JOURNAL OF MATERIALS SCIENCE 29 (1994) 99–102

# Preparation of YBCO superconductor thin film by spin-coating method with metal-organic precursors

S. C. FANG*‡, C. H. HUANG*, I. C. CHEN‡, C. F. LIAW‡, W.-M. HURNG‡
*Department of Chemistry, Soo Chow University, Shihlin, Taipei, Taiwan ‡Materials Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu 31015, Taiwan

YBCO thin film was prepared by the spin-coating method with metal-organic precursors. The precursors were synthesized by reacting metal acetates with 2-ethylhexanic acid or by reacting metal halides with ammonium 2-ethylhexanate directly. After proper heat treatments, YBCO film with $T_{c,\,onset} = 80$ K and $T_{c,\,zero} = 77$ K was obtained. SEM studies of a sample prepared at 990 °C showed the presence of CuO and $Ba_2YCuO_5$ (2 1 1 phase). This suggested the transient presence of a liquid phase which had been observed in preparing YBCO bulk material by the melt-texture method before the formation of YBCO phase. Furthermore, many voids were observed in the as-obtained film. These might be the origin of the relatively low $T_{c,\,zero}$ temperature.

## 1. Introduction

Since $La_{2-x}Ba_xCuO_4$ superconductor was discovered in 1987 [1], research activity on cuprate superconductors has been extremely high in both academic and industrial areas [2–6]. So far, more than 30 cuprates have been proved to be superconductors with various superconducting temperatures ($T_c$). Among them, YBCO ($YBa_2Cu_3O_{6+x}$ with $T_c \simeq 90$ K) has been well studied due to the ease of preparation of a pure phase and its early discovery. One of the most promising applications of this superconductor is in thin film form due to its high critical current ( $> 10^6$ A $cm^{-2}$) characteristics [7–9]. Many thin-film preparation methods such as chemical vapour deposition, sputtering and laser ablation were therefore adopted to prepare superconductor thin films from which devices could be made [10–15]. Among these methods, spin-coating is the least costly and most easily operated method although the film made by this way is in polycrystalline form [16, 17]. In this paper, we present the preparation of YBCO thin film by the spin-coating method with metal-organic (MO) precursors.

## 2. Experimental procedure

### 2.1. Preparation of precursors

MO precursors were prepared by the following two routes [18–20]:

(a) $$(CH_3COO)_aM + aRCOOH \xrightarrow[C_2H_5OH]{RH} (RCOO)_aM + aCH_3COOH$$

(b) $$NH_4OH + RCOOH \longrightarrow RCOONH_4 + H_2O$$

$$MX_a + aRCOONH_4 \longrightarrow M(RCOO)_a + aNH_4X$$

In route (a), metal acetate was mixed with 2-ethylhexanic acid according to the right stoichiometry and dissolved in anhydrous ethanol. The ethanol was then evaporated by using a hot-water bath, and refilled again until all the acetic acid was removed. The product was extracted by using *p*-xylene as solvent. In route (b), a suitable amount of ammonia was first mixed well with 2-ethylhexanic acid. Metal salts (chlorides or nitrates) were then added to the solution to form metal salts. The product was extracted from the mixture by using *p*-xylene as solvent and separated by a separation funnel. In our studies, yttrium precursor was prepared from route (a) while the barium one was synthesized from route (b). Copper precursor was purchased from Strem Chemical Co.

### 2.2. Determination of metal contents in the MO precursors

The yield of precursors from route (a) or (b) was always less than 60%, so the metal contents of precursors could not be derived from the starting materials directly. Even the commercially available product only provided a range of metal contents. Since the composition was a crucial requirement for superconductors, the actual metal contents of precursors were determined by using spectroscopy instead of thermal analysis results to improve the accuracy. First, a proper amount of precursor was weighed and put into a quartz crucible, then heated to 1000 °C under an oxygen atmosphere to remove all the organic components. After being identified by X-ray powder

0022-2461 © 1994 Chapman & Hall

diffraction, the heat-treated products were dissolved in dilute nitric acid and examined by induced coupled plasma (ICP) spectroscopy to determine metal contents.

