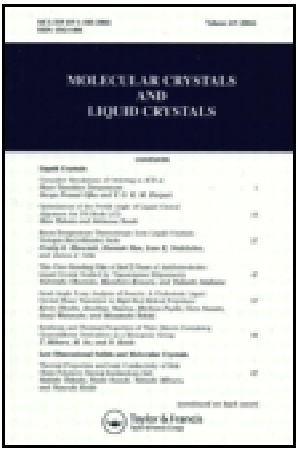

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Preparation of High Tc Superconducting Oxide Thin Films by ECR Sputtering

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PREPARATION OF HIGH Tc SUPERCONDUCTING OXIDE THIN FILMS BY ECR SPUTTERING

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Abstract Superconducting thin films of $YBa_2Cu_3O_{7-y}$ were prepared by ECR sputtering. The amorphous films obtained at relatively low substrate temperatures(up to 400°C) were annealed in an oxygen flow. The Tc of the annealed film was 90K and showed high c-axis orientation. The change of 124 phase to 123 phase was observed by changing annealing temperature.

INTRODUCTION

Since the discovery of superconducting oxide compounds[1] with transition temperatures above the boiling point of liquid nitrogen, much effort has been made to developing techniques for fabricating materials with good superconductivity. Various kinds of thin film fabrication methods[2,3,4] such as magnetron sputtering, ion beam sputtering, e-beam evaporation, and laser deposition have been proposed. The superconducting properties of the films have been improved by the development of the production methods. Thus we have now reached to a technical consensus for obtaining good superconducting films, i.e. to deposite stoichiometric films with good crystallinity.

In this paper, we report preliminary results for $YBa_2Cu_3O_{7-y}$ thin films prepared by a novel sputtering method which utilizes Electron Cyclotron Resonance(ECR) type microwave plasma. Matsuoka et.al. have developed an ECR sputtering system[5] which can be applied to conductive materials by introducing a rectangular microwave guide as a pressure window. The ECR sputtering system has the follwing advantages compared with other sputtering systems.

1)The Plasma state is easily generated under low gas pressure(<10^{-2} Pa).

2)Any kinds of gas can be used as the plasma former. This means that the oxygen rich plasma gas can be used for superconducting film preparation.

3)High energy particles are prevented from colliding with the film, because the substrates are placed in a vertical position against the target surface.

These unique features of the ECR-sputtering method seem very attractive for superconducting oxide film preparation in term of stoichiometry control and crystal growth. Goto et al. have reported the results of superconducting films fabricated by the ECR sputtering method[6]. Their films contain some other phases because they did not use a sintered target.

We have developed a method to produce a sintered cylindrical target for the ECR sputtering. The properties of the films prepared by ECR sputtering were examined in relation to the annealing temperature.

EXPERIMENTAL

a)Apparatus The configuration of the ECR sputtering system is shown in Figure 1. The ECR sputtering system used was AFTEX3000(Advanced Film Technology Inc.). Sputtering conditions are listed in Table 1.

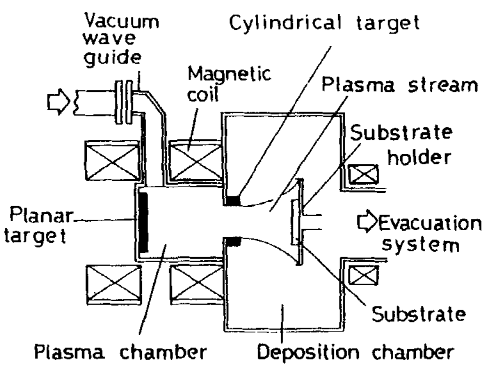

FIGURE 1 Schematic diagram of ECR sputtering system.

TABLE I Sputtering Conditions

Target	$YBa_{1.87}Cu_{3.8}O_x$
Substrate	$SrTiO_3(100)$
Sputtering gas	$Ar(33\%)+O_2(67\%)$
Gas pressure	$8.7x10^{-2}$ Pa
Power	140W
Growth rate	60A/mim
Target-substrate Space	120mm

Argon gas was introduced into the plasma chamber and oxygen was introduced just in front of the substrate to accelerate the oxidation of the films.

b)Target The dimensions of the target were 90mm(inner diameter), 110mm (outer diamter) and 50mm in length.

