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Preparation and characterization of Y-system superconducting thin films by mist microwave–plasma chemical vapour deposition

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Superconducting thin films of Y–Ba–Cu–O were prepared on single-crystal MgO (1 0 0) substrates by the mist microwave–plasma chemical vapour deposition (MPCVD) using an aqueous solution of metal nitrate. The growth rate was observed to be controlled by the concentration of metal nitrate in the solution. The X-ray diffraction patterns showed that the prepared films consisted of 123 phase with *c*-axis orientation perpendicular to the substrates. The dependence of $T_{c\text{-zero}}$ (zero resistance) of films on the microwave power was investigated. In addition, the effect of the ozone on the preparation of films was investigated. The maximum $T_{c\text{-zero}}$ (84 K) of as-deposited films was obtained at a metal concentration in the solution of 0.50 mol l^{-1}, a microwave power of 300 W and an ozone concentration in oxygen gas of 3.0%.

1. Introduction

The discovery of high $T_{c\text{-zero}}$ superconducting oxides [1, 2] has stimulated intensive research activities aimed at not only understanding the high-temperature superconductivity mechanisms [3], but further raising the superconducting $T_{c\text{-zero}}$ [4–6] and developing techniques for producing useful forms, such as wires [7], tapes [8] and thin films for practical application [9–12].

Y-system superconducting thin films were prepared by various techniques, such as electron-beam evaporation, sputtering, chemical vapour deposition, molecular beam epitaxy and laser ablation. However, these methods require too high a temperature or vacuum environment, and it is difficult to prepare starting source materials. We have already reported a new technique for the preparation of yttrium- [13, 14], bismuth- [15, 16] and thallium- [17–19] systems superconducting thin films by the mist microwave–plasma chemical vapour deposition (MPCVD) method. From the technological viewpoint, this method possesses several advantages so that it is easy to prepare the source as compared with metalorganic and halogen CVD systems, and it does not require post-annealing at high temperatures.

In the present study, superconducting thin films of Y–Ba–Cu–O were prepared on single-crystal MgO (1 0 0) substrates by the mist microwave–plasma chemical vapour deposition method (MPCVD) using a water solution of metal nitrate. The growth rate was observed to be controlled by the concentration of metal nitrate in the solution. In addition, the relationship between the microwave power and $T_{c\text{-zero}}$ of Y–Ba–Cu–O superconducting thin films has been investigated as a function of the microwave power, and the effect of ozone on the preparation of films was investigated.

2. Experimental procedure

The MPCVD system with a microwave generator and ultrasonic generator was used in the growth of thin films. The apparatus was the same as that reported previously [13, 15]. The substrate used was an MgO (1 0 0) single crystal, mirror-polished with 0.25 μm diamond paste. The typical growth conditions are summarized in Table I. The source materials for the superconductor were prepared by dissolving metal nitrate into deionized water. $Y(NO_3)\cdot 6H_2O$, $Ba(NO_3)_2$, $Cu(NO_3)_2\cdot 3H_2O$ were used as starting reagents. In the preparation of the Y–Ba–Cu–O system, the atomic ratio of Y:Ba:Cu was controlled to 1:2:3. Typical total metal concentration in the solution used was varied from 0.10–0.60 mol l^{-1}. The temperature of the substrate (1073 K) was measured by an optical pyrometer. The mist of the source solution (droplet size 1–2 μm), which was produced by an ultrasonic mist generator (6 MHz), was introduced into the reactor using argon as the carrier gas. Microwave (2.45 GHz) power was supplied by a magnetron generator. The supply rate of the mist was 80 standard cm^3 determined from the flow rate of argon carrier gas [14]. Furthermore, due to the oxidative reaction, oxygen gas was introduced into the reactor. The ozone was generated by passing a flow of oxygen through an ozone generator. The input molar ratio of oxygen

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TABLE I Typical growth conditions

Substrate	MgO (1 0 0)
Microwave power	240–320 W
Supply rate of mist	80 standard cm^3
Total flow rate	300 standard cm^3
Input molar ratio of oxyen	0.30
Total pressure of reactor	50 torr
Duration of deposition	5 h

$O_R = F_{\text{oxygen species}}/(F_{\text{oxygen species}} + \text{total } F_{Ar})$ [15] in the reactor was 0.30.

