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ARTICLE

Evaluating the Thermostability of Metal Precursors in MOCVD by Reaction Kinetic Analysis

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Abstract: The sufficient and stable evaporation of metal precursors is crucial for obtaining reproducible $YBa_2Cu_3O_{7-\delta}$ (YBCO) film with high quality in MOCVD technique. With the emergence of various metal precursors with high volatility, a practical way is needed to evaluate the thermal stability of metal precursors in evaporation. In this work, the thermal properties and decomposition kinetics of three precursors with different evaporation characteristics ($Y(DPM)_3$, $Cu(DPM)_2$, $Ba(DPM)_2$) were comparatively investigated by non-isothermal thermogravimetric analysis, and the apparent activation energy (E_a) of evaporation process was obtained by the classic kinetic analysis methods (Ozawa, Kissinger and Friedman methods). The thermal stability of metal precursors in evaporation was evaluated through the change regulation of E_a during the heating process. The results show that the decomposition reaction of $Ba(DPM)_2$ is indeed concomitant with its evaporation process and is highly sensitive to the change of temperature, while $Y(DPM)_3$ and $Cu(DPM)_2$ decompose stable. In addition, the consistent results of TGA-DSC and kinetic analysis can also confirm that evaporation kinetics study is reliable for investigating the thermostability of metal-organic compound in MOCVD process.

Key words: YBCO; MOCVD; metal precursor; thermostability; reaction kinetic analysis

In the metal-organic chemical vapor deposition technique (MOCVD), the sufficient and stable evaporation of metal precursors is crucial to obtain reproducible $YBa_2Cu_3O_{7-\delta}$ (YBCO) film with high quality. Among the used metal β-diketonates ($M(DPM)_n$; DPM=2, 2, 6, 6-tetramethyl-3, 5-heptanedionato; M=Y, Ba, Cu, Sm, Gd, Pr, etc.) in YBCO film fabrication, metal centers with larger ionic radii and strong polarities (such as Ba) prefer to be oligomeric or polymeric species with low volatility during evaporation process[1]. In some cases, increasing the vaporization temperature of precursors is usually used to achieve high vapor pressure, and 250~300 °C range or even higher temperature is employed for the evaporation of $Ba(DMP)_2$. High temperature will be a severe challenge for its long-term stability and stable vapor pressure characteristics[2,3].

Presently, the molecular tailoring design is usually used to improve the vaporization and mass transport properties of $M(DPM)_n$ by being coordinated with ancillary Lewis base ligands, and a lot of new precursors have appeared[4,5]. However, there is a lack of a practical and efficient way for evaluating evaporation of precursors with (or without) further side decomposition in MOCVD process, and some tedious isothermal evaporation or film deposition process have to be carried out for choosing metal precursors.

Various methods have been attempted to obtain useful information about volatility, stability and thermal decomposition of $M(DPM)_n$, such as Fourier transform infrared spectroscopy (FT-IR) or electron ionization mass spectrometer (EI-MS) methods combined with thermogravimetry-differential thermal analysis (TGA-DSC)[6-8]. However, the optical emission spectra from different components in the vapors usually overlap, which results in difficultly in distinguishing thermal decomposition from the evaporation process. In addition, the high-energy electron impact in EI-MS analysis can also break organic ligands into fragment ions besides thermal decomposition, which makes it difficult to truthfully reflect the

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stability and evaporation process of precursors.

The evaporation of *M*(DPM)$_n$ precursors in MOCVD technique is a solid-state decomposition process, in which the crystal lattice structure is destroyed (such as melting, evaporation, sublimation) and possible chemical reactions may occur with formation of new compounds. As a kinetic parameter of solid-state reactions, the apparent activation energy (E_a) can be used as a reactivity criterion to quantitatively judge whether the evaporation is a single or a multiple reaction process[9,10]. In this work, the evaporation characteristics of three precursors ($Y(DPM)_3$, $Cu(DPM)_2$, $Ba(DPM)_2$) for YBCO fabrication were comparatively investigated by non-isothermal thermogravimetric analysis, which is a useful tool to determine the kinetic parameters of solid-state reactions. Subsequently, different kinetic models (including Ozawa, Kissinger and Friedman methods) were used to evaluate the changes of E_a with the increase of conversion degree in order to prove that non-isothermal thermogravimetric analysis is reliable for investigating thermostability and evaporation characteristics of metal precursors.