### 2.3. Preparation of YBCO thin film

$(C_7H_{15}COO)_3Y$, $(C_7H_{15}COO)_2Ba$ and $(C_7H_{15}COO)_2Cu$ were mixed according to the following composition: $Y^{3+}:Ba^{2+}:Cu^{2+} = 1:2:3$, except for one reaction where the proportion of $Cu^{2+}$ was increased from 3.0 to 3.1. The concentration of the solution was adjusted by adding a suitable amount of *p*-xylene. The films were coated on MgO single-crystal substrates by using a spin-coater with a speed of 2000 r.p.m. and then heated at 500 °C to decompose organic components. After repeatedly coating and heating several times, a film with the desired thickness ( ~ 20 μm) was obtained. Eventually, the films were heated at various temperatures to form superconducting films. Three heating conditions were used to optimize the final product quality: 950 °C for 5 h and annealing at 500 °C for 5 h under oxygen (sample A); 960 °C for 5 h and annealing at 500 °C for 5 h under oxygen (sample B); and 990 °C for 5 h and annealing at 400 °C for 5 h under oxygen (sample C). In the last sample, the nominal copper composition was slightly increased from 3.0 to 3.1.

Thermal analyses including thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out in the air to study the thermal behaviour of precursors and decide proper calcination and sintering temperatures. An X-ray powder diffractometer (Shimazu XD3A with Cu$K_\alpha$ radiation) was used to monitor the reaction routes and confirm the products of samples. A four-probe resistance measurement was conducted to reveal the electrical properties of the samples. Scanning electron microscopy (SEM) (CamScan) with energy-dispersion spectroscopy (EDS) was utilized to examine the morphology of samples and identify impurity phases.

## 3. Results and discussion

### 3.1. Determination of metal contents in the MO precursors

The as-prepared yttrium, barium and copper precursors were analysed by ICP spectroscopy and the results are listed in Table I.

### 3.2. Thermal analysis studies of MO precursors

DTA and TGA results for the precursors are shown in Figs. 1 and 2, respectively, for the yttrium, barium and copper precursors. In the DTA results the copper precursor exhibited a sharp exothermic peak at 250 °C while relatively broad peaks were observed for yttrium and barium around 400 and 420 °C. Beyond 500 °C

TABLE I Metal content of metal-organic precursors derived from ICP analysis

| | Metal content (wt %) |
|---|---|
| Y precursor | 6.50 |
| Ba precursor | 9.96 |
| Cu precursor | 17.13 |

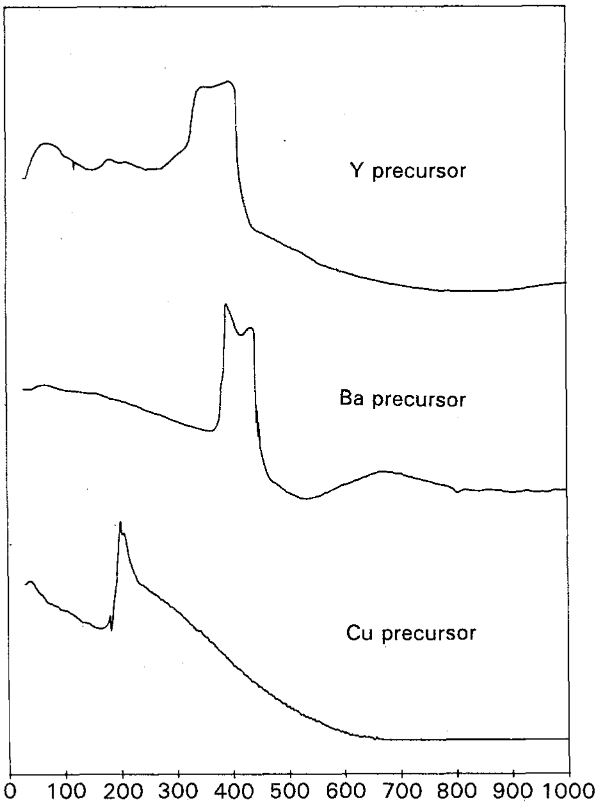

*Figure 1* DTA results for yttrium, barium and copper metal-organic precursors.