The grown thickness was measured by a surface roughness tester equipped with a diamond probe. An X-ray diffractometer with CuK_α radiation in the 2θ range from 0°–60° was used for the characterization of the as-deposited films. The surface morphology of the resultant films was observed by scanning electron microscopy (SEM). The chemical compositions in the as-deposited films were investigated by electron-probe X-ray microanalysis (EPMA), using a probe of 1 μm diameter, a probe current of 3×10^{-8} A, and an accelerating voltage of 15 kV. Electrical resistivity was measured by the standard four-probe method with silver paint contacts for as-deposited films over a range of temperatures from 50–250 K.

3. Results and discussion

One important feature of the MPCVD method is that the preparation of the source is easy compared with metalorganic and halogen CVD systems. Fig. 1 shows the dependence of the metal concentration in the solution on the growth rate for films prepared at the microwave power of 300 W. When the metal concentration in the solution was 0.10 mol l^{-1}, the growth rate of films was 40 nm h^{-1} and then the growth rate increased gradually with increasing metal concentration in the solution up to 0.50 mol l^{-1}. The growth rate of as-deposited films shows a maximum (200 nm h^{-1}) at the metal concentration in the solution of 0.50 mol l^{-1}. When the metal concentration in the solution was higher than about 0.60 mol l^{-1},the precipitate was deposited in the solution. Consequently, the films cannot be obtained at a metal concentration in the solution higher than about 0.60 mol l^{-1}. From this result, the highest growth rate of 200 nm h^{-1} was achieved for the films prepared at a metal concentration in the solution of 0.50 mol l^{-1}.

Fig. 2 shows typical X-ray diffraction patterns for Y–Ba–Cu–O superconducting thin films prepared under different microwave powers at a metal concentration in solution of 0.50 mol l^{-1}. X-ray diffraction patterns of the films were measured by a diffractometer operated at 25 kV with a filament current of 20 mA, using a nickel filter for CuK_α radiation. As seen in Fig. 2, the enhanced intensities of the (0 0 l) reflections for all films indicate that the c-axes are preferentially oriented perpendicular to the MgO (1 0 0) substrate surface. This type of orientation is frequently observed in films on MgO (1 0 0) substrates

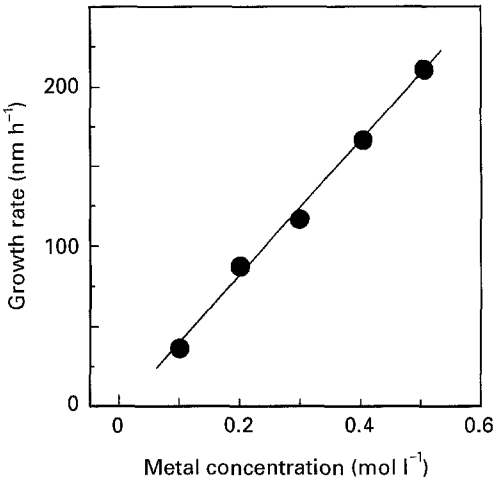

Figure 1 The dependence on the metal concentration of the solution of the growth rate of Y–Ba–Cu–O superconducting thin films. The microwave power is 300 W, O_R =0.30.

prepared by sputtering, laser ablation and CVD. Most reflections of Y–Ba–Cu–O thin films prepared at the atomic ratio 1:2:3 can be indexed by orthorhombic symmetry, in good agreement with those of the 123 phase. When the microwave power was 240 W, no diffraction peaks of the Y–Ba–Cu–O superconductor phase were confirmed for the as-deposited films. This may be attributed to the lack of oxidation which suppresses the formation of Y–Ba–Cu–O superconductor. The intensity of the diffraction peaks corresponding to the 123 phase increased initially with increased microwave power. The lattice parameter, c, estimated from Bragg angles of the (0 0 5) planes was constant at about 1.169 nm, despite variation of the microwave power. When the microwave power was 320 W, no diffraction peaks of the Y–Ba–Cu–O superconductor were observed for the as-deposited films. This is ascribed to the suppression of the formation of the Y–Ba–Cu–O phase due to the excess acceleration of oxidation. The X-ray peak intensity of Y–Ba–Cu–O phase (0 0 5) in Fig. 2 is shown in Fig. 3 as a function of the microwave power. The intensity of Y–Ba–Cu–O phase was normalized at the peak intensity of the MgO substrate. It is seen that the strongest peak intensity of Y–Ba–Cu–O phase is observed at a microwave power of 300 W. These results show that the c-axis orientation of Y–Ba–Cu–O superconducting thin film is enhanced by the increase of microwave power. The composition of Y–Ba–Cu–O phase observed by XRD was decided to be $Y_{0.98}Ba_{2.05}Cu_{2.98}O_x$ by the EPMA analysis. Fig. 4 shows scanning electron micrographs of Y–Ba–Cu–O superconducting thin films prepared at a microwave power of 300 W. As shown in Fig. 4, the films are composed of a uniform matrix portion and dispersed particles.

