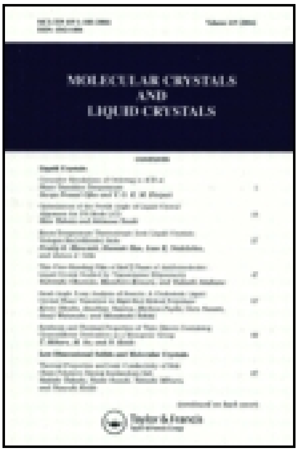

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Volatilities of Precursors for Chemical Vapor Deposition of Superconducting Thin Films

S. Yuhya [a] , K. Kikuchi [a] , M. Yoshida [a] , K. Sugawara [a] & Y. Shiohara [a]
[a] Superconductivity Research Lab. (SRL)-ISTEC, 10-13 Shinonome 1-Chome Koto-ku, Tokyo, 135, JAPAN

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Volatilities of precursors for chemical vapor deposition of superconducting thin films

S.YUHYA, K.KIKUCHI, M.YOSHIDA, K.SUGAWARA, and Y.SHIOHARA
Superconductivity Research Lab.(SRL)-ISTEC, 10-13 Shinonome 1-Chome
Koto-ku, Tokyo 135, JAPAN

ABSTRACT Volatilities of precursors for CVD of superconducting oxide materials have been investigated. The precursors studied were Cu, Y, Ba, Sr, Ca and Bi ß-diketonates and triphenyl Bi. Thermal stabilities for each precursors were measured by a thermal analysis. $Bi(DPM)_3$ was transformed into a Bi_2O_3 by a thermal decomposition and did not volatilize, while in the case of $Sr(DPM)_2$ and $Ba(DPM)_2$, evaporation and thermal decomposition occurred simultaneously. For $Cu(DPM)_2$, $Y(DPM)_3$, $Ca(DPM)_2$ and $Bi(ph)_3$, vapor pressures were estimated using a transpiration method. The temperature dependence of equilibrium vapor pressure has been measured. The latent heats of sublimation for $Cu(DPM)_2$ and $Y(DPM)_3$ were evaluated as 25.3 and 32.5 kcal/mol, respectively. The latent heats of evaporation for $Y(DPM)_3$ and $Bi(ph)_3$ were evaluated as 15.9 and 22.3 kcal/mol, respectively. In the case of $Ca(DPM)_2$, the latent heats of sublimation and evaporation were almost the same each other and its value was 17.2 kcal/mol.

INTRODUCTION

Since the discovery of the oxide superconductors of Y-Ba-Cu-O[1] and Bi-Sr-Ca-Cu-O[2], a number of physical and chemical film preparation techniques have been investigated.[3,4]

Chemical Vapor Deposition (CVD) is one of the promising methods to produce high-Tc superconductors because of the following reasons; the deposition is possible at a relatively high oxygen potential, the deposition rates can be high as compared with those achieved by other processes and it has an excellent capability to cover large areas which is required if complicated substrates (e.g. cavities, grooves and fibers) have to be coated.

Volatility is one of the important properties of precursors for CVD. Many organometal compounds have relatively high volatilities at low temperature. The desirable properties include thermal stability at the vaporization temperature and further thermal decomposition capability to form constituent elements for film fabrication.

For superconducting CVD, ß-diketonates are commonly utilized as the precursors.[4] Comparatively little has been reported about volatilities of the precursors for superconducting oxide thin films. In this work, the volatilities of precursors for superconducting CVD were investigated.

EXPERIMENTAL PROCEDURE

The precursors used in this work were ß-diketonates of Cu, Y, Ca, Ba, Sr and Bi with ligand of dipivaloylmethanate (DPM:$C_{11}H_{19}O_2$) and Bi(ph)3 (phenyl:C_6H_5). All samples were of reagent grades(TOSOH AKZO CORP.) in purity.

Thermal analysis was carried out by a thermogravimetric analysis (TG) and a differential thermal analysis (DTA). The sample weighed about 10 mg. All measurements were performed with conditions of 10 °C/min of heating rate and 100 ml/min of Ar gas flow rate.

The vapor pressure measurement was carried out by a transpiration method based on the results in measurements of evaporation rates at different carrier gas flow rates.[5] The isoteniscope technique has been commonly used for vapor pressure measurement.[6] However this method is very difficult to measure the low vapor pressure generally used for the CVD processing.

