〈연구논문〉

Formation of $YBa_2Cu_3O_{7-x}$ Superconducting Film on (100) MgO Substrate by a Spray Pyrolysis Method

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용액분무법으로 MgO (100) 면에 제조한 $YBa_2Cu_3O_{7-x}$ 초전도 박막

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Abstract — $YBa_2Cu_3O_{7-x}$ superconducting thin films were prepared on (100) MgO single crystal substrates by the spray pyrolysis method. The atomic concentration of Y, Ba and Cu in the film is 1 : 2 : 3 within the detection limit of energy dispersive X-ray analysis (EDX), which is the same as that in the starting solution. The X-ray diffraction pattern shows that the structure of the film is a single orthorhombic phase. It is also shown that the film is oriented along the c-axis perpendicular to the substrate. The onset (T_{c-on}) and completion (T_{c-zero}) of superconductive transition occur at 103 K and 80 K for the samples annealed at 950℃ in the flowing O_2 atmosphere, and they occur at 100 K and 80 K for the samples annealed in air. The microstructures, the grain size and the width of the grain boundary seem to be influenced strongly by the annealing ambient.

요 약 — 용액분무법으로 (100) MgO 단결정 기판위에 $YBa_2Cu_3O_{7-x}$ 초전도박막을 제조하였다. $YBa_2Cu_3O_{7-x}$ 초전도 박막의 Y, Ba, Cu 원자의 상대적인 비는 EDX의 검출 한계내에서 1 : 2 : 3이었고, 이는 분무 용액속의 금속이온의 비와 같았다. $YBa_2Cu_3O_{7-x}$ 초전도 박막의 결정구조는 단일 상의 사방구조이었으며, 기판에 수직인 c축 방향으로 grain이 성장되었고, 격자상수 c_o는 11.678 Å였다. 950℃ 의 공기중에서 10분간 열처리한 박막의 T_{c-on} = 100 K, T_{c-zero} = 80 K, J_c = 2.5 × 10⁴ A/cm²였고, 950 ℃ 의 흐르는 산소분위기에서 10분간 열처리한 박막의 T_{c-on} = 103 K, T_{c-zero} = 80 K, J_c = 1.0 × 10⁵ A/cm² 였다. $YBa_2Cu_3O_{7-x}$ 초전도 박막의 미세구조, grain 크기와 grain 경계폭은 제조후 열처리(post-annealing) 시간과 가스 분위기에 강한 영향을 받았다.

1. Introduction

Since the discovery of superconductivity at high temperature in rare and alkaline earth copper perovskites, the deposition of these materials in thin film forms has been demonstrated by a number of research groups[1-14]. The effort to make a film of $YBa_2Cu_3O_{7-x}$ superconductor phase has been one

of the most important approaches for utilization of these materials. Spary pyrolysis processing offers an inexpensive, non-vacuum, chemical method for thin film preparation with the potential to coat large-area substrates. Recently, reports on spray pyrolized films deposited from an ultrasonically nebulized solution have demonstrated improvements in film thickness control and film properties[15, 16]. This method enables accurate control of the film stoichiometry and produces films of reproducible properties. Ultrasonic nebulization also offers advantages over conventional pneumatic sprayers in that finer droplet sizes with a narrower droplet size distribution are achieved. This results in· better control of the thermal decomposition of the droplet to yield deposition of a homogeneous film.

In this paper we have investigated the deposition of $YBa_2Cu_3O_{7-x}$ thin films on (100) MgO single crystal substrates by the ultrasonic nebulization and spray pyrolysis method. The films were characterized by X-ray diffraction, EDX, SEM, and transport properties measurements. The effect of deposition and annealing conditions on film crystallinity and transport properties are presented.