Fig. 5 shows the electrical resistance normalized at 250 K versus the temperature relationship of the as-deposited films at a metal concentration in the solution of 0.50 mol l^{-1} for various microwave power. It is obvious from Fig. 5 that the resistivity behaviour is metallic and an extrapolated normal state resistance intercepts close to zero. It is found that the $T_{c\text{-zero}}$ is

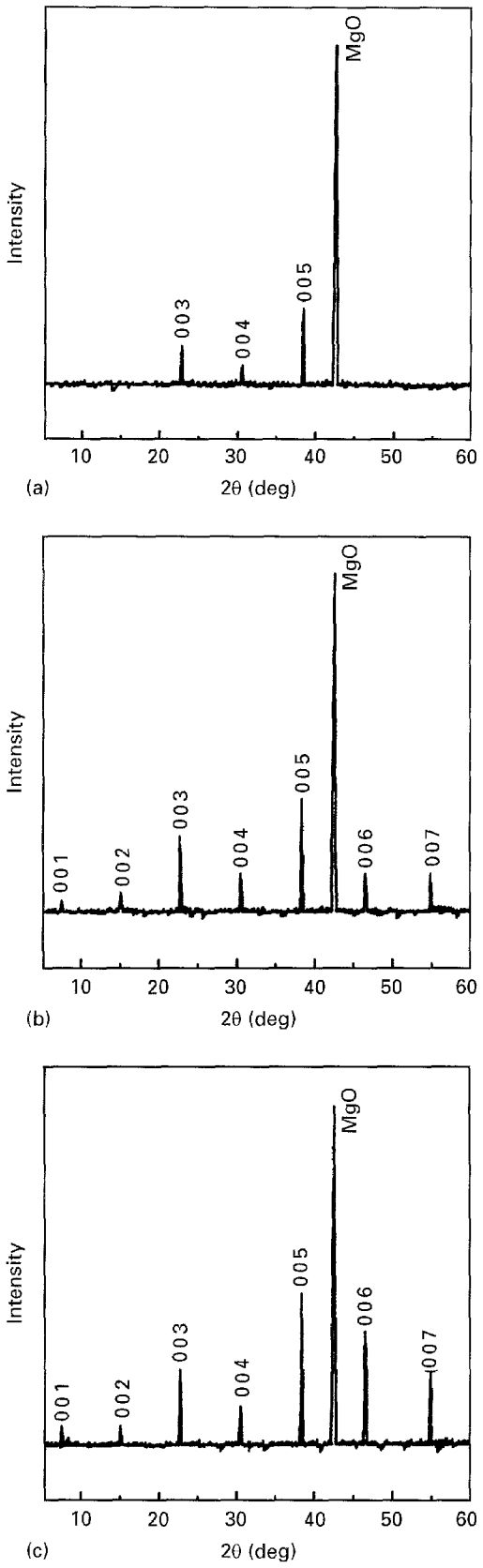

Figure 2 X-ray diffraction patterns of Y–Ba–Cu–O films deposited on MgO (1 0 0) substrates at various microwave powers: (a) 260 W, (b) 280 W, (c) 300 W.

changed by the microwave power. In order to clarify the relationship between $T_{c\text{-zero}}$ and microwave power during the deposition process, the value of $T_{c\text{-zero}}$ is shown in Fig. 6 as a function of the microwave power. When the microwave power was 240 W, no $T_{c\text{-zero}}$ was observed. This is attributed to the fact that the

