YBa₂Cu₃O_{7-x} thin films deposition on YSZ substrates by MOCVD

J. SANTISO and A. FIGUERAS

Institut de Ciència de Materials de Barcelona, C.S.I.C., Campus UAB, 08193 Bellaterra, Spain

Abstract.- The evaporation process of β -diketonate precursors for the MOCVD deposition of YBa₂Cu₃O_{7-x} superconducting films has been investigated by thermogravimetric analysis. Special attention has been paid to the Ba(thd)₂ precursor. A simple model of the reactions involved in this process has been described. YBa₂Cu₃O_{7-x} superconducting layers were deposited on YSZ substrates by MOCVD in a horizontal hot-wall reactor. Films showed a mixture of c-axis and a-axis orientation, and have a $T_c(R=0) = 88.2\text{K}$ and $T_c \text{ onset} = 91.6\text{K}$.

Introduction

MOCVD is a well established technique for the elaboration of high- T_c superconducting films [1-3]. Solid β -diketonate precursors of the type Cu(thd)₂, Y(thd)₃ and Ba(thd)₂ [(thd): 2,2,6,6-tetramethyl-3,5-heptanedione] are commonly used as source materials in the YBa₂Cu₃O_{7-x} preparation. Constant evaporation rates have to be achieved in order to control the stoichiometry in the layer. The stability of Ba(thd)₂ during the evaporation process is one of the main problems in the preparation of these materials [4].

In this paper, evaporation of precursors was studied in order to determine the experimental conditions for the YBa₂Cu₃O_{7-x} deposition process. Activation energies for the evaporation of precursors were evaluated.

Y-Ba-Cu-O thin films were deposited on YSZ(100) single crystal substrates. Morphology, structure and electrical response were characterized.

Experimental

Cu(thd)₂, Y(thd)₃ and Ba(thd)₂ organometallic compounds were supplied by Strem Chemicals. Thermogravimetric analysis was performed in a Perkin Elmer TGA7 microbalance. Evaporation rates were measured at different constant temperatures as function of time. Total pressure was 10 torr in flowing Ar atmosphere. The heating ramps were 5°C/min. Typical mass charges in the TGA were 20 mg.

Y-Ba-Cu-O thin films were deposited on YSZ(100) substrates (0.5x1cm²) by the MOCVD technique in a horizontal hot-wall reactor. Y, Ba and Cu precursors were evaporated in different lines by heating stainless steel containers (2cm² exposed surface, 100 mg mass charges). The precursors heating system was carefully stabilized in order to obtain high reproducibility in the evaporation rates.

Ar was used as carrier gas. O₂ was added to the flow. Gas flows were controlled by mass flow controllers. Intermediate line was heated in order to prevent condensation. Mixed gas flow was directed perpendicularly to the substrate surface through a nozzle. The substrate was attached to a stainless steel susceptor placed inside a 3 cm diameter quartz tube and heated by a tubular furnace. Total pressure in the reaction chamber was kept constant at 10 torr. The experimental conditions during the deposition process are listed in Table 1.

Table 1 Deposition conditions

precursors	T _{evap} (°C)	Ar flow (cm ³ /min)	O ₂ flow (cm ³ /min)
Y(thd) ₃	117.0	50	150
Cu(thd) ₂	220.0	50	
Ba(thd) ₂	103.4	50	
substrate: YSZ(100)		temperature 750 °C	
total pressure 10 torr			
run time 120 min			
line temperature 300 °C			
Oxygen treatment: 450°C, 10h, 1atm O ₂ :Ar (3:1)			

Substrate temperature was evaluated by placing a thermocouple in contact with the surface. Deposition runs lasted 2 hrs. Afterwards the substrate was cooled down to 400 °C and kept during 10 h in a 1 atm O₂:Ar (3:1) atmosphere.

Layer thickness was measured by profilometry. Y:Ba:Cu composition ratio was evaluated by microprobe analysis (Cameca). Morphological and structural analysis were performed by SEM (Hitachi) and XRD (Rigaku). Resistance versus temperature was measured by the standard four point measurement method (1mA current, 0.5x1cm²).

Results and Discussion

Mass losses in isothermal evaporation of Cu(thd)₂ and Y(thd)₃ compounds were constant in time during 2hr runs in the TGA apparatus. Temperature isotherms were ranged between 85 and 160 °C. An initial mass loss of 2% was observed in the heating-up period of Y(thd)₃. No decomposition of precursors after heating experiments was observed as revealed by FTIR and ICP analysis. Mass loss rates were independent of mass charges.