2. Experimentals

The $YBa_2Cu_3O_{7-x}$ films have been prepared in three consecutive steps. A mixed nitrate powder of Y, Ba and Cu with stoichiometric amounts of Y_2O_3 (Aldrich, 99.99%), $BaCO_3$ (Aldrich, 99.98%) and CuO (Aldrich, 99.99%) in the atomic ratio of Y : Ba : Cu＝ 1 : 2 : 3 were dissolved in a dilute nitric acid. After the nitrates had been formed, the nitrates were dried by evaporating any excess nitric acid and water using a rotary vacuum evaporator. This procedure, rather than starting from the nitrates precursors directly, in necessary in order to avoid uncertainty in the stoichiometry due to the unknown water content in the nitrates. A 0.01 M solution of the mixed nitrates was then prepared by adding the second distilled water. The solution in a flask was nebulized by an ultrasonic vibrator and then sprayed onto the (100) MgO substrate, which was kept at 300℃ in an electric furnace using a carrier gas (air or O_2). This nebulization and spray pyrolysis system

was manufactured in our laboratory (see details in Fig. 1). In the next step the nitrate film on (100) MgO substrate was preheated in air for 15 min at 500℃. The nitrates were therefore decomposed into the oxides by deaquation and denitration in the preheating process. The cycle of spraying and preheating was repeated 2 or 3 times in order to make a thicker and homogeneous film. Post-annealing in an air or flowing oxygen atmosphere is dedicated for the third step. The heat treatment schedule is as follows (see Fig. 2): The preheated films were annealed at temperatures up to 950℃ for 10 min in an air or flowing oxygen atmosphere. After the heat treatment, samples were cooled down to 500℃, and then annealed again at this temperature for 2 or 3 hours. After the samples were cooled down to room temperature they were removed from the electric furnace.
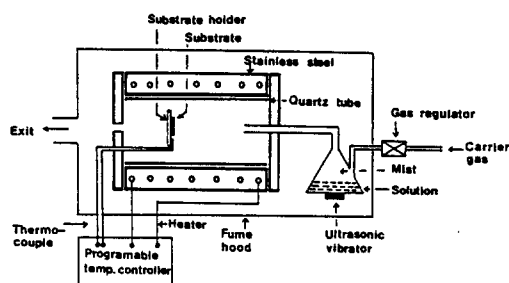

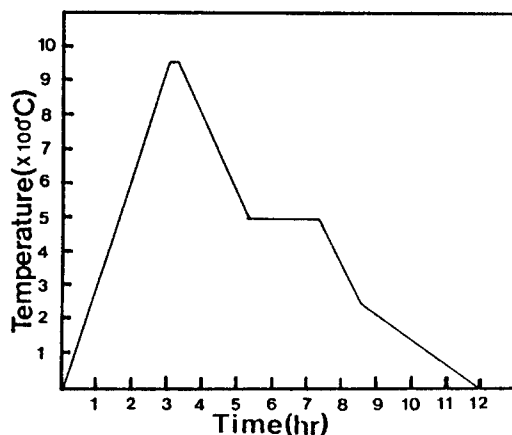**Fig. 1.** Schematic drawing of the simple spray pyrolysis system.

Fig. 2. Heat treatment schedule of the preheated samples.

X-ray diffraction in θ-2θ was used to investigate the crystallinity of the samples. The superconducting transition temperature (T$_c$) of the film was determined from the resistivity measurement carried out in the temperatures ranging from 300 K to 10 K by a standard four-point probe method. J$_c$ was determined by measuring current-voltage curve using same method for resistivity measurement. The surface morphology and the film thicknesss was measured by scanning electron microscopy (SEM) and the stoichiometry of the film was determined by energy dispersivee X-ray analysis (EDX).

