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Preparation of Superconducting Y-Ba-Cu-O Films by Aerosol Assisted Chemical Vapor Deposition Using Liquid Solution Sources

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Abstract−Superconducting Y-Ba-Cu-O thin films were prepared on MgO(100) substrate by aerosol-assisted chemical vapor deposition (AACVD). The process used a single solution source of Y, Ba and Cu β-diketonates dissolved in tetrahydrofuran (THF). This liquid precursor was passed through an ultrasonic aerosol generator and transported into a CVD reactor where solvent and precursor evaporation and deposition occurred on heated substrate. Experimental details of this process were described and the effects of preheating temperature were studied in order to improve the quality of the deposited films. When the preheating temperature was 380 °C, films deposited at 815 °C had sharp transitions to the superconducting state about 88 K. The best superconducting films deposited by AACVD were prepared in oxygen partial pressure of 3.2 Torr at a deposition temperature of 815 °C.

Key words: Y-Ba-Cu-O Thin Film, AACVD, Liquid Source

INTRODUCTION

Since the discovery of superconducting oxides, enormous amounts of research have been conducted for the preparation of high temperature superconductor (HTS) $Y_1Ba_2Cu_3O_{7-x}$ (YBCO) thin films. The fabrication of superconducting thin films with specific properties generally needs controlled chemical compositions and growth rates to produce high quality films. For film growth with these characteristics two types of techniques have been performed: the group of physical vapor deposition (PVD) techniques including molecular beam epitaxy (MBE), sputtering, and laser ablation; and the versatile class of methods represented by chemical vapor deposition (CVD) techniques [Cho and Shin, 1993]. Among these, CVD is expected as a promising technique for the practical application of HTS films, having special merits, such as a high deposition rate, the possibility of a long time deposition, no limitation of the shape and the scale.

Although the CVD process possesses many kinds of merits, there have still been various problems because of the lack of easy handling, stable precursors [Yoshida et al., 1996], particularly for alkaline earth metals such as barium, the relatively high processing temperature, and the large number of parameters that must be controlled to maintain stoichiometry during the period of deposition. Until recently, hydrocarbon based β-diketone chelate precursors such as $Ba(thd)_2$ (thd=2,2,6,6-tetramethyl-3,5-heptanedionate) have been used for fabrication of HTS films by CVD. The barium derivative, $Ba(thd)_2$, has been found to have an irreproducible and variable transport rate because of gas phase and solid state oligomerization and/or hydrolysis reactions. Because of the long residence time in the sublimation vessels and plumbing, the stability of the precursors is critical in maintaining deposition rate and stoichiometry under control. To solve the problems associated with the thermal decomposition of the source materials over a long time, that the $Ba(thd)_2$ appears to have, we have developed new precursors with sufficient and stable volatility. We refer to this as aerosol-assisted CVD (AACVD), which uses a single liquid solution source for the fabrication of YBCO films. This technique minimizes the residence time at high temperature that any of the precursors must survive before deposition [Salazar et al., 1992]. In AACVD of YBCO, the solution of precursors dissolved in a suitable solvent is introduced into an ultrasonic aerosol generator. The aerosol is then transported into the preheated zone of the reactor, where the temperature is maintained sufficiently high. The solvent chosen to dissolve the precursors must be unreactive with the precursor and at the same time must have a sufficiently high vapor pressure to be completely evaporated at the temperature of the preheating zone [Klippe and Wahl, 1997].

In the present paper, we reported preparation of YBCO thin films by AACVD method, focusing on the effects of the preheating temperature using a new single-source technique.

EXPERIMENTAL

The ranges of condition for deposition are summarized in Table 1. Fig. 1 shows a schematic diagram of the AACVD apparatus. This system consists of four parts: a feed system/vaporizer that supplies and evaporates the precursor solution continuously, preheating system, deposition system, and exhaust system. The deposition of YBCO by the AACVD process was accomplished by a THF (tetrahydrofuran) mixed single solution of β-diketone chelates of $Y(thd)_3$, $Ba(thd)_2$ and $Cu(thd)_2$ (thd=2,2,6,6-tetramethyl-3,5-heptanedionate) (Strem Co., Ltd., USA). The precursor solution was kept outside the vacuum system in a reservoir, from which it was continually fed by a mass flow controller (MFC) into the system. The molar ratio of the precursors, Y : Ba : Cu, was 1 :

