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Modeling of evaporation rates of cerium β-diketonate

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Abstract

The effect of sublimation rate from the surface of solid precursor was included in our model for predicting the evaporation rates of cerium β-diketonate ($Ce(thd)_4$). This model suggested that when the rate of mass transfer was comparable to that of sublimation from surface, the organometallic (OM) concentration at the solid surface would become lower than its saturation pressure. On the other hand, when the sublimation rate was fast, such as in the case of $Cu(thd)_2$, the OM surface concentration would reach its saturated value. In addition, $Ce(thd)_4$ also exhibited solid-state decomposition whose contribution to weight losses should also be included for better fitting of the evaporation results. This was especially important when the evaporation rates were slow at low temperatures and high pressures. When the measured fluxes were plotted versus $1/T$ under different operating pressures, we obtained different "apparent" activation energies ranging from 26.7 to 34.5 kcal mol^{-1} for $Ce(thd)_4$. Nevertheless, this activation energy remained constant for $Cu(thd)_2$ at 29.4 kcal mol^{-1} regardless of operating pressures. The above difference was successfully simulated with our proposed model.

Keywords: Cerium diketonate; Evaporation rate; Modeling; Solid precursor

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1. Introduction

The organometallic vapor phase epitaxy (OMVPE) technique has been successfully applied to the growth of various thin films for microelectronic applications [1-4]. In spite of these successes, however, there are still areas of research to be carried out to improve our understanding about the mechanism of these chemical vapor deposition (CVD) processes. The evaporation behavior of solid OM precursors is one such example. A complete understanding of this behavior includes at least the following aspects:

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(1) evaporation rate as a function of system design and operating conditions;
(2) stability of the evaporation process;
(3) possible solid-state decomposition during evaporation.

The rates of evaporation have been investigated for a few solid diketonates [5–8]. Factors that were found to exhibit some effects on evaporation rates included:

(1) operating conditions, such as temperature, pressure, carrier gas flow rate, sample quantity, etc.;
(2) system design, such as evaporator and sample cell geometry; and
(3) other factors, such as "effective" surface area of solid particles and storage history (and hence surface characteristics).

In this work, cerium diketonate was chosen as an example to illustrate the usefulness of our revised mathematical model for predicting evaporation rates. This precursor was used to deposit CeO_2 buffer layer on various substrates for superconducting yttrium barium copper oxide (YBCO) films [9–11]. We would demonstrate that the evaporation of $Ce(thd)_4$ could be satisfactorily simulated only when we took into consideration the resistance due to sublimation from the solid surface as well as weight losses caused by the solid-state decomposition.

2. Modeling

The major difference between this model and our previous one [5] lies in the inclusion of sublimation rate from precursor surface into mass transfer considerations. In other words, the evaporation process is now assumed to consist of the following three steps:

(1) sublimation of precursor molecules from solid surface to gas phase;
(2) diffusion of these molecules from solid surface to the rim of sample cell, i.e. diffusion within the cell; and
(3) forced convection into the flowing carrier gas.

In our previous model, the first step, i.e. sublimation of solid precursor molecules into the gas phase, was assumed to proceed instantaneously and therefore a saturation vapor pressure could be maintained at the solid surface at all times, i.e. $C_s = C_{sat}$. However, in some cases, the rates of diffusion and convection (i.e. steps 2 and 3) may become comparable to that of the first step. Cerium 2,2,6,6-tetramethyl-3,5-heptane dionate ($Ce(thd)_4$) is one such example. The respective fluxes due to the three steps can be expressed as follows [5, 12]:

$$N = (\gamma C_{sat} \text{-} \alpha C_s)/(2\pi M/RT)^{1/2} \tag{1}$$

$$N = (C_s - C_i) D/h \tag{2}$$

$$N = k(C_i - C_b) \tag{3}$$

where γ: evaporation coefficient
α: condensation coefficient
C_{sat}: saturation concentration of OM at temperature T
C_s, C_i and C_b: OM concentrations at the solid surface, at the rim of sample cell, and in the bulk of carrier gas, respectively
D: diffusion coefficient of OM molecule in carrier gas
h: distance for stagnant diffusion
k: mass transfer coefficient due to convection effect.