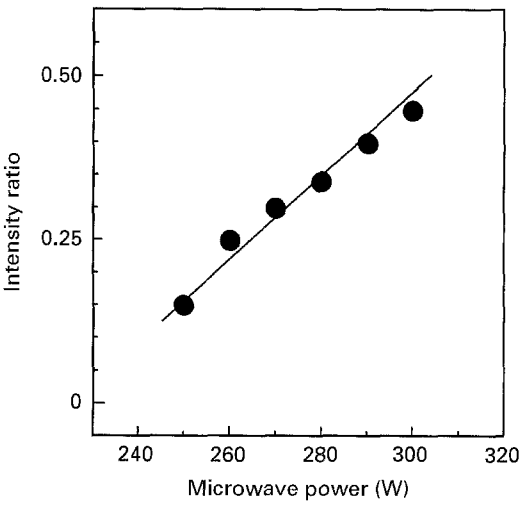

Figure 3 X-ray diffraction peak intensity ratio of Y–Ba–Cu–O phase (0 0 5)/MgO as a function of microwave power. O_R =0.30.

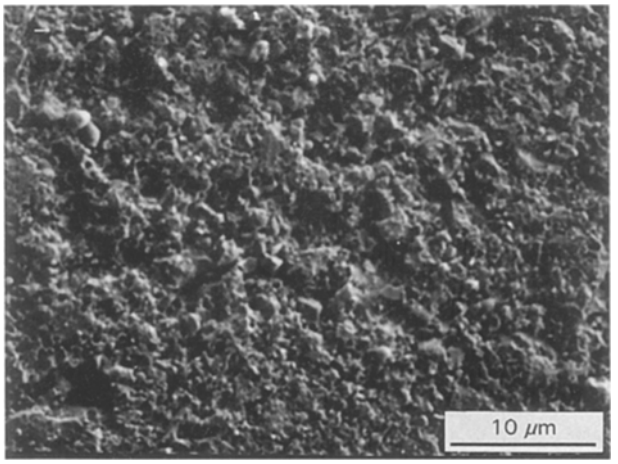

Figure 4 Scanning electron micrograph of Y–Ba–Cu–O superconducting thin films prepared at the microwave power of 300 W and an input molar ratio of oxygen of 0.30.

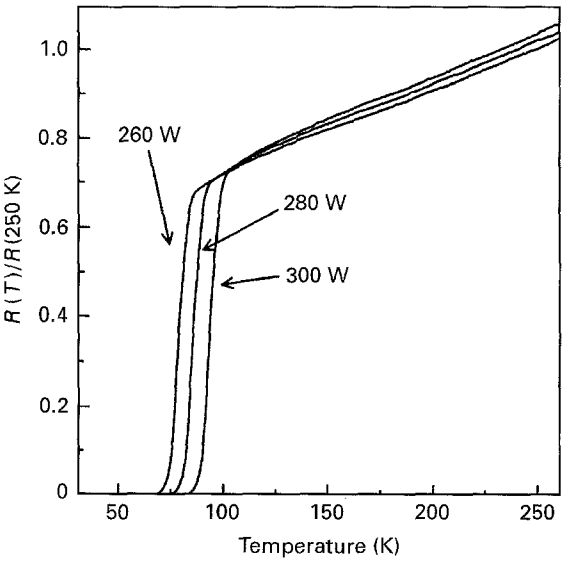

Figure 5 Resistance normalized at 250 K versus temperature for as-deposited films prepared at various microwave powers. O_R =0.30.

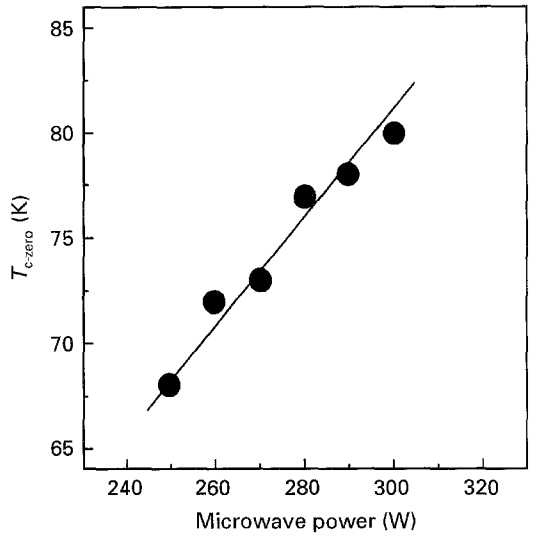

Figure 6 The dependence on microwave power of $T_{c\text{-}zero}$ for the as-deposited Y–Ba–Cu–O films. O_R =0.30.