3. Results and Discussion

The thickness of the as-sprayed nitrate film was found to be 6~8 μm by SEM observation. X-ray diffraction patterns of the films formed in each step are shown in Fig. 3. The X-ray diffraction spectrum of the as-sprayed sample showed that the film is not YBa$_2$Cu$_3$O$_{7-x}$ but mixed BaCuO$_2$ and Ba(NO$_3$)$_2$ crystallites (Fig. 3(a)). Diffraction peaks of yttrium nitrate are not observed, but it is probably present at an amorphous phase. The X-ray diffraction patterns of the preheated films show a peak of CuO and Y$_2$O$_3$ (Fig. 3(b)). Some other peaks could not be positively identified, though they belong to the hydrate phase of barium oxide or a mixed phase. The X-ray diffraction patterns of films annealed at 950℃ for 10 min in an air or in flowing oxygen are shown in Fig. 3(c) and 3(d), where peaks for the orthorhombic superconducting phase of the YBa$_2$Cu$_3$O$_{7-x}$ can easily be identified and no obvious difference was found between them. The lines due to diffraction from the (002), (003), (004), (005), (006), and (007) planes are strongly detectable. The thickness of the YBa$_2$Cu$_3$O$_{7-x}$ thin film was found to be 3~5 μm. The position and the intensity of each line is in good agreement with those for the (00l) lines[17], which implies that an oriented superconducting thin film of YBa$_2$Cu$_3$O$_{7-x}$ with its c-axis perpendicular to the surface of (100) MgO substrate is formed. The lattice constant c$_o$ calculated from the X-ray diffraction patterns of (00 l) lines was 1.678 Å, which is the same value as that reported in the previous studies[18].
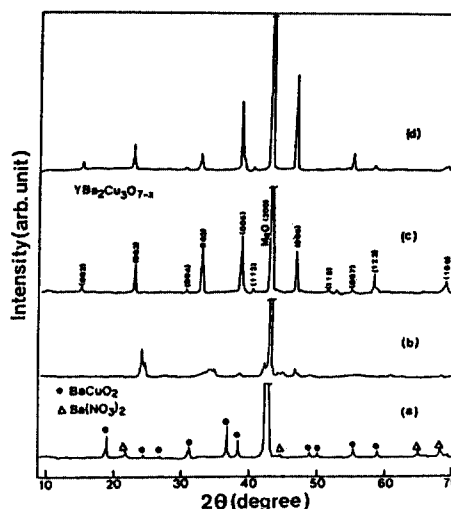

Fig. 3. X-ray diffraction patterns of the sample, (a) as-sprayed, (b) after preheating at 500℃ for 15 min in air, and (c) after annealing at 950℃ for 10 min in air and (d) after annealing at 950℃ for 10 min in the flowing O$_2$ ambient.

The resistivities of the samples measured at RT are ρ ~150~200 mΩ-cm, which are slightly higher than those reported by Miller et al.[19], and Cukauskas et al.[20]. The temperature dependence of resistivities of the samples shows that the film is either metallic or semiconducting. One group (samples post-annealed in flowing O$_2$ ambient) shows metallic behavior, and another (samples post-annealed in air) shows semiconducting behaviour above the superconducting transition. Two representative resistivity-temperature profiles are shown in Fig. 4. Curve (a) in Fig. 4 indicates the semiconducting behavior and curve (b) stands for the metallic behavior. Sample 1 (curve (a)) shows a sharp superconducting transition with onset (T$_{c-on}$) at 100 K and completion (T$_{c-zero}$) at 80 K, and sample 2 (curve (b)) shows a superconducting transition with a T$_{c-on}$ at 103 K and a T$_{c-zero}$ at 80 K. The critical current density (J$_c$) of the films measured at 77 K are 2.5×10^4 A/cm^2 and 1.0×10^5 A/cm^2 for sample 1 and 2, respectively. The onset and completion temperatures of our samples are, within our knowlege, higher than in any other reports using a similar method[21], but the value of J$_c$ is nearly the same as that reported by Gupta et al.[22]. There
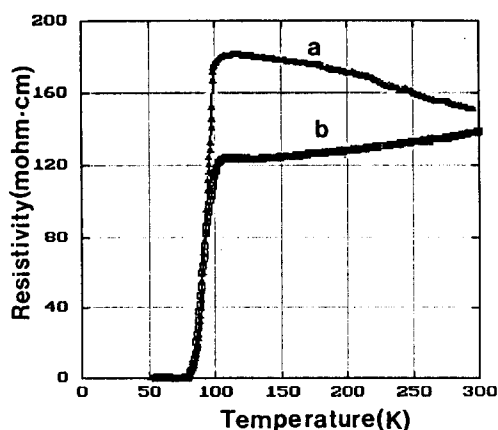
Fig. 4. Temperature dependence of resistivity of YBa_2 Cu_3O_{7-x} superconducting films, (a) annealed in air and (b) annealed in the flowing O_2 atmosphere.