1 Experiment

Metal β-diketonates including $Y(DPM)_3$, $Cu(DPM)_2$ and $Ba(DPM)_2$ were synthesized according to the previous reports[11-13]. Their structures were confirmed by nuclear magnetic resonance (^{1}H NMR) on a Bruker AV-400 NMR spectrometer (Switzerland) with deuterated chloroform ($CDCl_3$) as the solvent: 1.12 (18H, $-CH_3$) and 5.89 (H, -CH-) for $Y(DPM)_3$; 1.18 (18H, $-CH_3$) and 5.62 (H, -CH-) for $Cu(DPM)_2$; 1.12 (18H, $-CH_3$) and 5.5 (H, -CH-) for $Ba(DPM)_2$.

The dynamic thermogram of three metal β-diketonates was recorded on a STARe system TGA/DSC thermogravimeter (Metter-Toledo International Inc, Switzerland), and the recording was carried out over the temperature range of 25~600 °C at a heating rate of 10 °C/min. The flow rate of high purity nitrogen as the purge gas was 100 mL/min, which ensures that the concentration of substance at the top of the crucible remains nearly zero throughout the measurement.

The nonisothermal thermogravimetric tests were carried out at various heating rates of 5, 10, 15, and 25 °C/min in streams of N_2. The kinetics of decomposition was studied through the analysis of TGA-DTG curves by the Flynn-Wall-Ozawa, Kissinger, and Friedman methods.

2 Results and Discussion

2.1 Thermogravimetric analysis

Thermogravimetric analysis is extensively used especially in a study of mass loss versus temperature, and valuable information on thermal behavior of materials over a wide temperature range may be obtained. The TGA and DSC curves of $Y(DPM)_3$, $Cu(DPM)_2$ and $Ba(DPM)_2$ in the N_2 flow atmosphere are shown in Fig.1. For $Y(DPM)_3$ and $Cu(DPM)_2$, two sharp endothermic peaks in DSC curve are associated with the melting and evaporation, and the mass loss occurs in a single step ending with a nil residue. No DSC peaks caused by thermal decomposition are observed during the whole process. Hence, it is considered that $Y(DPM)_3$ and $Cu(DPM)_2$ do not thermally decompose in the heated gas line between a vessel of precursors and a reactor in MOCVD apparatus, where argon is used as a carrier gas. In addition, the mass loss occurs in a single step with a nil residue, showing that the precursor is stable up to vaporization temperatures, which indicates substantial vapor phase stability and exceptionally clean transport characteristics.

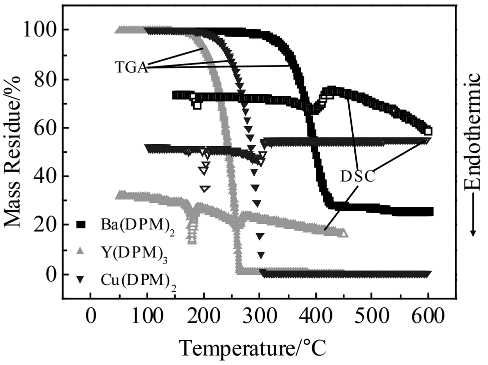

Fig.1 Ambient pressure TGA and DSC of $Y(DPM)_3$, $Cu(DPM)_2$ and $Ba(DPM)_2$ at a heating rate of 10 °C/min under a nitrogen atmosphere at a flow rate of 100 mL/min