Under steady state and assuming $C_b = 0$ and $\gamma = \alpha$, we can obtain the equation:

$$N = C_{sat}/[1/k + h/D + (2\pi M/RT)^{1/2}/\gamma] \tag{4}$$

It can be seen that the total resistance to evaporation consists of three terms corresponding to the three steps mentioned above. The parameters C_{sat}, k and D can then be converted into process parameters such as temperature (T in K), pressure (P_t: in Torr), and carrier gas velocity (u), through the following equations:

$$C_{sat} = P_{sat}/RT = P_o/RT \exp(-\Delta H/RT) \tag{5}$$

$$D = D_o (T/273)^{1.75} (760/P_t) \tag{6}$$

$$Sh = kd/D = 1 + (1 + Pe)^{1/3} \tag{7}$$

$$Pe \text{ (Peclet number)} = d\,u/D \tag{8}$$

Here d is the cell diameter ($= 1.9$cm in this case). After appropriate mathematical manipulation [13], we obtain:

$$N = P_o \exp(-\Delta H/RT)/[(2\pi M/RT)^{1/2}/\gamma + 28.5\,R\,P_t(h + C_o + C_1\,u)/(D_o T^{0.75})] \tag{9}$$

where C_o and C_1 are constants relating to system design. When the sublimation resistance is negligible, the above equation can be simplified to:

$$N = P_o \exp(-\Delta H/RT)/[28.5RP_t(h + C_o + C_1 u)/(D_o T^{0.75})] \tag{10}$$

This equation was used to simulate evaporation rates for Cu(thd)$_2$. Our calculation indicated that the temperature term of $T^{0.75}$ exhibited almost no influence on the Arrhenius behavior for the temperature range studied here.

Finally, if there is some solid-state decomposition reaction during evaporation, it would also cause weight losses. We need then to add an additional term to account for such a situation:

$$N = K_{rxn} \exp(-\Delta E/RT) + P_o \exp(-\Delta H/RT)/[2\pi M/RT)^{1/2}/\gamma + 28.5\,R\,P_t\,(h + C_o + C_1\,u)/(D_o T^{0.75})] \tag{11}$$

Eq. (11) was then used for Ce(thd)$_4$ results.

3. Experimental

The OM compound employed in this work was Ce(thd)$_4$ from Strem Chemical Co. It was used as received. The experimental setup and procedures were the same as for our previous studies on $Y(thd)_3$, $Cu(thd)_2$ and $Ba(thd)_2$ [5,6]. Stated briefly, a Cahn balance (model C2000) was utilized to record weight losses of the OM sample under various evaporation temperatures, pressures and carrier gas (argon) flow rates. About 30mg of sample was used for each experiment. The duration of evaporation was kept at 30min for all runs reported here. During this period, the evaporation rates remained nearly constant. The long-term stability of this OM precursor was not studied in this work.

During the evaporation experiments, we noticed that some white residues remained on top of $Ce(thd)_4$ powder. This suggested that some solid-state decomposition reaction might occur. We then analyzed these white residues for their Ce content by inductively coupled plasma–atomic emission spectroscopy (ICP–AES) and their chemical bonding by FTIR spectroscopy.

4. Results and discussion

4.1. *Evidence of solid-state decomposition*

If $Ce(thd)_4$ decomposes during evaporation to give off thd ligands, one would expect an increase in Ce content in the remaining sample. Our ICP–AES data show that the white residue indeed contains more Ce than the original sample (32.2 wt% vs 15.2 wt%). The FTIR spectra of the original $Ce(thd)_4$ and white residue are shown in Fig. 1. It can clearly be seen that most of the peaks between 600 and 1600 cm^{-1} disappear after evaporation. According to Harima et al. [14], these peaks originate from chemical bonding in the ligands, e.g. CC, CO, CH, CH_3, $C–CH_3$. Based on these data, we can therefore reasonably assume that $Ce(thd)_4$ decomposes during evaporation.