Fig. 5. Surface morphologies of $YBa_2Cu_3O_{7-x}$ superconducting films, (a) annealed in air and (b) annealed in the flowing O_2 atmosphere.

might to be three reasons leading to the difference in J_c of samples 1 and 2: (1) difference in oxygen content in the Cu-O of orthorhombic structure; (2) the difference in orientations of grains; (3) the effect of grain boundaries. According to Wang *et al.*[23] oxygen content can be estimated by the difference of the lattice constant (b-a)/b. The values were determined by X-ray diffraction and are 0.0175 and 0.0181 for sample 1 and 2, respectively, and the difference is within experimental error. Therefore (1) cannot be the main reason. There is no marked difference in X-ray diffraction patterns for the two samples. This excludes (2) as the reason for the difference in J_c. The main reason must be the effect of grain boundaries. We attribute the difference in J_c between the two samples mainly to the different microstructures of the samples.

In order to characterize the structural dependence of the electrical properties we have investigated the microstructures of the samples. Fig. 5 shows the SEM photographs of surface morphologies of the samples. The crystallities of sample 1 (post-annealed in air) are large plane-like shape grains with wide grain boundaries, while those of sample 2 (post-annealed in the flowing O_2) are fine but irregular in shapes whose grain boundaries are not distinct. These facts indicate that the oxygen partial pressure during the heat treatment produces a marked effect
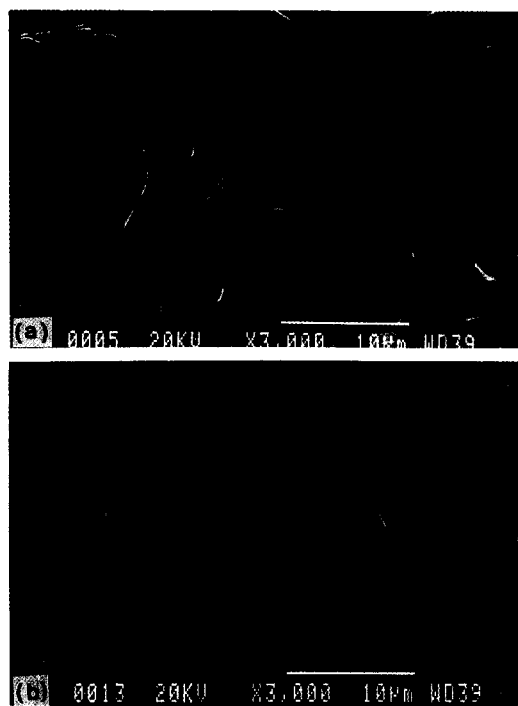
on the morphology of the $YBa_2Cu_3O_{7-x}$ superconducting thin film. The widths of the grain boundaries shown in Fig. 5(a) are 5 μm, which results in poor links between the grains and is responsible for the low J_c. On the other hand the grain boundaries shown in Fig. 5(b) seem to be much narrower and the size of the grains are much smaller than those shown in Fig. 5(a). This may account for the better connection for the superconducting phase in sample 2 leading to a comparably larger J_c. We attributed the difference in J_c between the two samples mainly to the different microstructures of the samples. From the above results, we suggest that the lack of oxygen during the heating and cooling process not only reduces the oxygen content in the crystal but also results in larger grain size and a wider grain boundary.

