated dissociation of intact thd ligands. In contrast LnO was thought to derive from some cracking process of the bound ligands. It is interesting to note that although LnO⁺ shows a comparable intensity to Ln⁺ in the photoionization mass spectrum, the LnO⁺ feature is entirely absent in the electron ionization (70 eV) mass spectrum of Ln(thd)₃.

In Figure 1 it appears that, for Eu(thd)₃, dissociation of the ligands is fairly clean (excepting a few postionization daughter fragments) until Eu(thd). However, between $Eu(thd)^+$ and EuO^+ there is significant structure in the mass spectrum. That region of the spectrum is shown in expanded form and under optimized conditions in Figure 5. The two isotopes of europium, ¹⁵¹Eu and ¹⁵³Eu, are evident in the spectrum. An analogous chemistry appears to be captured for $Gd(thd)_3$, $Tb(thd)_3$, and $Er(thd)_3$ in Figure 4, but, in those cases, the ligand cracking starts earlier in the dissociation, the spectrum showing fine structure between $Ln(thd)_2^+$ and LnO^+ . Figure 6 shows a comparison for the fine structure in $Eu(thd)_3$, $Gd(thd)_3$, $Tb(thd)_3$, and $Er(thd)_3$ on the low-mass side of $Ln(thd)^+$. The mass of the metal (as an isotopic average) is subtracted from the total fragment mass in order to align fragments with the same organic component. For example, the feature labeled as "8" in Figures 5 and 6 is assigned to Ln[(CH₃)₃CC(O)CHC(O)C(CH₃)=CH₂]⁺ which is formed by loss of CH₄ from Ln(thd) or from $Ln(thd)^+$. In Figure 5, feature 8 falls on the coordinate axis as an isotopic doublet at m/z = 318 and 320 for $Eu[(CH_3)_3CC(O)CHC(O)C(CH_3)=CH_2]^+$. In Figure 6, where the metal mass is subtracted, the feature falls with a center at m/z = 167 for all four metals. The feature assigned to $Ln(thd)^+$, which had previously been observed as strong for Eu(thd)₃ and weak for Gd(thd)₃ and Tb(thd)₃, falls at m/z = 183 in Figure 6, representing the mass of the intact thd⁻ ligand.

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^{*a*} The process begins (top left center) with the Eu(thd) complex eliminating either methane (left arrow) or isobutene (right arrow). The numbering scheme refers to the order in which the features appear in the mass spectrum.



Figure 5. PI-TOF mass spectrum of $Eu(thd)_3$ with photolysis at 266 nm and 20 mJ/pulse (300 MW/cm²), sublimation at 150 °C, and He backing pressure of 40 kPa. This expanded region of the mass spectrum illustrates how the thd⁻, dionate ligand cracks in the Eu(thd) complex to yield the EuO product.

The chemistry yielding the fragments falling between the Eu(thd)⁺ and EuO⁺ is hypothesized to begin with the β -diketonate anion rather than with the radical as is illustrated in Scheme 2. Note for example, that feature **5** represents the loss of 56 rather than the 57 mass units which latter value is typical of *tert*-butyl loss in the radical rearrangements. In Scheme 2, in order to produce fragment **5**, the anionic ligand rearranges with a hydrogen migration, replacing the *tert*-butyl group with a hydrogen and eliminating the closed-shell isobutene, CH₂=C(CH₃)₂. Analogous isobutene elimination has been previously observed in the



Figure 6. PI-TOF mass spectra of $Eu(thd)_3$, $Gd(thd)_3$, $Tb(thd)_3$, and $Er(thd)_3$ with photolysis at 266 nm and 20 mJ/pulse (300 MW/cm²), sublimation at 150 °C, and He backing pressure of 40 kPa. The isotopic average of the metal mass is subtracted from the ordinate to illustrate the similarity in the fragmentation pattern of the ligand.

thermal decomposition of *tert*-butyl acetyl acetonate on $Si(100)^{24}$ as well as from Hthd on $Si(100)^{.25}$

In an alternate path illustrated in Scheme 2, Eu(thd) can eliminate CH_4 , as mentioned previously, to produce feature 8. In fact, all of the steps leading to the proposed penultimate Eu(OCCH) may be achieved with elimination of stable molecular fragments and most with simple

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Figure 7. PI-TOF mass spectra of $Gd(thd)_3$, $Tb(thd)_3$, and $Er(thd)_3$ with photolysis at 266 nm and 20 mJ/pulse (300 MW/cm²), sublimation at 150 °C, and He backing pressure of 40 kPa. The isotopic average of the metal mass is subtracted from the ordinate to illustrate the similarity in the fragmentation pattern of the ligand. Cracking of the ligand anion is seen to begin after dissociation of the first ligand for these three species.