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Table 1. Deposition conditions of Y-Ba-Cu-O thin films prepared by AACVD

Source materials	$Y(thd)_3$, $Cu(thd)_2$, $Ba(thd)_2$
Solvent	THF (tetrahydrofuran)
Molar ratio of precursors	1 : 1.8 : 2.7
Injection rate of solution	0.2 ml/min
Flow rate of carrier gas (Ar)	600 sccm
Flow rate of reactant gas (O_2)	400 sccm
Total pressure	8.0 Torr
Deposition temperature	815 °C
Pre-heating temperature	270-400 °C
Deposition time	30 min

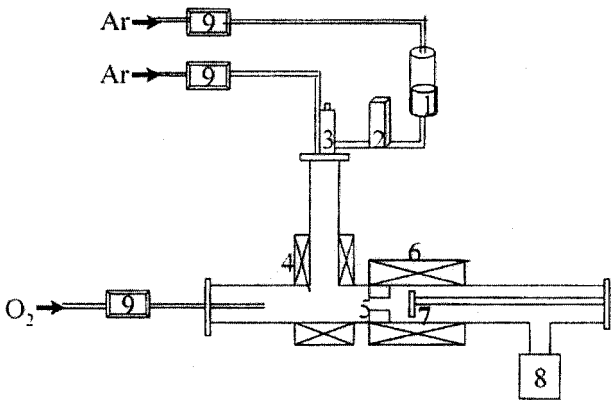

Fig. 1. Schematic diagram of AACVD system.

1. Precursor solution
2. L-MFC
3. Atomizer
4. Preheater
5. Nozzle
6. Furnace
7. Substrate
8. Pump
9. MFC

1.8 : 2.7 and the precursor solution was transformed into a mist by an aerosol generator at a constant rate of 0.2 ml/min. The mist was then transported, with a carrier gas of Ar, to the preheating zone, prior to entering the deposition area. The preheat zone was heated at 270-400 °C during deposition. Deposition of films was performed on MgO(100) substrate placed normal to the gas stream at 815 °C.

In the case of forming YBCO films by AACVD process using single precursor solution, the following reaction is proposed:

$$Y(thd)_3+2Ba(thd)_2+Cu(thd)_2+2THF+206O_2 \rightarrow Y_1Ba_2Cu_3O_{7-x}+119CO_2+123.5H_2O$$

The films were characterized by X-ray diffraction (XRD) using Cu-K_α radiation. Zero-resistance T_c was measured by the dc four-probe method. Surface morphology of the films prepared at various preheating temperatures was investigated by scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

We fabricated YBCO thin films using a liquid source. YBCO thin films were prepared on MgO(100) substrate, changing preheating temperature with the total gas pressure and flow rate kept at 8 Torr and 1,000 sccm, respectively. Fig. 2 shows a change of the

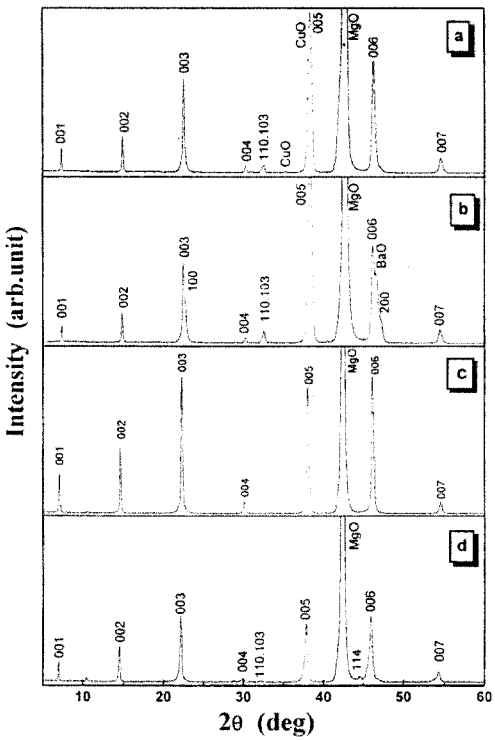

Fig. 2. X-ray diffraction patterns for the films prepared at various preheating temperatures of (a) 270 °C, (b) 300 °C, (c) 380 °C, and (d) 400 °C.