In the isothermal evaporation of Ba(thd)₂ a 9% mass loss was observed in the heating-up period (5 °C/min ramp). Figure 1 shows mass losses of Ba(thd)₂ precursor versus time, at different temperatures. Up to 230 °C mass loss rates were almost constant during the first 2hrs of isothermal heating. Experiments performed above this temperature (up to 260 °C) showed decreasing mass loss rate with time. Progressive degradation of product with temperature and time was observed by IR analysis. The Ba content increased as revealed by Atomic Absorption analysis from 26.2 (±0.9)% (as supplied) to 31(±2)% after a 2h, 10 torr, and 250 °C run, similar to those reported by Fitzer et al.[4]. Mass loss rates depended on mass charge. Mass decreased exponentially as function of time and tended to a residual constant value (m_{sat}). This residual mass decreased with temperature.

The mass losses could be well fitted for each temperature assuming the combination of two

Figure 1.- Mass loss percent of Ba(thd)₂ precursor as function of time at different temperatures.

different processes. The first process corresponds to the homogeneous evaporation of the product (A) and follows a law

where m_A is the remaining mass of the non-decomposed product able to evaporate, and k_1 its reaction rate constant.

The second process is the decomposition of the molecule into a residual solid product (B) and a vapour product (C) and follows the laws

where k_2 is the decomposition reaction rate constant, m_B the decomposed mass B, and r a proportionality factor.

Solving the equation system (1,2) total mass loss rate becomes

$$\left(\frac{dm}{dt} \right)_{1,2} = -k(m - m_{sat}) \quad (3)$$

$$\text{where } m = m_A + m_B, \quad k = k_1 + k_2 \quad \text{and} \quad m_{sat} = m_B^\circ + r \left(\frac{k_2}{k} \right) m_A^\circ \quad (4)$$

where m_A° and m_B° are the initial masses of A and B at the start of the isotherm.

This model fitted well the experimental measurements. Thus k and m_{sat} values corresponding to equation (3) were obtained for different temperatures. Figure 2 represents the Arrhenius plot of k versus reciprocal temperature. Up to 250°C one can observe that the process shows an almost linear

Figure 2.- Arrhenius plot of k versus the reciprocal temperature for the $\text{Ba}(\text{thd})_2$ evaporation process. The activation energy was calculated from the slope of the continuous line

Figure 3.- Saturation mass of the $\text{Ba}(\text{thd})_2$ evaporation process at different temperatures.

dependence with an apparent activation energy of 56 KJ/mol. Above this temperature the slope of the curve increases due to the presence of a second process with higher activation energy.

It could be observed, from the equation (4), that constant values of m_{sat} should be obtained if only one process dominates. When only decomposition process is considered ($k_2 \gg k_1$) then m_{sat} becomes $m_B^0 + r m_A^0$, decreasing to a lower value, m_B^0 , in the case that normal evaporation process dominates ($k_1 \gg k_2$). Figure 3 shows the values of residual mass percent versus temperature. Two different zones can be observed. At temperatures lower than 250°C residual masses decrease linearly as function of temperature, corresponding to a region where k_1 and k_2 values are comparable. Above 250°C a constant residual value has been obtained, corresponding to a region where homogeneous evaporation process dominates. Consequently, the evaporated to decomposed mass ratio increases with temperature.

In the MOCVD process it is necessary to have constant evaporation rates. Thus, Ba(thd)₂ precursor must be kept at temperature lower than 230°C to have an almost constant evaporation rate in the first 2 hours (as seen in figure 1), but the evaporated to decomposed mass ratio is lower than at higher temperatures. Special temperature programs could be applied to keep an almost constant evaporation rate value, at least for 1 hour, at temperatures ranging from 240 to 260°C then increasing the Ba(thd)₂ evaporation yield.

Figure 4.- Arrhenius plot of the evaporation rate of organometallic precursors Y(thd)₃, Cu(thd)₂ and Ba(thd)₂ measured in the MOCVD setup.

Evaporation rates were obtained directly in the MOCVD setup by measuring the mass differences before and after a deposition run. Figure 4 shows the Arrhenius plot of the evaporation rates versus the reciprocal temperature of the Y(thd)₃, Cu(thd)₂ and Ba(thd)₂ precursors. Apparent activation energies of 135 and 111 KJ/mol for the Y and Cu precursors respectively, could be attributed, similar to those obtained by Yuhya et al.[5]. The mass losses were measured for the Ba(thd)₂ precursor in a 2hr run and 100 mg mass charge. A depletion in the apparent activation energy

was observed at temperatures above 250°C because the saturation mass, unable to evaporate, has been reached.