Y–Ba–Cu–O superconductor phase cannot be obtained at a microwave power of 240 W, as shown in Fig. 2. $T_{c\text{-}zero}$ increased with increasing microwave power: $T_{c\text{-}zero}$ of as-deposited films shows a maximum (80 K) at a microwave power of 300 W. When the microwave power was 320 W, no $T_{c\text{-}zero}$ was observed. This is ascribed to the suppression of the formation of Y–Ba–Cu–O phase due to the excess acceleration of oxidation, as described in X-ray analysis. Consequently, the microwave power dependence of the $T_{c\text{-}zero}$ of as-deposited films may be explained by the increase of *c*-axis orientation, as described previously. The earlier paper reported the effect of oxygen and supply rate of the mist on the preparation of Y–Ba–Cu–O superconducting thin films by the MPCVD method [19]. From these results, the highest $T_{c\text{-}zero}$ of 80 K was achieved for the films prepared at a metal concentration in the solution of 0.50 mol l^{-1}, a microwave power of 300 W, an input molar ratio of oxygen of 0.30 and a supply rate of mist in the range from 80–100 standard cm^3.

Ohnishi *et al.* [20] studied the influence of ozone concentration on the preparation of stoichiometric superconducting Y–Ba–Cu–O films by a metalorganic chemical vapour deposition technique (MOCVD). They reported the synthesis of superconducting Y–Ba–Cu–O phase with $T_{c\text{-}zero}$ of 85 K. In order to obtain films with $T_{c\text{-}zero}$ higher than 80 K, the effect of ozone on the preparation of Y–Ba–Cu–O superconductors by the MPCVD method was studied. The effects of ozone have been investigated under optimum preparation conditions (metal concentration in the solution 0.50 mol l^{-1}, microwave power 300 W, input molar ratio of oxygen 0.30, supply rate of mist 80 standard cm^3), as described previously. Fig. 7 shows typical X-ray diffraction patterns for Y–Ba–Cu–O superconducting thin films prepared under different ozone concentrations. The peaks of the (0 0 *l*) planes for the Y–Ba–Cu–O phase are clearly observed over the range of ozone concentrations in oxygen from 0.0%–3.0%, as shown in Fig. 7. When the ozone concentration in oxygen gas was higher