The results of the EDX spectra of samples 1 and 2 are shown in Fig. 6. No difference is observed in the EDX spectra of the two samples, which implies
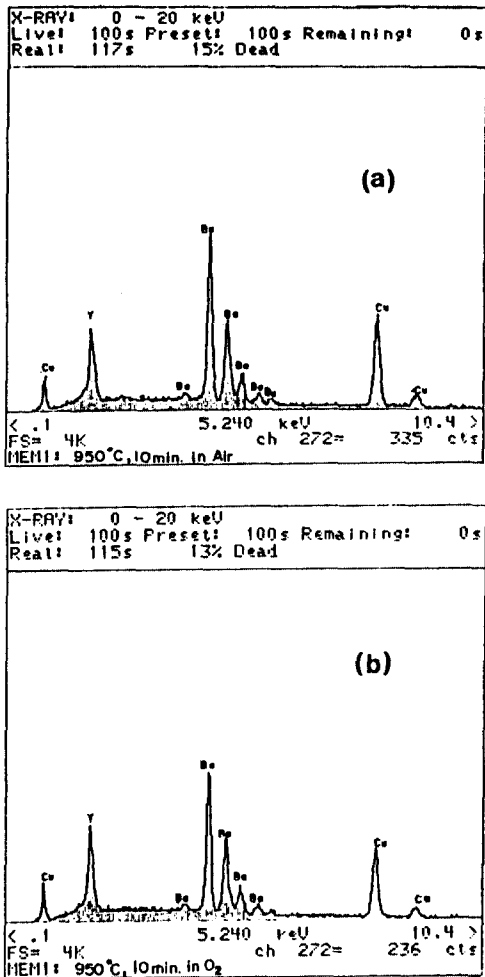
X-RAY: 0 - 20 keV
Live: 100s Preset: 100s Remaining: 0s
Real: 117s 15% Dead

(a)

< .1   5.240 keV   10.4 >
FS= 4K   ch 272=   335 cts
MEM1: 950°C,10min. in Air

X-RAY: 0 - 20 keV
Live: 100s Preset: 100s Remaining: 0s
Real: 115s 13% Dead

(b)

< .1   5.240 keV   10.4 >
FS= 4K   ch 272=   236 cts
MEM1: 950°C, 10min. in O₂

Fig. 6. Energy dispersive X-ray analysis (EDX) spectra obtained from samples, (a) annealed in air and (b) in flowing O_2, respectively, show that the concentration of Y : Ba : Cu = 1 : 2 : 3.

that the atomic concentration of Y, Ba and Cu are the same. The X-ray yield from a thin film $\Delta(t)$ at depth t is expressed by[24]

$$Y_X(t) = N \, \Delta t \, \sigma_e(t)\omega_x \, e^{-\mu/\cos\theta} \, I(t)\varepsilon \frac{d\Omega}{4\pi} \qquad (1)$$

where, N is the number of atoms in the unit volume, σ is the ionization cross section at depth t, μ is the X-ray absorption coefficient, ω is the fluorescence yield, θ is the detector angle, $\varepsilon d\Omega$ is the efficiency and solid angle of the detector, $I(t)$ is the intensity

Table 1. Chemical composition analysis of EDX

Sample	Metal fraction					
	Solution			Film		
	Y	Ba	Cu	Y	Ba	Cu
1	0.17	0.33	0.50	0.15	0.34	0.51
2	0.17	0.33	0.50	0.16	0.33	0.51

of electron beam. Then the amount of a metal atom can be calculated by

$$Y = \int_{t=0}^{R} Y(t)dt + \text{Secondary fluorescence} \qquad (2)$$

In practice we should account for the matrix effect, eg, (1) the change in cross section as a function of depth due to the change in electron energy as the beam penetrates the sample and (2) the attenuation of the beam as it penetrates the sample due to backscattering of the electron. The correction for the matrix effect of the samples should be included for determining the atomic concentration. One way to avoid such correction is using a standard sample of known compositions. We used a known composition of $YBa_2Cu_3O_{7-x}$ ceramic as a standard for determining the composition of our samples. The relative concentration of Y : Ba : Cu in the film was determined to be 1 : 2 : 3 from the results of EDX within the detection limit of 5% (see Table 1). This stoichiometry is the same as that of the starting materials when they were weighed, which implies that the composition of the metal atoms in the solution remains unchanged during the formation of the films in spray pyrolysis method.

4. Conclusion

Films of $YBa_2Cu_3O_{7-x}$ with 103 K of high T_{c-on} temperature and 80 K of T_{c-zero} temperature can be formed on the (100) MgO substrate by the spray pyrolysis method. The crystal structure of the films was a single orthorhombic phase. Moreover, an oriented film with the c-axis perpendicular to the substrate surface can be formed by careful control of the heat treatment condition. The oxygen atmosphere during heat treatment can influence not

only the microstructures but also the grain size and the width of the grain boundaries. The grain boundaries of the film are the most important among all the factors in determining J_c.

Acknowledgement

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