Different from $Y(DPM)_3$ and $Cu(DPM)_2$, the TGA plot of $Ba(DPM)_2$ shows that there are two mass loss steps with about 22% residue left at 600 °C. The major mass loss of about 68% occurs at 188~410 °C, due to the evaporation of $Ba(DPM)_2$. The second step shows a 10% mass loss in the range of 410~550 °C and is associated with the decomposition of the precursor possibly. The DSC data of $Ba(DPM)_2$ shows that two endothermic peaks at 188 and 391 °C are associated with the melting and evaporation. Subsequently, several endothermic peaks in the range 410~550 °C are observed, which confirms the thermal decomposition in the second step. However, the endothermic peak at 391 °C corresponding to the evaporation process is unusually broad, and it is likely that another kind of process may be hidden under the same peak. Combining this broad peak and high residue left, it is concluded that the evaporation process of the precursor in the first step is accompanied by a decomposition reaction possibly, which is consistent with the dissociation of DPM ligand above 200 °C in previous reports.

All of the above shows that $Y(DPM)_3$ and $Cu(DPM)_2$ are more stable than $Ba(DPM)_2$ up to their vaporization temperatures.

2.2 Kinetics analysis

Commonly, TGA cannot distinguish unequivocally decomposition and sublimation. Therefore the kinetic model, the values of the apparent activation energy (E_a) and pre-exponential factor (A) of evaporation were investigated in order to reveal the mass loss process of Y(DPM)$_3$, Cu(DPM)$_2$ and Ba(DPM)$_2$.

All kinetic studies use the basic rate equation Eq.(1), in which dα/dt is a function of temperature and mass of sample, t is the time, α is the extent of conversion defined by the expression as $\alpha=(w_i-w_t)/(w_i-w_f)$, where w_t is the mass percent at any time t, w_i and w_f are the initial and final mass percent of sample, respectively. $k(T)$ is the rate constant, and $f(\alpha)$ is the reaction model associated with a certain mechanism. The temperature dependence of the rate constant is traditionally presented by the Arrhenius equation and Eq.(1) can be rewritten as Eq.(2), where A and E_a are the Arrhenius parameters and R is the gas constant. By the separation of variables in Eq.(2), Eq.(3) can be obtained, where $g(\alpha)$ denotes the integral form of the kinetic model $f(\alpha)$. Non-isothermal tests are more convenient to be carried out because it is not necessary to perform a sudden temperature jump for the sample at the beginning. Thus, most experiments are performed non-isothermally, and the heating rate is kept constant. Defining the heating rate as β= dT/dt, Eq.(2) and Eq.(3) can be rewritten as Eq.(4) and Eq.(5), respectively, which are the fundamentals for non-isothermal kinetic analyses.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)f(\alpha) \tag{1}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A\mathrm{e}^{-E_a/RT}f(\alpha) \tag{2}$$

$$g(\alpha)=\int\mathrm{d}\alpha/f(\alpha)=A\int\mathrm{e}^{-E_a/RT}\mathrm{d}t \tag{3}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}\mathrm{e}^{-E_a/RT}f(\alpha) \tag{4}$$

$$g(\alpha)=\frac{A}{\beta}\int\mathrm{e}^{-E_a/RT}\mathrm{d}T \tag{5}$$

In order to obtain more reliable results, most popular multi-scan methods including Flynn-Wall-Ozawa Eq.(6)[14], Friedman equation Eq.(7)[15] and the Kissinger equation Eq.(8)[16] have been proposed for the determination of the kinetic triplet factors.

$$\log(\beta)=\log[\frac{AE_a}{Rg(\alpha)}]-2.315-0.4567\frac{E_a}{RT} \tag{6}$$

$$\ln(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T})=-\frac{E_a}{R}\frac{1}{T}+\ln f(\alpha) \tag{7}$$

$$\ln(\frac{\beta}{T_p^2})=-\frac{E_a}{R}(\frac{1}{T_p})+\ln\frac{AR}{E_a} \tag{8}$$