X-ray diffraction patterns by a θ-2θ method using Cu-K_α radiation as a function of preheating temperature. The strong c-axis peaks from YBCO(00*l*) were mainly observed, in addition to slight a- or b-axis peaks, and a very small peak from CuO was also revealed. We could obtain a good, c-axis-oriented YBCO film at a deposition temperature of 815 °C when the preheating temperature was 380 °C. The scanning electron micrographs of YBCO thin films prepared at deposition temperature 815 °C for 30 min are shown in Fig. 3. Sample (c) shows a smooth ground surface of c-axis oriented YBCO containing small holes. Sample (d) shows some precipitations on its surface. The effects of temperature on electrical resistivity are shown in Fig. 4. Sample (c) with the highest T_c (=88 K) shows an onset transition temperature above 92 K, and the transition width (ΔT) is small (about 4 degrees). Sample (d) shows broad transition width (about 10 degrees) that might be related to factors including poor interconnectivity of the grains and voids.

YBCO thin films were deposited on MgO(100) substrate as a function of substrate temperature (T_s) and oxygen partial pressure (P_{O2}) with the total gas pressure and volumetric flow rate kept at 8 Torr and 700 sccm, respectively. Fig. 5 shows the X-ray diffraction patterns by the θ-2θ method as a distance between the nozzle and the substrate. The strong c-axis peaks from YBCO(00*l*) were mainly observed, in addition to a slight a- or b-axis peaks. A very small peak from BaO and CuO was also revealed. We could obtain a good, c-axis-oriented YBCO film at 2 cm away from the nozzle when the substrate temperature was 815 °C.

Fig. 6 shows the XRD patterns of YBCO films prepared at a temperature of 815 °C and an oxygen partial pressure between 2.25 to 4.5 Torr. We could obtain a good, c-axis oriented YBCO film

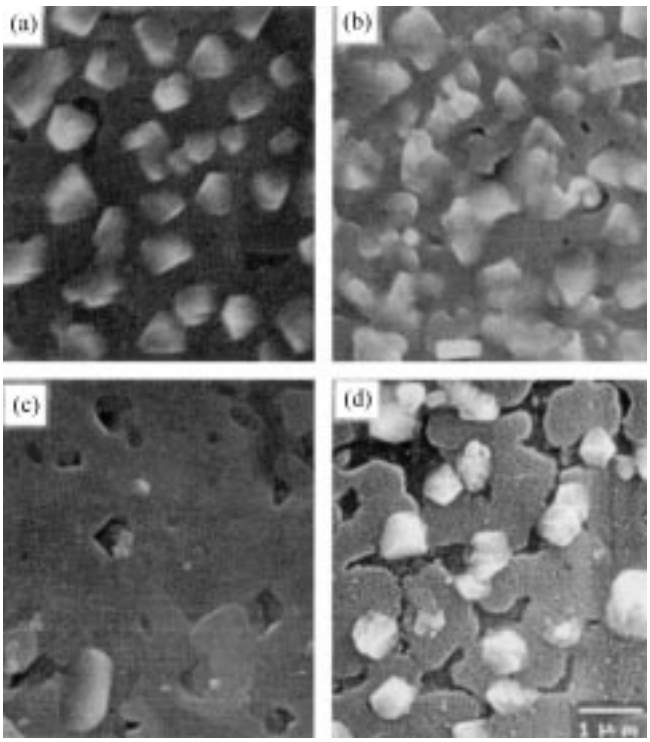

Fig. 3. Surface SEM micrographs of the thin films prepared at various preheating temperatures of (a) 270 °C, (b) 300 °C, (c) 380 °C, and (d) 400 °C.