4.2. *Results and modeling on evaporation rates*

Shown in Figs. 2 and 3 are the $\ln N$ vs $1/T$ diagrams for $Cu(thd)_2$ and $Ce(thd)_4$ respectively. For $Cu(thd)_2$, the slopes of all straight lines are nearly the same. The activation energy for evaporation was calculated to be 29.4 kcal mol^{-1}, which is about the same as reported by Waffenschmidt et al. [8]. The solid lines shown in this figure represent simulation results (Eq. (10)). Agreement between experimental data and prediction is rather good. In this case, neither solid-state decomposition nor sublimation resistance was included.

However, in Fig. 3, the slopes changed operating pressure for $Ce(thd)_4$, producing "apparent" activation energies ranging from 26.7 to 34.5 kcal mol^{-1}. To simulate this situation, we utilized Eq. (11) with the following set of parameters (derived via a trial-and-error procedure):

$$\gamma = 0.01;\ P_o = 1.1 \times 10^9\ \text{Torr};\quad \Delta H = 32.7\ \text{kcal mol}^{-1};\quad \Delta E = 15.8\ \text{kcal mol}^{-1};$$

$$K_{rxn} = 8.6 \times 10^4\ \text{mol s}^{-1};\quad D_o = 2.8 \times 10^{-6}\ \text{m}^2\,\text{s}^{-1};\quad C_1 = 8.9 \times 10^{-3}\ \text{s};$$