carbon-carbon bond breaking and hydrogen migration. Exceptions to this simplicity include the step from fragment 2 to the fragment at m/z = 206 and 208 identified as $Eu(OCH=C=CH_2)$, whose formation, with loss of ethene, C₂H₄ appears to require a 1,2-elimination reaction, and the steps from fragments 8 and 3, where ethane elimination from the tert-butyl group requires a formal 1,1-elimination. The most complex rearrangement is in the step from 5 to 1b, where the latter is assigned as the europium complex of 3-hydroxypropanal. This step requires loss of the tert-butyl group coupled to reduction of the carbon-carbon double bond in the coordination ring. The eliminated C₄H₆ fragment, derived from the branched *tert*-butyl group is most likely linear, as no stable branched isomers of C4H6 are possible. However, a similar rearrangement has precedent, wherein isobutene, which would be the product of tert-butyl elimination without the reduction step, has been shown to convert to linear 1,3-butadiene under metal-catalyzed dehydrogenation.26

In Figure 4, it is clear that the ligand cracking for the Gd, Tb, and Er species begins at $Ln(thd)_2$, whereas for Eu, the fragmentation only appears on the low mass side of Eu(thd), as illustrated in Figures 1 and 5. The mass spectrum in Figure 7 illustrates a similar fragmentation pattern for the Gd, Tb, and Er species. The ligand cracking mechanism, in fact, appears to be similar for all four species. The numbered features in Figures 5, 6 and 7 are analogous. For example, feature 8 corresponds to $Ln[(CH_3)_3CC(O)CHC(O)C(CH_3)=CH_2]^+$ in Figures 5 and 6 and corresponds to $Ln(thd)[(CH_3)_3CC(O)CHC-(O)C(CH_3)=CH_2]^+$ in Figure 7 are features corresponding to $LnC_2(thd)$ and LnO(thd) which can be converted to the final LnO and LnC_2 products with loss of intact thd.

As suggested earlier, we have concluded from the fragmentation pattern that the ligand cracking begins with the thd⁻ anion and therefore not through a ligand-to-metal charge-transfer state. However, the oxidation

state of the metal is unclear. In the Eu case, the chemistry may result from a postionization fragmentation of $Eu(thd)^+$ or derive from fragmentation of the neutral Eu(thd), with subsequent ionization of the fragments, or both of these processes may occur in parallel. The answer may relate, if the metal is acting as a catalyst, to which electronic configuration is more effective, Eu²⁺:[Xe]4f⁷ in $Eu(thd)^+$ or Eu^+ : [Xe]5d¹4f⁷ in the neutral species, Eu(thd). For the Gd case the two options would be a starting point of Gd³⁺:[Xe]4f⁷ in the postionization fragmentation of cationic $Gd(thd)_2^+$ or, alternatively, a starting point of Gd^{2+} :[Xe]5d¹4f⁷ in the fragmentation of neutral Gd(thd)₂. The mechanism in Scheme 2 would predict different oxidation states for the products of fragmentation of $Ln(thd)^+$ vs the neutral, Ln(thd), yielding, for example, LnO⁺ in the former case and LnO in the latter. The presence of neutral LnO in the products can be determined with Resonance Enhanced Multiphoton Ionization (REMPI) and will be explored in future work.

Deposition of the Lanthanide Oxide. To examine the characteristics of films deposited from laser-assisted chemical vapor deposition using the Eu(thd)₃ precursor, sparse films on fused-silica slides were created in a static cell, using the 532 nm output of a Nd:YAG laser for activation. The deposition chamber was evacuated to $< 10 \,\mathrm{mTorr}$ during operation but the films were exposed to atmosphere immediately after cooling under vacuum. Figure 8 shows the AFM image of the deposition consisting of isolated micrometer-sized mounds on a background essentially free of deposition. SEM and TEM images both suggest a largely amorphous material with small regions of crystallinity. In Figure 9, a confocal luminescence microscope image ($\lambda_{ex} = 532 \text{ nm}$) shows that the mounds are brightly luminescent compared to an essentially dark, deposition free background. Dispersed emission from the same region of the slide is compared to the dispersed emission of a polycrystalline Eu2O3 standard. The broadened spectrum of the deposited material is consistent with largely amorphous Eu₂O₃. One might presume that the initial deposit was a mixture of Eu and EuO products evident from the mass spectrum and that subsequent exposure to atmospheric oxygen resulted in further oxidation.

For the TEM images, deposition was onto a copper grid rather than on silica. Most of the sample is amorphous consistent with the luminescence, but in isolated areas, clear fringes in the TEM images reveal lattice spacings which fall into three categories, with *d*-spacings of 4.27, 3.91, and 3.83 Å. Electron diffraction on the same sample reveals more than a dozen lattice spacings as given in Table 1. Errors in these measurements are $\pm 1\%$ or less. The three measured spacings are a poor match for cubic Eu₂O₃. However, the 3.83 Å spacing (3.82 Å from electron diffraction) is a good match for the $d_{012} = 3.82$ Å of hexagonal Eu₂O(CO₃)₂. The observed 4.27 Å is potentially a match (within the 1% error bars) for d = 4.24 Å in Eu₂O(CO₃)₂·H₂O. These carbonate species are likely products of reaction of Eu₂O₃ with atmospheric CO₂

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Figure 8. Atomic force microscopy of results from LCVD using a static deposition chamber, a Eu(thd)₃ precursor and 532 nm laser activation. Deposition on a fused silica substrate results in a sparse distribution of separate micrometer-sized mounds.