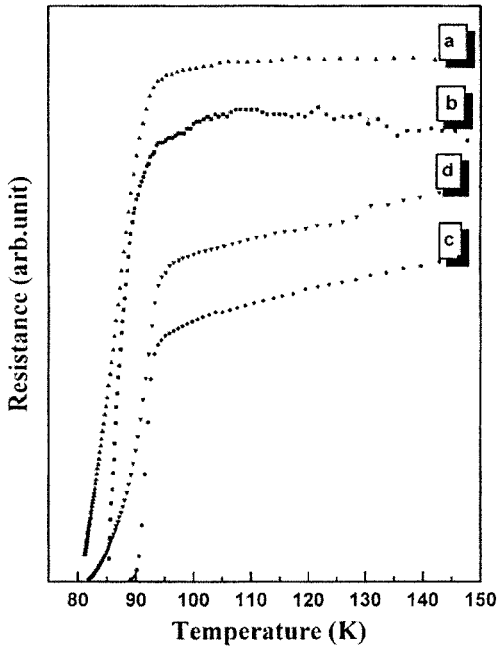

Fig. 4. Temperature vs. electrical resistance for the films prepared at various preheating temperatures of (a) 270 °C, (b) 300 °C, (c) 380 °C, and (d) 400 °C.

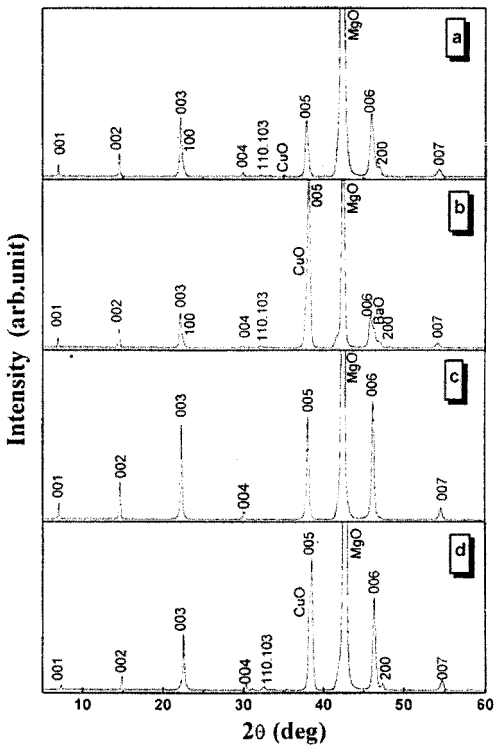

Fig. 5. X-ray diffraction patterns for the films. The interval between the nozzle and the substrate was (a) 0 cm, (b) 1 cm, (c) 2 cm, and (d) 3 cm.

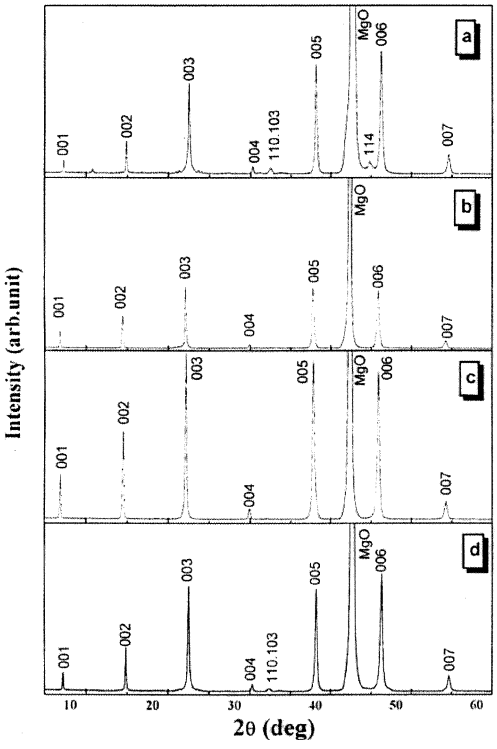

Fig. 6. X-ray diffraction patterns for the films prepared on MgO (100) substrates at various oxygen partial pressures of (a) 2.28 Torr, (b) 2.4 Torr, (c) 3.2 Torr, and (d) 4.2 Torr.

when the P_{O2} value was 2.4-3.2 Torr. The scanning electron micrograph of YBCO thin films prepared at 815 °C for 30 min are shown in Fig. 7. The rough surface and the large precipitates were observed in the film deposited at P_{O2} below 2.4 Torr. Sample (c) showed a smooth ground surface of c-axis oriented YBCO containing small holes. Sample (d) showed some precipitations on its