$$C_o = d/2$$

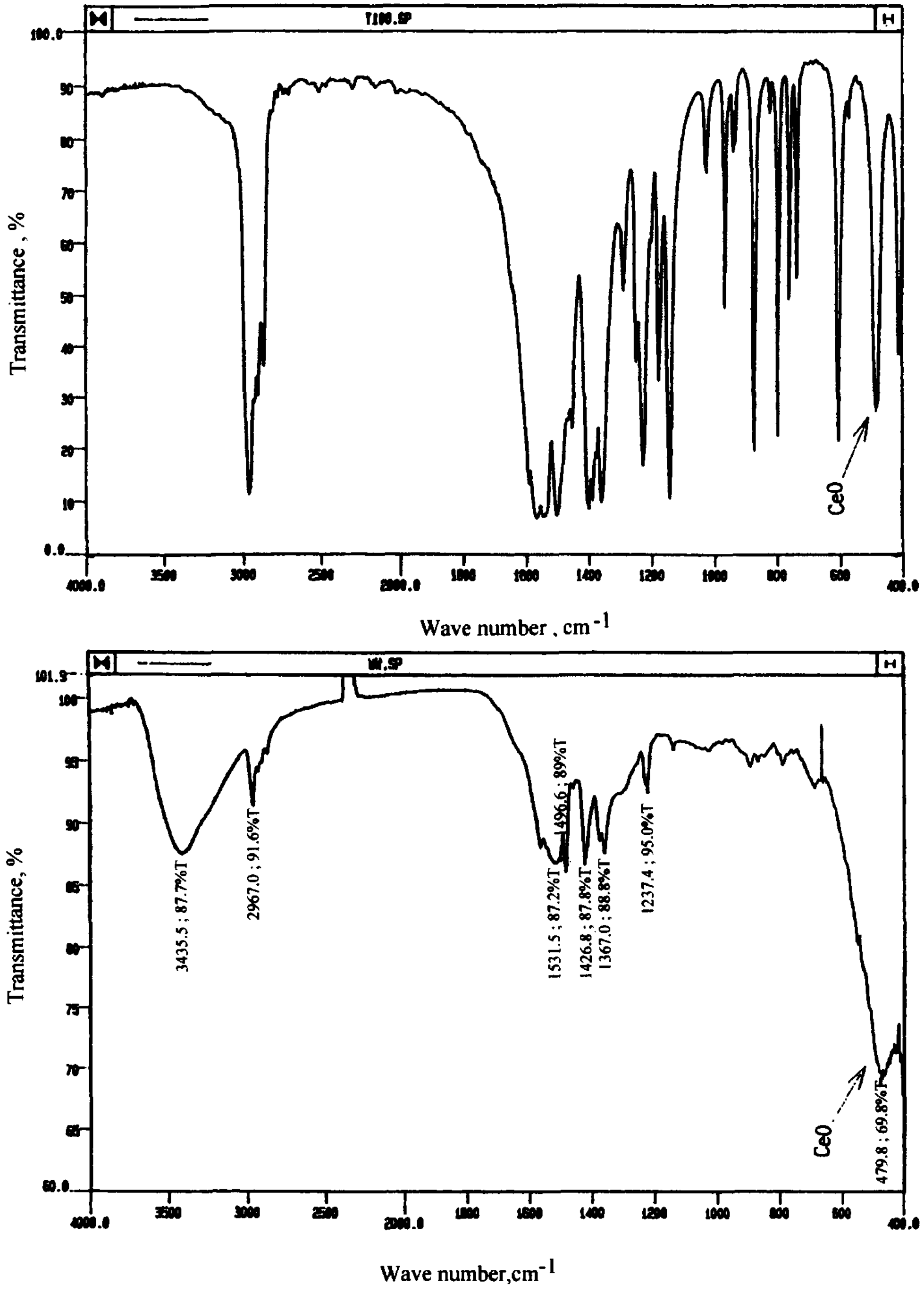

Fig. 1. FTIR spectra of (a) original Ce(thd)$_4$ sample and (b) white residue obtained after evaporation experiment.

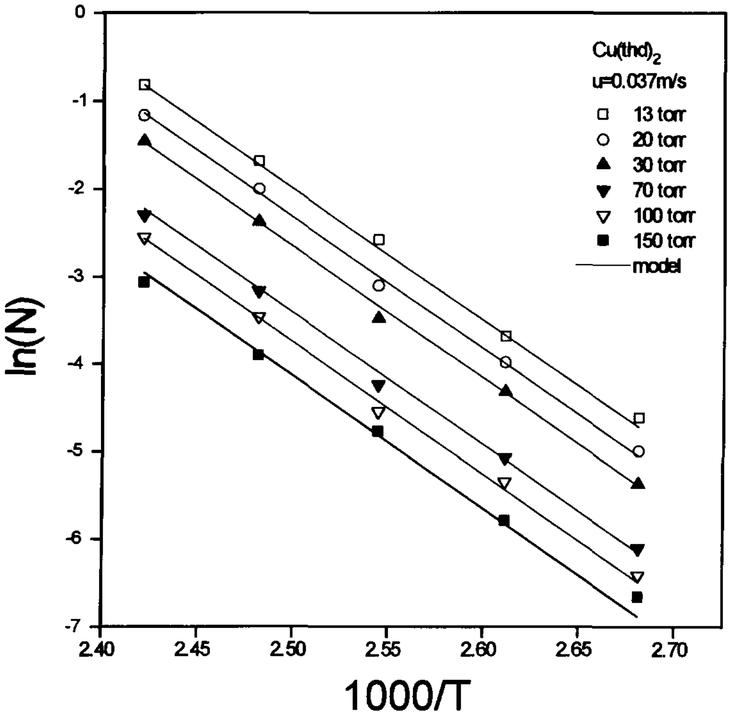

Fig. 2. Arrhenius plots for Cu(thd)$_2$ under various operating pressures. Simulated results are shown as solid lines.

The fit between experimental data and prediction is very satisfactory. The changes in slopes of these Arrhenius plots can now be explained by considering the solid-state decomposition reaction. This contribution of the decomposition reaction to weight losses can be easily calculated and is shown in Table 1. It clearly matters most when the evaporation rate is slow under low temperature and high pressure conditions. Although this set of parameters was not really optimized, it is still a satisfactory choice. Since the temperature range is rather small (140 to 175°C), the simulation results can be reasonably represented by straight lines as exhibited in Fig. 3.

Finally, shown in Fig. 4 are the effects of carrier gas velocity on evaporation fluxes. The contribution from solid-state decomposition under these conditions (170°C and 20 Torr) is only 3.8% (Table 1) and can thus be neglected. As a result, Eq. (9) was used instead of Eq. (11). We can, therefore, plot $1/N$ versus u and expect straight line relationships. The effects of h, distance for stagnant diffusion, are also indicated in this Fig. 4. The fit between experimental data and calculation is again satisfactory.