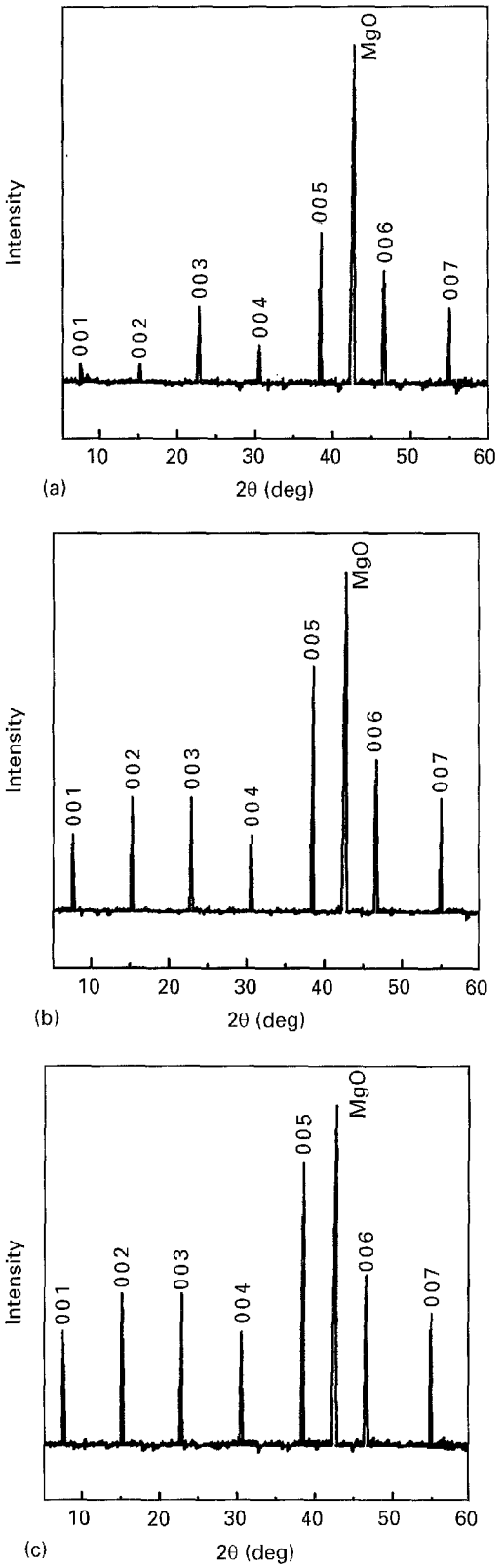

Figure 7 X-ray diffraction patterns of Y–Ba–Cu–O films deposited on MgO (1 0 0) substrates at different ozone concentrations: (a) 0%, (b) 1.5%, (c) 3.0%.

than 4.0%, no diffraction peaks of the Y–Ba–Cu–O phase were observed for the as-deposited films. The peak intensity ratio of (0 0 5)/MgO is shown in Fig. 8 as a function of the ozone concentration in oxygen gas. The peak intensity ratio of (0 0 5)/MgO increases gradually from 0.50–1.20 with increasing ozone concentration in oxygen gas from 0.0%–3.0%. This indicates that the *c*-axis orientation is promoted by the

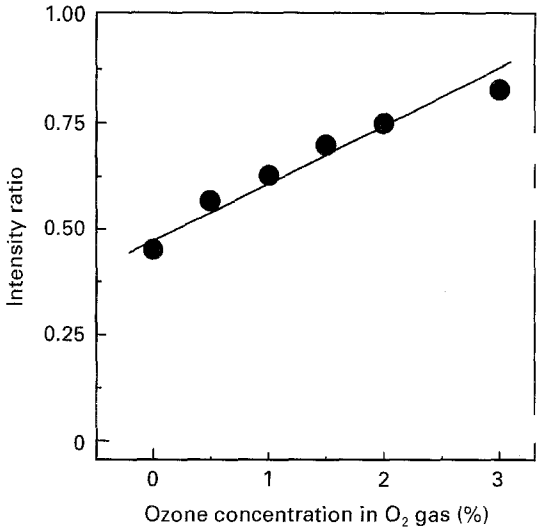

Figure 8 X-ray diffraction peak intensity ratio of Y–Ba–Cu–O phase (0 0 5)/MgO as a function of ozone concentration. Microwave power =300 W, O_R =0.30.

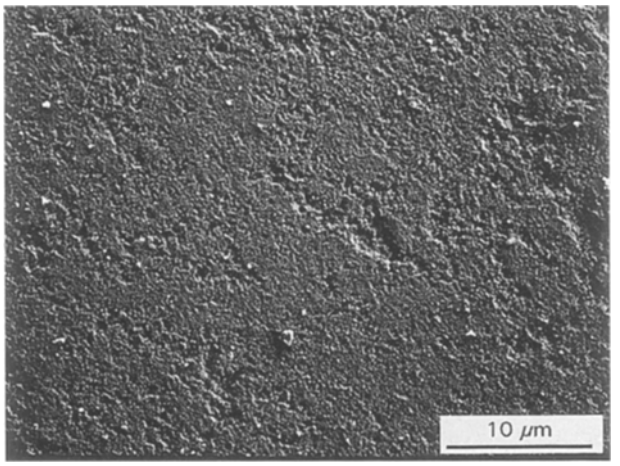

Figure 9 Scanning electron micrograph of Y–Ba–Cu–O superconducting thin films prepared after ozone addition.