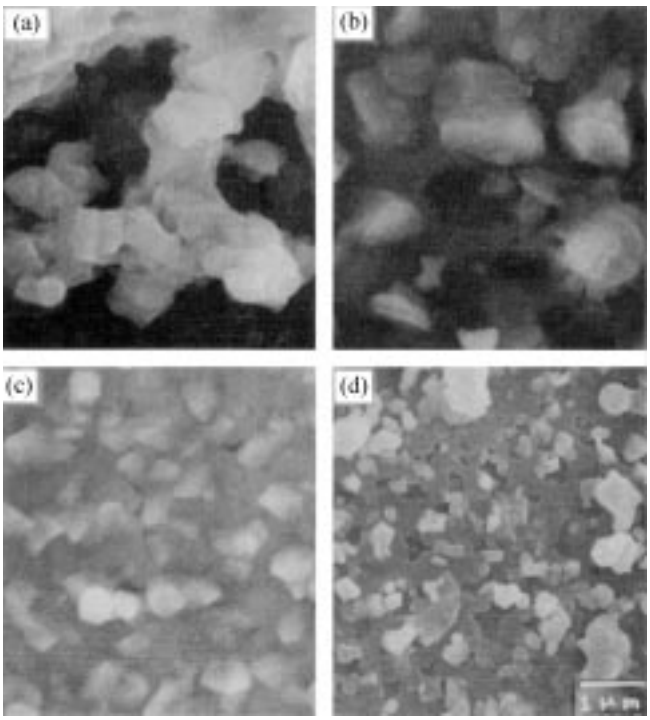

Fig. 7. Surface SEM micrographs of the thin films prepared on MgO(100) substrates at various oxygen partial pressures of (a) 2.28 Torr, (b) 2.4 Torr, (c) 3.2 Torr, and (d) 4.2 Torr.

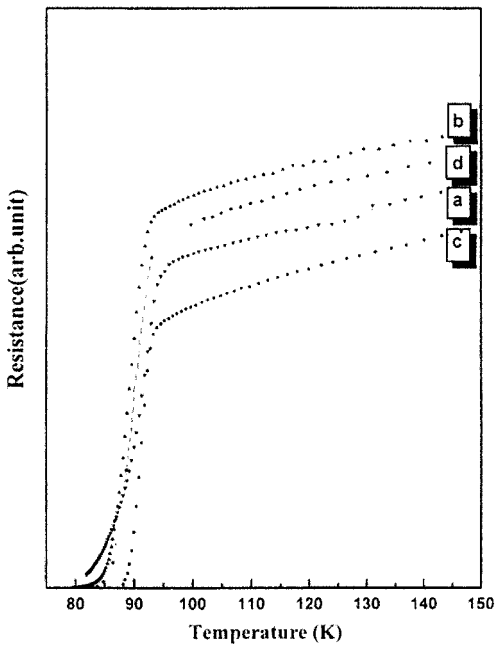

Fig. 8. Temperature vs. electrical resistance for the films prepared on MgO(100) substrates at various oxygen partial pressures of (a) 2.28 Torr, (b) 2.4 Torr, (c) 3.2 Torr, and (d) 4.2 Torr.

surface. It indicates P_{O2} has a strong influence on the properties of YBCO film. The temperature dependences of electrical resistivity are shown in Fig. 8. Sample (c) with the highest Tc (=87 K) shows an onset transition temperature ($T_{c,\,onset}$) above 90 K, and the transition width ($\Delta T=T_{c,\,onset}-T_{c,\,zero}$) is small (about 3 degrees). Samples (b) and (d) show broad transition width (about 6 degrees), that might be related to factors including poor interconnectivity of the grains and voids.

CONCLUSION

Aerosol-assisted CVD (AACVD) has been developed for preparing c-axis oriented superconducting YBCO thin films using THF (tetrahydrofuran) mixed single solution of β-diketone chelates of $Y(thd)_3$, $Ba(thd)_2$ and $Cu(thd)_2$. The process involves forming an aerosol of a precursor solution to transport into a CVD reactor. When the preheating temperature was 380 °C, films deposited at 815 °C had sharp transitions to the superconducting state about 88 K. The best superconducting films deposited by AACVD were prepared in oxygen partial pressure of 3.2 Torr at a deposition temperature of 815 °C.

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