CHEMISTRY LETTERS, pp. 551-552, 1988.

Preparation of Superconducting $YBa_2Cu_3O_{7-\delta}$ Films by the Dipping-Pyrolysis Process Using Metal Acetylacetonates

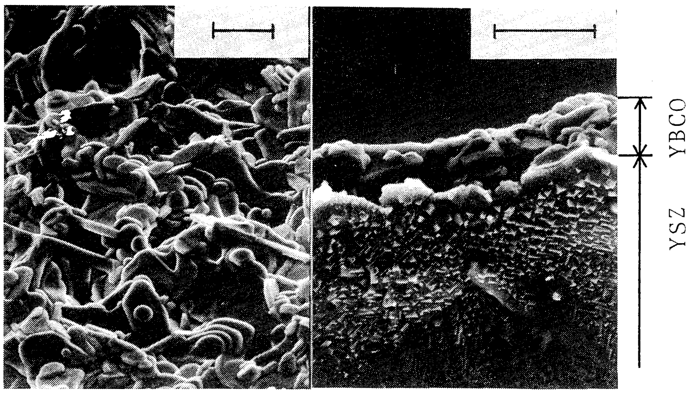
Toshiya KUMAGAI,* Wakichi KONDO, Hiroshi YOKOTA,† Hidehiro MINAMIUE,†† and Susumu MIZUTA*
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305
†Ebara Corp., 11-1, Haneda-asahi, Ohta, Tokyo 144
††Nihon Kagaku Sangyo Co., 2-20, Shitaya, Taito, Tokyo 110

Superconducting $YBa_2Cu_3O_{7-\delta}$ films were prepared on yttria stabilized zirconia substrates by the dipping-pyrolysis process using metal acetylacetonates (Y/Ba/Cu = 1.0/3.0/4.3) as starting materials; T_c(onset) of 97 K and T_c(end) of 89 K were achieved in the resistivity measurement for the films annealed at 950 °C in O_2.

Currently, the dipping-pyrolysis has widely been noticed as a simple and convenient process to prepare the thin films of the superconductor $YBa_2Cu_3O_{7-\delta}$ (YBCO). Metal organic acid salts such as stearates,[1] naphthenates,[1,2] laurates,[3] or 2-ethylhexanoates[4] have been so far reported as starting materials.

As results of the X-ray diffraction, Auger electron spectroscopy, and thermal analyses (TG and DTA) on the pyrolysis process of those organic acid salts and the subsequent reactions among Y_2O_3, $BaCO_3$, and CuO, the present authors have found out the following problems: (i) reduction of copper ion to metal copper by the higher hydrocarbons evolved in the pyrolysis process; (ii) differences in pyrolysis temperatures among Y, Ba, and Cu organic acid salts which may cause the heterogeneous segregation of (Cu, Cu_2O, CuO), Y_2O_3, and $BaCO_3$; (iii) formation of $BaCuO_2$ phase[5] above 800 °C; and (iv) diffusion of Ba^{2+} into the substrates. In this work Y-, Ba-, and Cu- acetylacetonates (acac's) were used as starting materials to solve the problems (i) and (ii) since the numbers of carbon contained in these acac's are far smaller and their pyrolysis temperatures are closer to one another than those of Y, Ba, and Cu organic acid salts. Starting mixing ratio of Y/Ba/Cu was also set at 1.0/3.0/4.3 to correct the deviation of the metal composition associated with the problems (iii) and (iv).

The starting materials, i.e., acac powders of Y, Ba, and Cu, all from Nihon Kagaku Sangyo Co., with chemical pure grade, were dissolved in a mixture of pyridine (Py) and propionic acid (PA), Py/PA = 5/3 in volume ratio, to make homogeneous solutions (~10 wt%) with molar ratios, (A) Y/Ba/Cu = 1.0/2.0/3.0 and (B) 1.0/3.0/4.3. The mixed solutions were coated on YSZ (10 mol% Y_2O_3) substrates, dried in air and in an oven at 110 °C for 10 min, and pyrolyzed in air for 10-20 min at 500-700 °C. After this procedure was repeated 20 times to increase film



(a) (b)

Fig. 1. SEM photographs of YBCO films with starting mixing ratio Y/Ba/Cu = 1.0/3.0/4.3, annealed at 950 °C in O_2. (a) free surface, (b) fractured surface. Scale bars are 5 μm.

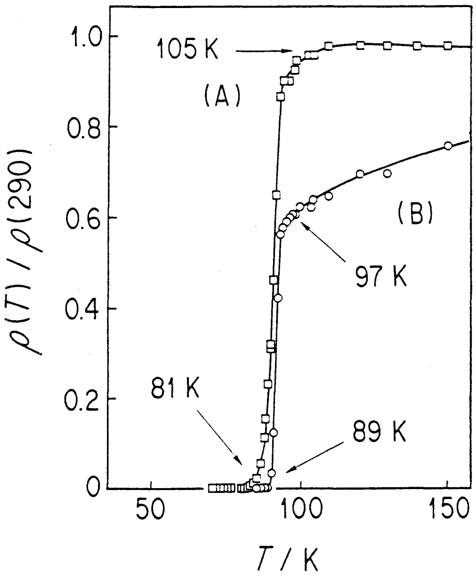


Fig. 2. Resistivity vs. temperature relationship for the YBCO films annealed at 950 °C in O_2. (A) Y/Ba/Cu = 1.0/2.0/3.0, annealed for 10 min; (B) 1.0/3.0/4.3, annealed for 20 min.

thickness, the films were subjected to annealing in pure oxygen at 950 °C for 10-30 min, followed by gradual cooling. The films thus prepared gave XRD patterns corresponding to the orthorhombic YBCO phase. Both free and fractured surfaces of these YBCO films were observed by SEM, Fig. 1. One may easily find the remarkable grain growth on the free surface as well as the considerable densification inside the film. The thickness was also observed 3-6 μm. Resistivities (ρ's) of these films were measured by the dc four probe method as shown in Fig. 2. The specimen with the starting molar ratio of Y/Ba/Cu = 1.0/3.0/4.3 gave the T_c(end) of 89 K, while that with 1.0/2.0/3.0 the T_c(end) of 81 K. The temperature dependence was mostly metallic.

Based on the results described above, it is concluded that the 90 K class YBCO films are successfully prepared by the dipping-pyrolysis process using metal acetylacetonates.

The authors would like to thank Drs. I. Kojima and M. Kurahashi of NCLI for the AES measurement on YBCO films.

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(Received December 25, 1987)