Based on the Flynn-Wall-Ozawa equation Eq.(6), the activation energies (E_a) can be obtained from a logarithmic plot of heating rates (β) as a function of the reciprocal of temperature (T^{-1}) for a constant $g(\alpha)$, since the slope of such a line is given by $-0.4567E_a/R$. This plot and the apparent activation energy of Ba(DPM)$_2$ calculated from different heating rates are shown in Fig.2 and Fig.3, respectively. For 10%~60% conversions, the lines in Fig.2 are parallel and the average apparent activation energy are about 116~120 kJ/mol with a slight increase tendency, which also reveals that Ba(DPM)$_2$ is almost stable in evaporation with the possibility of other side reaction, such as the decomposition process or formation of oligomers.

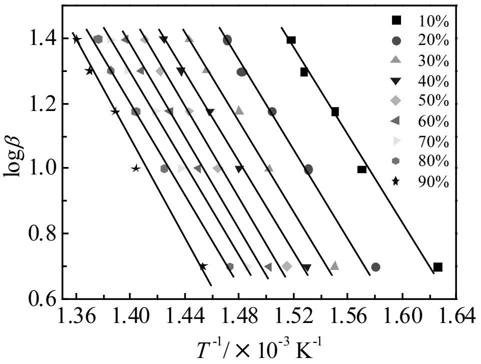

Fig.2 Ozawa plots of logβ versus T^{1} at different heating rates (β) for compound Ba(DPM)$_2$

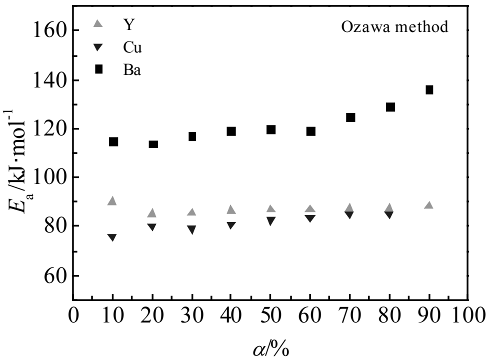

Fig.3 Apparent activation energy (E_a) versus different extents of conversion (α) by Ozawa method for compound Ba(DPM)$_2$, Y(DPM)$_3$, and Cu(DPM)$_2$

With the conversion exceeding 60%, the parallelism of lines is not good and the apparent activation energy gradually increases from 120 kJ/mol to 137 kJ/mol in Fig.3. This suggests that the reaction mechanism in evaporation process can vary with the degree of conversion increase, and the decomposition process or formation of oligomers is accelerated during this stage. Using the same method, the apparent activation energy of Y(DPM)$_3$ and Cu(DPM)$_2$ was calculated and has no remarkable change, about 86.7 and 83.0 kJ/mol, respectively (Fig.3), which reveals that Y(DPM)$_3$ and Cu(DPM)$_2$ are stable in evaporation without any other side reaction, such as the decomposition process or formation of oligomers.

Subsequently the apparent activation energy was also determined by Friedman technique using Eq.(7). The apparent activation energy of volatilization was calculated based on the linear dependence of the ln(*β*d*α*/d*T*) versus 1/*T* plot for various heating rates. This plot and the apparent activation energy calculated from the different heating rates are shown in Fig.4 and Fig.5, respectively. Similar to the results of Ozawa method, for 10%~60% conversions, the lines in Fig.4 are parallel and the average apparent activation energy in Fig.5 is 109~118 kJ/mol with a slight increase tendency. After the conversion exceeding 60%, the parallelism of lines is not good and the apparent activation energy obviously increases from 120 kJ/mol to 157 kJ/mol. All of the above shows that the decomposition process or formation of oligomers can occur in evaporation process and is accelerated with the degree of conversion increase. Using the same method, the apparent activation energy of $Y(DPM)_3$ and $Cu(DPM)_2$ was calculated and has no remarkable change, about 83.9 and 87.2 kJ/mol, respectively (Fig.5), which reveals that $Y(DPM)_3$ and $Cu(DPM)_2$ are stable in evaporation without any other side reaction, such as the decomposition process or formation of oligomers.