YBa₂Cu₃O_{7-x} thin films were obtained on YSZ(100) substrates. The deposition rate was 0.5 μm/h (1 μm film thickness). The average composition of the film was 1:1.5:2.4 as measured by microprobe analysis.

Figure 5 shows a SEM micrograph of the layer surface. Stepped morphology reveals an almost layer by layer growth habit. Some rectangular precipitates corresponding to a/b-oriented domains are clearly seen

Figure 5.- SEM micrograph of the surface of the YBCO layer grown on YSZ by MOCVD at 750°C

An XRD analysis of the layer is shown in figure 6. It can be seen that only (00h) and (h00) reflections are present in a θ -2 θ analysis. Layers are a mixture of c-axis and a-axis oriented domains perpendicular to the substrate surface. In the figure inset the rocking curve of the (006) reflection is shown. The FWHM is 1.4°. This reveals a high degree of orientation of the c-axis domains. The c parameter was evaluated in 11.677 Å from the average of the (00h) reflections, and the a parameter to 3.829 Å from the (h00) reflections.

Figure 7 shows the resistance of the layer as function of temperature. $T_c(R=0)$ is 88.2K and $T_{c\text{onset}}= 91.6\text{K}$. Above the critical temperature resistance is linear dependent and extrapolates to a nonzero value at $T= 0\text{K}$ probably due to the presence of a small amount of non-superconducting domains in the layer.

Figure 6.- XRD pattern of an YBCO film on YSZ(100). Substrate peaks were eliminated. The inset shows the rocking curve of the (006) reflection.

Figure 7.- Temperature dependence of electrical resistance for a YBCO/YSZ layer. The inset shows a magnified plot of the transition region

Conclusions

From the study of the evaporation process of organometallic precursors and the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ deposition we can conclude:

- 1.- $\text{Y}(\text{thd})_3$ and $\text{Cu}(\text{thd})_2$ present constant evaporation rates at least during the first 2hrs of an isothermal heating. $\text{Y}(\text{thd})_3$ shows a 3% mass loss in the heating up period. Activation energies were evaluated in 135 and 111 KJ/mol respectively.
- 2.- $\text{Ba}(\text{thd})_2$ presents an exponentially decreasing evaporation rate. Although, at temperatures up to 230°C, it could be considered that the $\text{Ba}(\text{thd})_2$ evaporation rate remains constant at least for 2h. This fact could be explained by the combination of a homogeneous evaporation and decomposition process. An activation energy of 56 KJ/mol could be assigned to the combined process up to 250°C. An increase in the evaporation temperature enhances the evaporation over the decomposition process.
- 3.- $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ were deposited on YSZ(100) substrates in a MOCVD reactor. Deposition rate was 0.5 $\mu\text{m/h}$.
- 4.- Layer morphology reveals a layer by layer growth habit.
- 5.- Films show a mixture of c-axis and a-axis orientation. The c parameter corresponding to the c-oriented domains was 11.677 Å, and the a parameter of the a-domains was 3.829 Å. The FWHM of the (006) rocking curve was 1.4°.
- 6.- Films were superconducting with $T_{\text{c onset}} = 91.6\text{K}$ and $T_{\text{c}}(R=0) = 88.2\text{K}$.

Acknowledgments

This work has been partially supported by a CICYT program (MAT 468/92) of the Spanish Government and the MIDAS program.

References

- [1] T. Hirai and H. Yamane, J. Cryst. Growth 107 (1991) 683-691
- [2] L.M. Tonge, D.S. Richeson, T.J. Marks, J. Zhao, J. Zhang, B. W. Wessels, H.O. Marcy and C.R. Kannewurf, Adv. in Chem. Series ISS 226 (1990) 351-368
- [3] M. Schieber, S.C. Han, Y. Ariel, S. Chokron, T. Tsach, M. Maharizi, C. Deutscher, D. Racah, A. Raizman and S. Rotter, J. Cryst. Growth 115 (1991) 31-42
- [4] E. Fitzer, H. Oetzmann, F. Schmaderer and G. Wahl, Journal de Physique IV, Colloque C2, suppl. au Journal de Physique II, vol 1 (1991) C2-713
- [5] S. Yuhya, K. Kikuchi, M. Yoshida, K. Sugawara and Y. Shiohara, Mol. Cryst. Liq. Cryst., vol.184 (1990) 231-235