5. Conclusion

By taking sublimation from the solid surface into consideration, we have developed a better model for predicting evaporation rates of solid OM precursors. The rates of

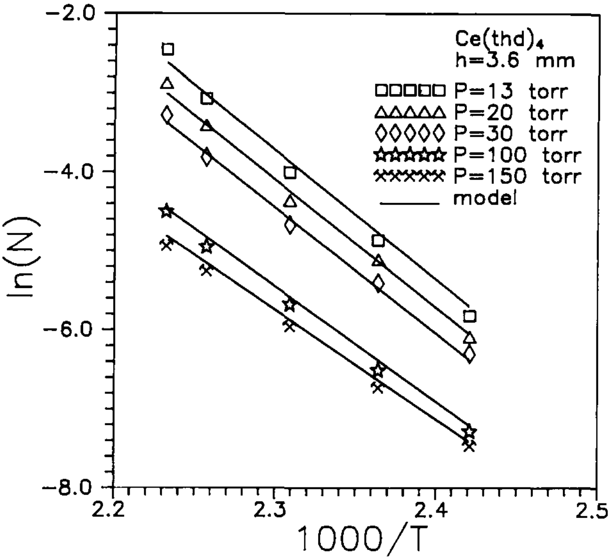

Fig. 3. Arrhenius plots for $Ce(thd)_4$ under various operating pressures. Simulated results are shown as solid lines.

Table 1

Fraction of weight losses due to solid-state decomposition as calculated by Eq. (11)

Evap. condition	140°C	150°C	160°C	170°C	175°C
13 Torr	10.0	6.3	4.0	2.6	2.1
20 Torr	14.2	9.1	5.8	3.8	3.1
30 Torr	19.5	12.8	8.3	5.4	4.4
100 Torr	43.9	32.1	22.6	15.6	12.9
150 Torr	53.9	41.4	30.4	21.6	18.1

evaporation are influenced by three factors: sublimation rate from the solid surface, diffusion rate within the sample cell, and convection rate into the carrier gas. Experimental results for $Ce(thd)_4$ showed that all three factors should be included, especially under low pressures when the diffusion rate is fast, whereas for $Cu(thd)_2$, the sublimation rate is always faster than the other two factors and can therefore be neglected from our model.

As for $Ce(thd)_4$, there is yet another factor to be included, i.e. the solid-state decomposition reaction. Our data indicated that part of $Ce(thd)_4$ would evolve thd ligands prior to sublimation. The contribution of this decomposition reaction to weight losses of $Ce(thd)_4$ becomes significant when the evaporation proceeds slowly, i.e. under low temperature and high pressure conditions.

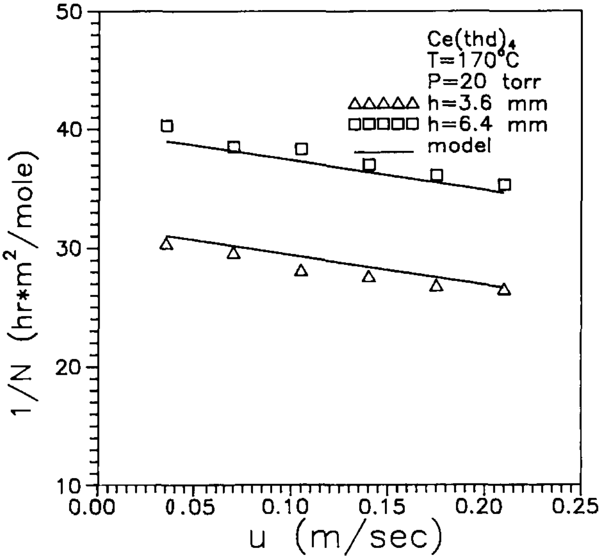

Fig. 4. Plots of $1/N$ versus carrier gas velocity (u) with two different h values.

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