The apparent activation energy of one reaction process can be calculated by Kissinger equation Eq.(8) from the linear dependence of the $\ln(\beta/T_p^2)$ versus $1/T_p$ plot for various heating rates, where T_p is the absolute temperature at the maximum mass-loss rate for different heating rates in Fig.6. The average apparent activation energy for whole evaporation process of $Ba(DPM)_2$, $Y(DPM)_3$ and $Cu(DPM)_2$ is obtained, and the value is 109.2, 84.7 and 89.6 kJ/mol, respectively. All these show that $Ba(DPM)_2$ is more difficult to be evaporated than $Y(DPM)_3$ and $Cu(DPM)_2$.

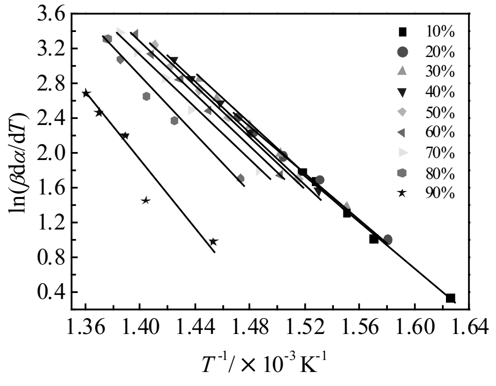

Fig.4 Friedman plot of ln(*β*d*α*/d*T*) versus T^{-1} at different heating rates (*β*) for compound $Ba(DPM)_2$

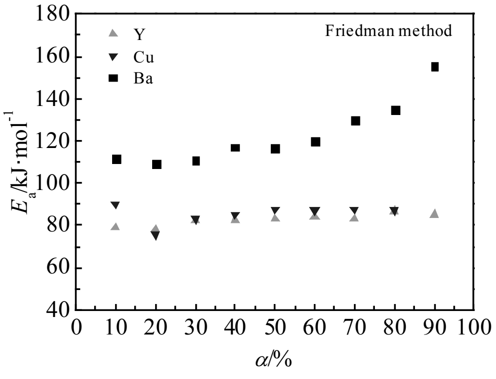

Fig.5 Apparent activation energy (E_a) versus different extents of conversion (*α*) by Friedman method for compound $Ba(DPM)_2$, $Y(DPM)_3$, and $Cu(DPM)_2$

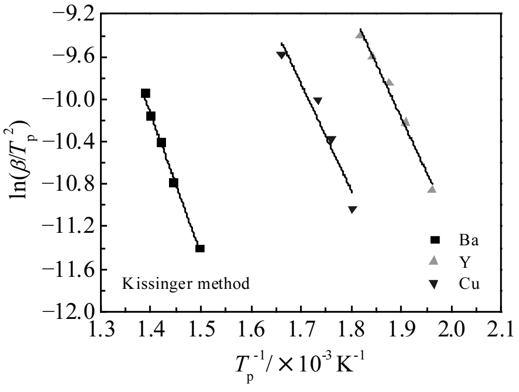

Fig.6 Kissinger plots of $\ln(\beta/T_p^2)$ versus T_p^{-1} at different heating rates (*β*) for compound $Ba(DPM)_2$, $Y(DPM)_3$, and $Cu(DPM)_2$

Based on the similar results of evaporation kinetic from Flynn-Wall-Ozawa, Friedman and Kissinger methods, it is clear that the obtained apparent activation energy of $Ba(DPM)_2$ is reliable, which is between 109 and 120 kJ/mol for 10%~60% conversions. With the conversions exceeding 60%, the decomposition or formation of oligomers may be accelerated in the evaporation process due to the dissociation of *β*-diketone ligand. Different from $Ba(DPM)_2$, the steady apparent activation energy of $Y(DPM)_3$ (84~87 kJ/mol) and $Cu(DPM)_2$ (83~90 kJ/mol) indicates their stability during the whole evaporation process. However, the apparent activation energy also increases in trace with the extent of conversion and temperature increase, which indicates that there is a possibility of decomposition or formation of oligomers in the evaporation process due to the dissociation of *β*-diketone ligand. Therefore, it is very important to choose suitable evaporation technology and conditions for avoiding precursor breakdown (or thermal aging).