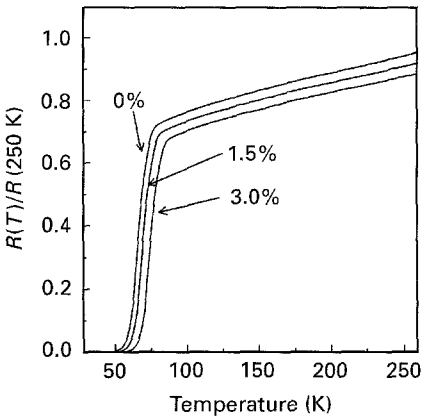

Figure 10 Resistance normalized at 250 K versus temperature for as-deposited films prepared at various ozone concentrations. Microwave power =300 W, O_R =0.30.

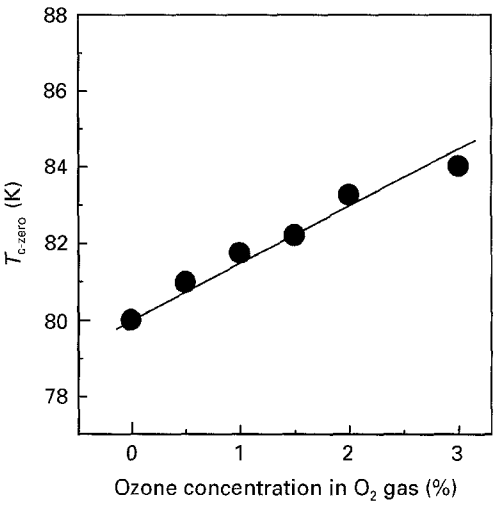

Figure 11 The dependence on ozone concentration of the $T_{c\text{-}zero}$ for the as-deposited Y–Ba–Cu–O films. Microwave power =300 W, O_R =0.30.

ozone addition. The composition of Y–Ba–Cu–O superconducting thin films prepared by ozone addition was found to be $Y_{1.05}Ba_{2.00}Cu_{2.97}O_x$ by the EPMA analysis. This composition almost agreed with the composition of Y–Ba–Cu–O superconducting thin films prepared without ozone addition. A scanning electron micrograph of Y–Ba–Cu–O superconducting thin films prepared at the ozone concentration in oxygen gas of 3.0% is shown in Fig. 9. Compared with scanning electron micrographs of films prepared without ozone addition (see Fig. 4), the matrix becomes dense and flat with the ozone addition. From these results, it is found that the Y–Ba–Cu–O superconducting thin films with a good *c*-axis orientation and a smooth surface morphology was obtained by introducing ozone.

Fig. 10 shows the electrical resistance normalized at 250 K versus the temperature relationship of the as-deposited films for various ozone concentrations. It is obvious from Fig. 4 that all as-deposited films show a metallic behaviour above $T_{c\text{-onset}}$, in analogy with Fig. 5. It was found that the $T_{c\text{-zero}}$ is changed by the ozone concentration. In order to clarify the relationship between the $T_{c\text{-zero}}$ and ozone concentration during the deposition process, the value of $T_{c\text{-zero}}$ is shown in Fig. 11 as a function of the ozone concentration. The $T_{c\text{-zero}}$ increased gradually from 80–84 K with increasing ozone concentration from 0.0%–3.0%. A similar dependence was reported by Ohnishi *et al.* [20]. From this result, the ozone concentration dependence of the $T_{c\text{-zero}}$ of as-deposited films may be explained by the promotion of *c*-axis orientation and the improvement of structure, as described previously. However, the exact reason is not well understood at present.

4. Conclusions

Superconducting thin films of Y–Ba–Cu–O were prepared on single-crystal MgO (1 0 0) substrates by the mist microwave–plasma chemical vapour deposition (MPCVD) using an aqueous solution of metal nitrate. The growth rate was observed to be controlled by the concentration of metal nitrate in the solution. The X-ray diffraction patterns showed that the prepared

films consisted of 123 phase with c-axis orientation perpendicular to the substrates. The dependence of $T_{c\text{-zero}}$ (zero resistance) of films on the microwave power was investigated. In addition, the effect of the ozone on the preparation of films were investigated. The maximum $T_{c\text{-zero}}$ (84 K) of as-deposited films was obtained at a metal concentration in the solution of 0.50 mol l^{-1}, a microwave power of 300 W, and an ozone concentration in oxygen gas of 3.0%.

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