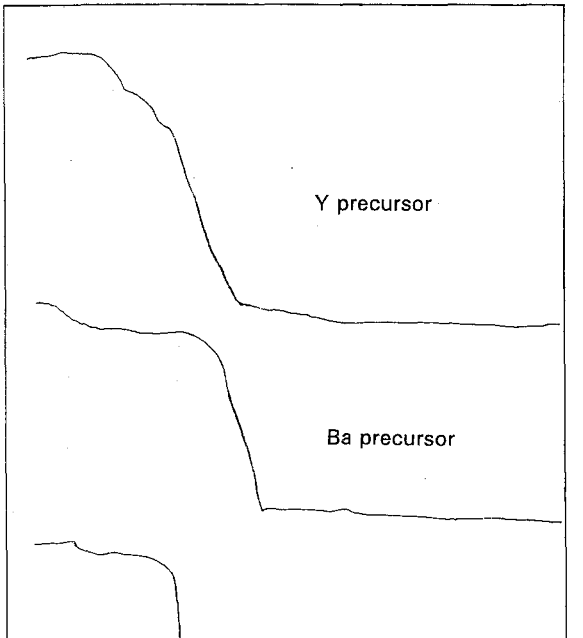

*Figure 2* TGA results for yttrium, barium and copper metal-organic precursors.

there were no peaks in the DTA spectra. Moreover, the TGA results showed a gradual weight loss until 500 °C. Thus the calcination temperature was set at 500 °C. The final products of precursors after the analysis were confirmed by X-ray diffraction (XRD) to be $Y_2O_3$, $BaCO_3$ and CuO as shown in Fig. 3.

### 3.3. Characterization of sintered samples

Sample A, B and C were characterized by XRD as shown in Fig. 4. Clearly, the major phase of the samples is YBCO phase with trace amounts of impurities. Preferred orientation phenomena were observed due to the MgO substrate effect. The temperature dependences of the resistance of the samples are depicted in Fig. 5. They all show metallic behaviour with $T_{c,\ onset}$ at 80 K and $T_{c,\ zero}$ at 77 K. A $T_{c,\ onset}$ lower than the reported $T_c$ of 90 K [5] might have resulted from insufficient oxygen content or poor connection between the grains in the samples. This point will be further discussed in the next section.

### 3.4. Microstructure of samples in different stages

Sample heating at 500 °C for 5 h yields flat, uniform and small grains (Fig. 6a) with a particle size less than 1 μm, while the grains in sintered samples became ~ 10 μm in size as shown in Fig. 6b for sample C. Also, voids and impurities are observed in the sintered samples. To emphasize the impurity phases, a back-scattering electron image of sample C was taken as shown in Fig. 6c. The impurity phases were confirmed by EDS analysis to be $Y_2BaCuO_5$ (2 1 1 phase) and CuO with irregular and rectangular shapes. This resulted from the decomposition of the sample to form 2 1 1 phase, CuO and a liquid phase which eventually generated a YBCO phase as the sample cooled down [21–23]. This phenomenon has been observed in the growth of YBCO bulk material by the melt-texture route. The melt-texture route had been shown to enhance the $J_c$ of the bulk material as well as maintaining the $T_c$ at 91 K. In our case, melting of the sample caused voids and impurity phases (such as 2 1 1 phase and CuO) due to the limited material products present in the substrate. The presence of voids and impurities inhibited the connection of the superconducting grains so that $T_c$ became lower than 90 K.

