Mechanisms of Thermal and Photo Assisted MOCVD Processes from M(hfac)$_2$tetraglyme (M=Sr, Ba) Precursors

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In recent years, alkaline-earth β-diketonate complexes have been extensively used as precursors in the Metal Organic Chemical Vapor Deposition (MOCVD) of various electroceramic oxides including HTc superconductors (1,2), ferroelectrics (3) and high-k materials (4) as well as in the fabrication of optical coatings and host materials for luminescent devices (5,6). This paper focuses on the mechanicistic aspects of the MOCVD processes adopting M(hfac)$_2$tetraglyme (M=Sr,Ba and H-hfac =1,1,1,5,5,5-hexafluoroacetylacetone) precursors. The thermal activated decomposition of Ba(hfac)$_2$tetraglyme has been investigated combining "in situ" FTIR techniques and "ex situ" techniques for chemical, morphologic and structural analyses (EDX, XPS, and XRD). The obtained results have been compared with those found for Sr(hfac)$_2$tetraglyme and a general scheme for the deposition from M(hfac)$_2$tetraglyme precursors have been proposed. An heterogeneous mechanism is operating at low temperature, while an homogeneous decomposition becomes relevant at high temperature.

In particular, at 300°C, precursor does not decompose in the gas phase and deposition pathway involves the adsorption of the precursor on the film surface with glyme dissociation. Therefore, adsorbed M(hfac)$_2$ undergoes heterogeneous decomposition leading to MF$_2$ and to fluorinated surface species, responsible of CF$_x$ surface contamination observed by XPS measurements.

"In situ" FT-IR spectra obtained above 400°C show evidence of much more complex decomposition processes. The precursor decomposition involves the break down of the β-diketonate ring with formation of new fluorinate products such as acylketenes and CF$_2$O. The proposed reaction scheme is shown in Figure 1.

Some experiments were performed to evaluate the effects of UV irradiation at 254 nm and 300 nm. On the basis of previous solution studies, two sets of photo MOCVD experiments were designed: in the first set, deposition was performed under pure O$_2$ irradiating at 300nm; in the second set, CHCl$_3$ vapors were added to the reaction gasses under irradiation at 254 nm. Data have shown that irradiation enhances the deposition rate and that faster growth rates are obtained in the presence of CHCl$_3$. F/Sr atomic ratio of sample deposited in the absence of CHCl$_3$ vapors is close to 2 , thus suggesting the presence of SrF$_2$.

Films deposited in the presence of CHCl$_3$ vapors show a lower F/Sr ratio (~ 1.5) and a significant Cl/Sr atomic ratio (~ 0.7), indicating the presence of chlorinated phases.

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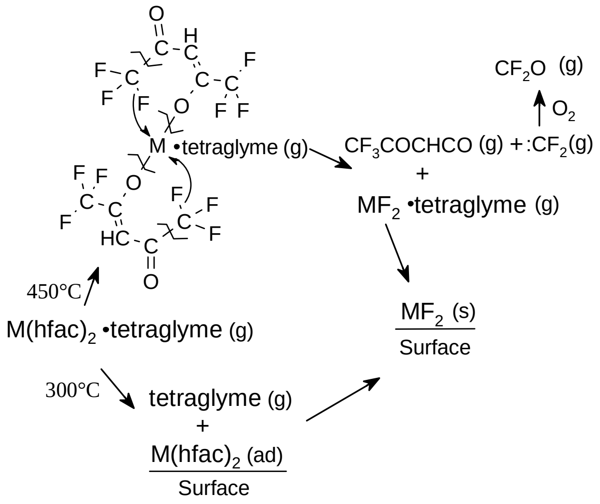

Figure 1. Proposed reaction scheme for thermally activated MOCVD processes .