TEM





Figure 9. Confocal luminescence microscopy reveals that the deposited material contains luminescent Eu^{3+} . The left micrograph on the bottom provides an optical image of the LCVD deposits from the $Eu(thd)_3$ precursor. The right micrograph is the luminescence image of the same area. The two spectra in the top panel provide a comparison of microcrystalline Eu_2O_3 (top trace) and LCVD europium deposits (bottom trace).

and H_2O as has been previously documented.^{27,28} However, reaction of deposited carbide, EuC₂ with atmospheric oxygen might also be considered.

The spacing of 3.91 Å (3.89 Å from electron diffraction) is not characteristic of the hydrate, $Eu_2O(CO_3)_2 \cdot H_2O$, but no data exists at such low angles (large *d*-spacing) for

Table 1. Crystallographic *d*-Spacings from TEM Fringes and from Electron Diffraction (ED) of LCVD Products in This Work^{*a*}

	· · · · ·		
fringes	ED	XRD	material ^b
.27		4.24	Α
.91	3.89	3.87	\mathbf{C} (or \mathbf{B}^c)
.83	3.82	3.82	B
	3.50	3.54	Α
	3.21	3.23	В
	2.97	2.97	В
	2.77	2.78	D
	2.53	2.52	C and D
	2.45	2.45	Α
	2.38	2.38	A and C
	2.27	2.27, 2.28	D, A
	2.25	2.25	С
	2.23	2.23,2.24	A and C, B
	2.21	2.21	A and D
	2.10	2.11	Α
	2.07	2.07, 2.07, 2.08	A, D, B
	1.66	1.66, 1.67	C and D, A

^{*a*} Also given for comparison are the matching *d*-spacings derived from powder X-ray diffraction (XRD) of potential products. ^{*b*} A, Eu₂O-(CO₃)₂·H₂O; B, Eu₂O(CO₃)₂ (hexagonal); C, Eu₃O₄ (orthorhombic); D, Eu₂O₃ (monoclinic). ^{*c*} No data exists for B (Eu₂O(CO₃)₂ (hexagonal)) at low angle (large *d*-spacing).

Eu₂O(CO₃)₂. Thus the possibility of the 3.91/3.89 Å spacing arising from the unhydrated carbonate is not eliminated, but the fringes might also be assigned to orthorhombic Eu₃O₄ with d = 3.87 Å. The assignments for the identity of the crystalline material is made more convincing by additional matches at the smaller lattice spacings revealed by electron diffraction. Thirteen of the fourteen additional lattice spacings that are observed with electron diffraction can also be attributed to these same three materials.

Conclusion

Photochemical production of LnO from the MOCVD precursor, $Ln(thd)_3$ appears to proceed through multistep cracking of the bound ionic ligand, thd^- , with each step ejecting a stable neutral fragment from the complex and leaving an anionic fragment bound to the metal. The chemistry in Eu(thd)₃ is unique among the metals tested

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in that the cracking commences only after the complex has been stripped of two of the three ligands, proceeding from a Eu(thd) complex to the competing Eu⁰ and EuO products. In contrast, for the Gd, Er, and Tb complexes, only the first ligand is ejected from the complex before the cracking process begins from the Ln(thd)₂ complex. However, in all four cases the intraligand cracking steps, whose details are given above, are similar.

The fundamental tool used in this study, laser photoionization mass spectrometry, also reveals the presence of the metal dimer, $Ln_2(thd)_6$ in the molecular source. The gas-phase dimer likely arises from condensation of the monomer in the expansion cooling of the molecular-beam source and is not expected in the static CVD chamber. Precursor dimerization is potentially more relevant in molecular beam epitaxy experiments. It is interesting to note that the significant dimerization occurs at very low He backing pressures (P > 15 kPa) and occurs even for Er_{2^-} (thd)₆, though in the crystal structure, $Er(thd)_3$ exists as a monomer, in contrast to the bridged-dimer structures reported for the larger cations, Eu^{3+} , Gd^{3+} , and $Tb^{3+}.^{21.22}$ Laser-assisted MOCVD, using the Eu(thd)₃ precursor and a silica substrate, with subsequent exposure to atmosphere, produces a sparse coverage of amorphous Eu₂O₃ with small areas of crystallinity consistent with formation of the carbonate, Eu₂O(CO₃)₂ and its hydrate Eu₂O-(CO₃)₂·H₂O, expected products of reaction of high surface area Eu₂O₃ with atmospheric CO₂ and H₂O.^{27,28}

In summary, a detailed mechanism for the gas-phase formation of lanthanide oxides from a classic metal—organic CVD precursor has been revealed using a molecularbeam-source laser-photoionization, mass spectrometry experiment. In this and previous work, the experimental methodology has proven to be a powerful tool for deducing the complex unimolecular chemistry relevant to deposition of thin films of metal and metal binary compounds.

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