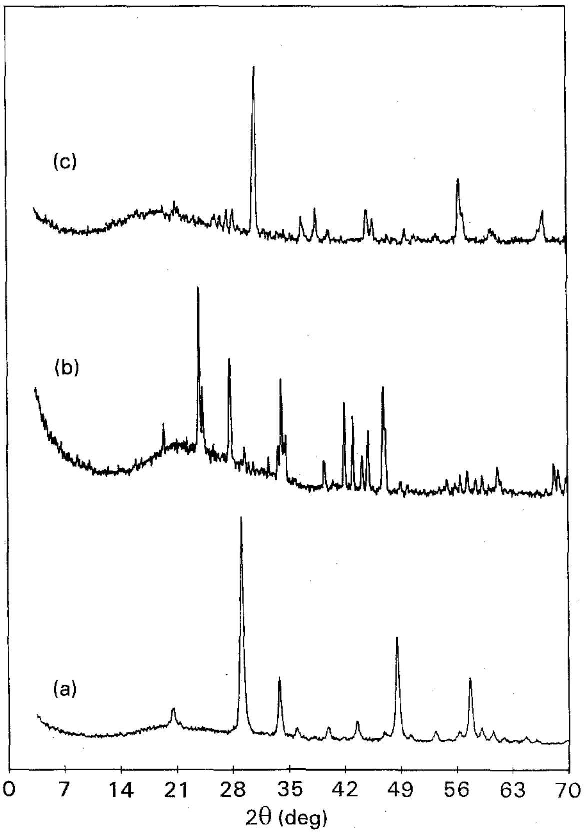

*Figure 3* XRD patterns of final products of precursors after thermal analysis. (a) $YO_x$, (b) $BaO_x$ and (c) $CuO_x$.

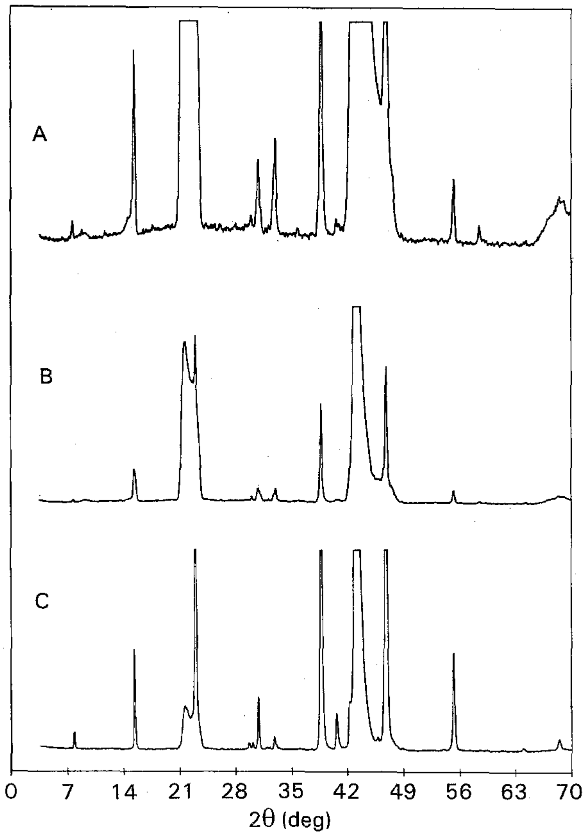

*Figure 4* XRD patterns of sintered samples A, B and C.

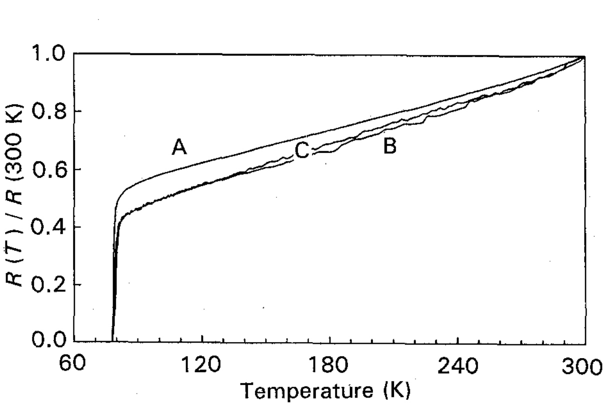

*Figure 5* Temperature dependence of resistance for samples A, B and C.