For the transpiration method, the vapor pressure is given by the following equation based on the Boyle-Chrales' law.

$$P = \frac{k}{r} \bullet \frac{V}{M} \bullet \pi$$

Where k is an evaporation rate (mg/min), r is a carrier gas flow rate (ml/min), V is a molar volume of carrier gas (l), M is a molecular weight of vapor molecule, and π is a pressure of measurement system (torr).

Under a carrier gas flow, evaporated gas is never saturated. The vapor density (k/r: g/l) at the zero flow rate has been estimated by extrapolating the data points at certain flow rates to the zero flow rate. This value was assumed to be corresponding to the equilibrium vapor pressure.

Figure 1 shows a schematic diagram of the experimental apparatus. It consists of a hanging type balance and a down flow Ar gas system adjusted by the mass flow controller (MFC). The sample weight was about 200mg. The values of k and r have been obtained by the thermal balance and the MFC, respectively. The value of V is 24 l/mol at 20 °C and at 1atm. The value of M has been calculated from a molecular formula of specimen.

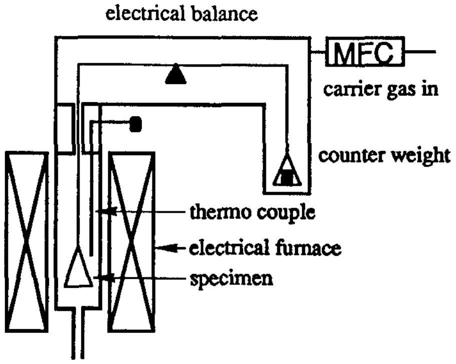

Figure 1 Experimental apparatus for vapor pressure by a transpiration method

The π is an ambient pressure (760 torr).

RESULTS AND DISCUSSION

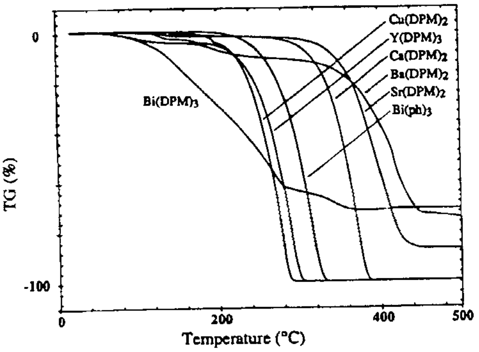

Figure 2 TG curves of precursors

Figure 2 shows the results of thermograms of the precursors. $Y(DPM)_3$ and $Ca(DPM)_2$ exhibited a two-step weight loss due to evaporation and/or sublimation of volatile impurities (solvent etc.) and vaporization of the precursors. Similar two-step weight losses were observed for $Sr(DPM)_2$ and $Ba(DPM)_2$, however these left about 15 % and 25 % of the mass of the precursors as residue at the 500 °C after heating. It is estimated that the evaporation along with thermal decomposition occurred up to 450 °C for $Sr(DPM)_2$ and $Ba(DPM)_2$. In the case of $Bi(DPM)_3$, about 30 % as the residue was observed. It seems that the precursor is transformed into a Bi_2O_3 by thermal decomposition with oxidation and not volatile. $Cu(DPM)_2$ and $Bi(ph)_3$ showed only the evaporation of their molecules.

Accordingly, the vapor pressure measurement was carried out for $Cu(DPM)_2$, $Y(DPM)_3$, $Ca(DPM)_2$ and $Bi(ph)_3$ whose vapor molecules correspond to the solid molecule. In order to remove the volatile impurities, the vapor pressure was measured after the preheating by which samples were kept for 2 hours in the measurement chamber at 70 °C for $Bi(ph)_3$, 100 °C for $Cu(DPM)_2$ and $Y(DPM)_3$ and 150 °C for $Ca(DPM)_2$. After reaching the predetermined temperatures, the weight loss was measured maintaining those temperatures constant for 3 to 30 minutes at different carrier gas flow rates. The rates of weight loss were from 10^{-4} to 10 mg/min.

Figure 3 shows the Clausius-Clapeyron plots for each precursors. For $Y(DPM)_3$, the plots are not on the straight line because of its melting. Similarly, the plot of $Bi(ph)_3$ at 70 °C ($1/T=2.92*10^{-3}$) which is lower than its melting point, shifted below the line extrapolated from higher temperatures of evaporation region.