3 Conclusions

1) The decomposition reaction of $Ba(DPM)_2$ is indeed concomitant with its evaporation process and is highly sensitive to the change of temperature. With the extent of conversion and temperature increase, the decomposition or formation of oligomers will be accelerated in the evaporation process.

2) The apparent activation energy of the evaporation process evaluated by Flynn-Wall-Ozawa, Kissinger and

Friedman methods is consistent, and the evaporation kinetics study is suitable for investigating the thermostability of metal-organic precursors in MOCVD technique.

References

1 Condorelli G G, Malandrino G, Fragala I L. *Coordination Chemistry Reviews*[J], 2007, 251: 1931

2 Zhao P, Ito A, Tu R *et al. Material Letters*[J], 2010, 64: 102

3 Molodyk A, Novozhilov M, Bitkowsky S *et al. IEEE Transactions on Applied Superconductivity*[J], 2009, 19: 3169

4 Malik M Z, Afzaal M, O'Brien P. *Chemical Reviews*[J], 2010, 110: 4417

5 Cai H Z, Chen L, Wei Y *et al. Rare Metal Materials and Engineering*[J], 2010, 39(2): 209

6 Song H Z, Jiang Y Z, Xia C G *et al. Journal of Crystal Growth*[J], 2003, 250: 423

7 Harima H, Ohnishi H, Hanaoka K *et al. Japanese Journal of Applied Physics*[J], 1990, 29: 1932

8 Jiang Y Z, Liu M F, Wang Y Y *et al. Journal of Physical Chemistry A*[J], 2006, 110: 13 479

9 Chatterjee K, Dollimore D, Alexander K. *Journal of Thermal Analysis and Calorimetry*[J], 2001, 63(3): 629

10 Sun Y, Wan Z P, Hu L X *et al. Rare Metal Materials and Engineering*[J], 2017, 46(8): 2080

11 Zhang T, Gu H W, Ding F Z *et al. Rare Metal*[J], 2013, 32(1): 67

12 Zhang T, Gu H W, Ding F Z *et al. Rare Metal*[J], 2012, 31(4): 343

13 Zhang T, Gu H W, Ding F Z *et al. Journal of Rare Earths*[J], 2012, 30(10): 1041

14 Ozawa T. *Bulletin of the Chemical Society of Japan*[J], 1965, 38(11): 1881

15 Tanaka H. *Thermochimica Acta*[J], 1995, 267: 29

16 Kissinger H E. *Analytical Chemistry*[J], 1957, 29: 1702

反应动力学法评价 MOCVD 过程中金属前驱盐的稳定性

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摘 要：基于 MOCVD 法制备 YBCO 超导体过程中常用的、具有不同蒸发特性的 3 种金属前驱盐（$Y(DPM)_3$, $Cu(DPM)_2$, $Ba(DPM)_2$），采用非等温热重分析法对比研究 3 种金属前驱盐在蒸发过程中的热稳定性和分解动力学特性，并依据典型动力学方法（Ozawa, Kissinger 和 Friedman 法）获得各金属前驱盐在蒸发过程中的表观活化能（E_a）及其变化规律，进而分析其在蒸发过程中的热稳定性。结果表明：$Ba(DPM)_2$ 金属前驱盐在蒸发过程中伴随发生热分解反应，且分解过程对温度变化敏感，而 $Y(DPM)_3$ 和 $Cu(DPM)_2$ 可以稳定蒸发。结合 TGA-DSC 分析证实，采用固相反应动力学方法来评价 MOCVD 过程中金属前驱盐的热稳定性是可靠的。

关键词：YBCO；MOCVD；金属前驱盐；热稳定性；化学反应动力学

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