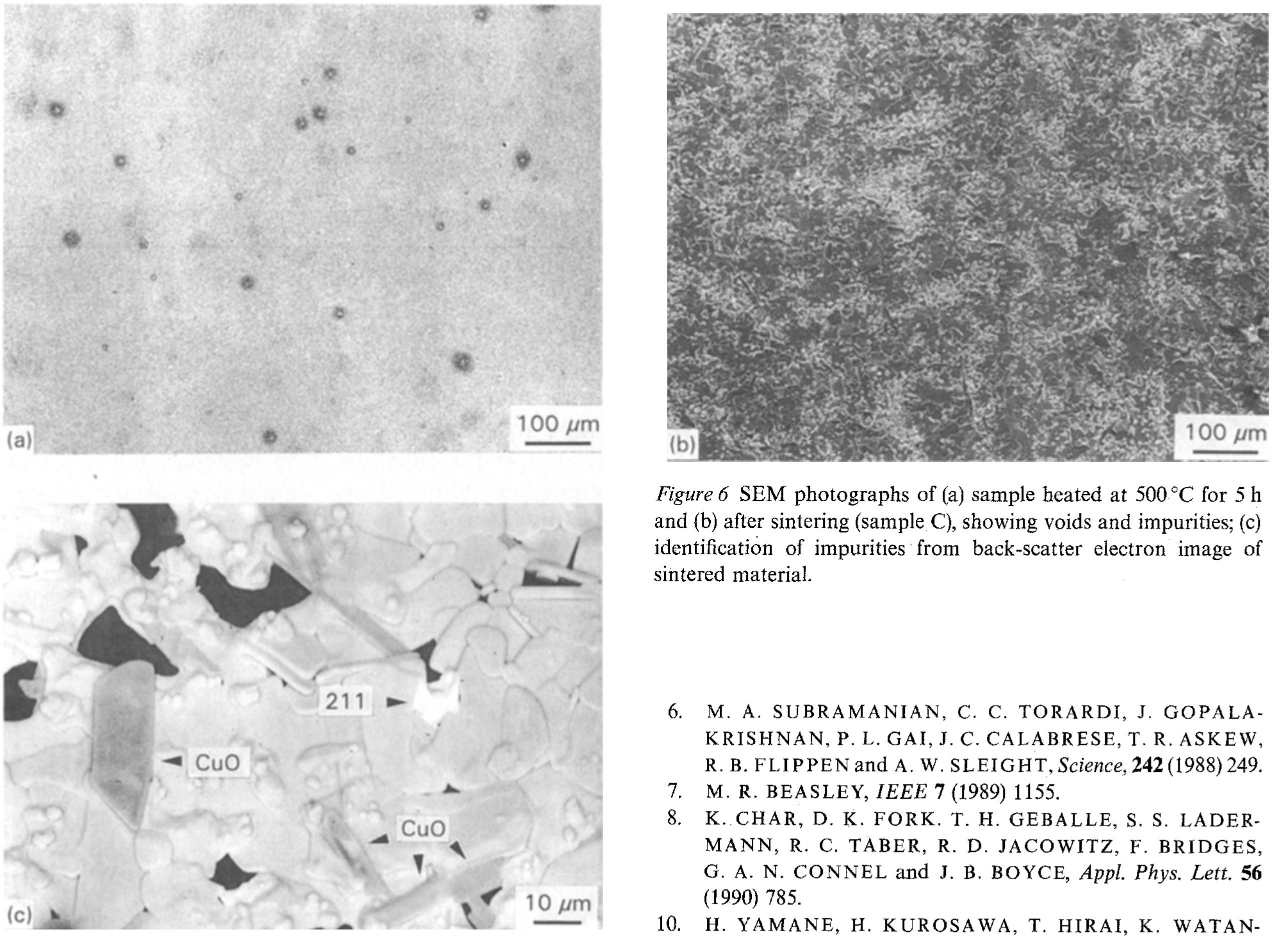

*Figure 6* SEM photographs of (a) sample heated at 500 °C for 5 h and (b) after sintering (sample C), showing voids and impurities; (c) identification of impurities from back-scatter electron image of sintered material.

## 4. Conclusions

A YBCO thin film has been successfully prepared by the spin-coating method from metal-organic precursors with $T_c \simeq 80$ K. This method is easy and economical compared to other delicate PVD or CVD thin-film processes. However, the relatively low $T_c$ which was caused by the melting of YBCO in the heat treatment needs further work to overcome it.