Table 1 shows the melting point and the data fitted to the following equation,

$$\log P = \frac{1}{2.303R}\left(\frac{-\Delta H}{T} + \Delta S\right)$$

where ΔS is the entropy change and R is a gas constant. These values are comparatively consistent with the values reported in the literatures.[7,8]

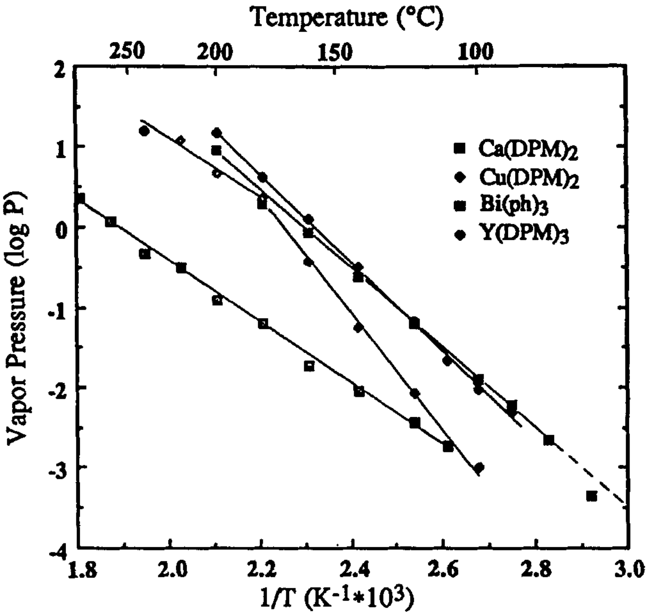

Figure 3 Clausius-Clapeyron plots for precursors

Table 1 Melting points and Clausius-Clapeyron fits for each precursors

precursors	melting point (°C)	log P (torr)	literatures
$Cu(DPM)_2$	196	-5542/T+12.88 (sub.)	-5843/T+10.45 (sub.)[7] -4069/T+ 6.68 (eva.)[7]
$Y(DPM)_3$	176	-7107/T+16.00 (sub.) -3485/T+ 7.95 (eva.)	-8740/T+19.97 (sub.)[8] -3567/T+ 8.30 (eva.)[8]
$Ca(DPM)_2$	230	-3760/T+ 7.06 (sub.,eva.)	
$Bi(ph)_3$	79	-4885/T+11.19 (eva.)	

For $Ca(DPM)_2$, the values of ΔH for sublimation and vaporization are almost the same values experimentally. This seems to be due to so small value of the latent heat of fusion compared with that for other precursor materials, as shown in figure 4.

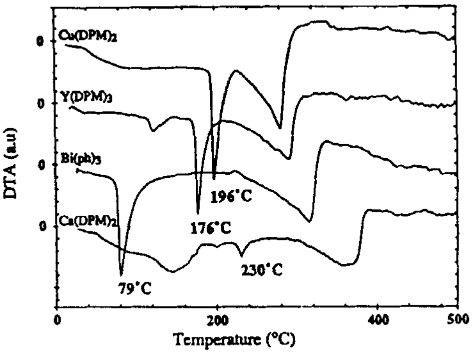

Figure 4 DTA curves of precursors

CONCLUSION

Precursor volatility for superconducting CVD processing has been investigated by a thermal analysis and a vapor pressure measurement which might be helpful to determine the process temperature practically used in CVD. Bi(DPM)$_3$ was transformed into a Bi_2O_3 by the thermal decomposition with oxidation and not volatile. For Sr(DPM)$_2$ and Ba(DPM)$_2$, the evaporation along with thermal decomposition occurred. For Cu(DPM)$_2$, Y(DPM)$_3$, Ca(DPM)$_2$ and Bi(ph)$_3$, the temperature dependences of their equilibrium vapor pressures were measured. In the case of Cu(DPM)$_2$, log P (torr) is equal to $-5542/T+12.88$ for sublimation. In the case of Y(DPM)$_3$, log P (torr) is equal to $-7107/T+16.00$ for sublimation and to $-3485/T+7.95$ for evaporation. In the case of Bi(ph)$_3$,log P (torr) is equal to $-4885/T+11.19$ for evaporation. In the case of Ca(DPM)$_2$, log P (torr) is equal to $-3760/T+7.06$ both for evaporation and sublimation.

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