## Acknowledgement

This work was supported by the Ministry of Economic Affairs, Taiwan under contract No. 3 651 300 to ITRI.

## References

1. J. B. BEDNORZ and K. A. MÜLLER, *Z. Phys.* **B64** (1986) 189.
2. M. K. WU, J. R. ASHBURN, C. J. TORNG, P. H. HOR, R. L. MENG, L. GAO, Z. J. HUANG, Y. Q. WANG and C. W. CHU, *Phys. Rev. Lett.* **58** (1987) 908.
3. H. MAEDA, Y. TANAKA, M. FUKUTOMI and T. ASANO, *Jpn. J. Appl. Phys.* **27** (1988) L209.
4. Z. Z. SHENG and A. M. HERMANN, *Nature* **332** (1988) 55.
5. S. S. P. PARKIN, V. T. LEE, A. I. NAZZAL, R. SAVOY, R. BEYERS and S. J. LaPLACA, *Phys. Rev. Lett.* **61** (1988) 750.
6. M. A. SUBRAMANIAN, C. C. TORARDI, J. GOPALAKRISHNAN, P. L. GAI, J. C. CALABRESE, T. R. ASKEW, R. B. FLIPPEN and A. W. SLEIGHT, *Science*, **242** (1988) 249.
7. M. R. BEASLEY, *IEEE* **7** (1989) 1155.
8. K. CHAR, D. K. FORK. T. H. GEBALLE, S. S. LADERMANN, R. C. TABER, R. D. JACOWITZ, F. BRIDGES, G. A. N. CONNEL and J. B. BOYCE, *Appl. Phys. Lett.* **56** (1990) 785.
10. H. YAMANE, H. KUROSAWA, T. HIRAI, K. WATANABE, H. IWASAKI, N. KOBAYASI and Y. MUTO, *Supercond. Sci. Technol.* **2** (1989) 115.
11. K. WATANABE, T. MATSUSHITA, N. KOBAYASI, H. KAWABE, E. AOYAGI, H. YAMANE, H. KUROSAWA, T. HIRAI and Y. MUTO, *Appl. Phys. Lett.* **56** (1990) 1490.
12. X. Xi, G. LINKER, O. MEYER, E. NOLD, B. OBST, F. RATZEL, R. SMITHEY, B. STREHLAM, F. WESCHENFELDER and J. GREEK, *Z. Phys.* **B74** (1989) 13.
13. G. KOREN, A. GUPTA, E. A. GIESS, A. SEGMULLER and R. B. LAIBOWITZ, *Appl. Phys. Lett.* **54** (1989) 1054.
16. T. N. BOWMER and F. K. SCHOKOOHI, *J. Mater. Res.* **6** (1991) 670.
17. J. A. AGOSTINELLI, G. R. PAZ-PUJALT and A. K. MEHROTRA, *Physica C* **156** (1988) 208.
18. T. KUMAGI, H. YOKOTA, K. KAWAGUCHI, E. KONDO and S. MIZUTA, *Chem. Lett.* (1987) 1645.
19. C. E. RICE, R. B. van DOVER and G. J. FISANICK, *Appl. Phys. Lett.* **51** (1987) 1842.
20. H. NASU, S. MAKIDA, T. KATO, Y. IBARA, T. IMURA and Y. OSAKA, *Chem. Lett.* (1987) 2403.
21. A. H. HAMDI, J. V. MANTESE, A. L. MICHELI, R. C. O. LAUGAL, D. F. DUNCAN, Z. H. ZHANG and K. R. PADAMANBKAN, *Appl. Phys. Lett.* **51** (1987) 2152.
22. M. E. GROSS, M. HONG, S. H. LIOU, P. K. GALLAGHER and J. KWO, *ibid.* **52** (1987) 160.
23. R. W. VEST, T. J. FITZSIMMONS, J. XU, A. SHAIKH, G. L. LIEDL, A. I. SCHINDLER and J. M. HONG, *J. Solid State Chem.* **73** (1988) 283.

*Received 7 July 1992*
*and accepted 27 April 1993*