The powder for the target was synthesized by the oxalic acid method and calcinated at 900°C for 10 hours and at 920°C for 10 hours in an oxygen flow. The cylindrical target was molded by the CIP method and sintered at 930°C. The target composition ratio of the metal elements was as follows: Y:Ba:Cu=1:1.87:3.80.

c)Deposition Films were deposited onto a $SrTiO_3(100)$ substrate to a thickness of about 8000 Å. The target was biased at -400V(dc), and the deposition rate was approximately 60 Å/min.

d)Film characterization The crystal orientation and texture of the films were examined using the X ray diffraction method. The compositional ratio of the metal elements in the films was determined by the ICP method. The surface morphology was observed using SEM . The Tc was measured by the standard four probe method.

RESULTS AND DISCUSSION

The films obtained by ECR sputtering at substrate temperatures below 500°C were amorphous and dark brown in color. The metal composition of the films varied depending on the substrate temperature.

The stoichiometric ratio Y:Ba:Cu=1:2:3 was obtained at a substrate temperature of 400°C. These stoichiometric films were annealed in an oxygen flow at various temperatures.

Figure 2 shows the X-ray diffraction patterns and the SEM photographs of the films annealed at 800°C(a), 830°C(b) and 850(c)°C. For the film annealed at 800°C, the (001) peak of the 124 phase was predominant. The 124 phase peak disappeared as the annealing temperature was increased above 850 °C.

For the film annealed at 850°C, the (001) peak of the 123 phase predominated. SEM photographs also show this phase change. From the photographs it can be seen that, film (a) has a very porous ground and that the state of the ground becomes smoother as the annealing temperature is increased. The Tc of the films is shown in Figure 3.

The Tc of film (c) shows a very sharp drop in resistance at 90 K. As the volume fraction of the 124 phase increases, the Tc decreases and also the transition width becomes larger. Figure 4 shows the X-ray diffraction pattern of film (c). This Figure shows the strong c-axis orientation of the film. Liou et al.[3] reported that an annealing temperature as high as 950°C was needed to obtain highly c-axis oriented films from amorphous films. The films fabricated by the ECR sputtering show c-axis orientation after annealing at 850°C.

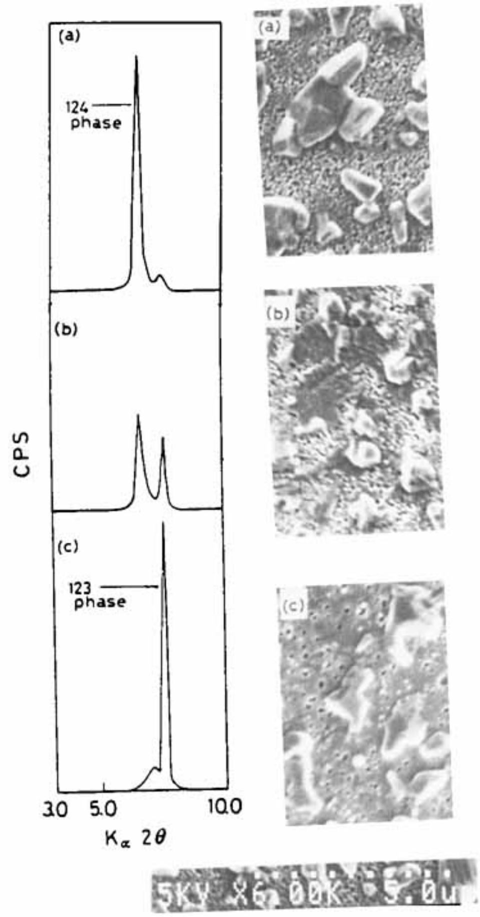

FIGURE 2 X-ray diffraction patterns of annealed film (001) peak and SEM photographs.
800°C(a), 830°C(b) and 850°C(c)

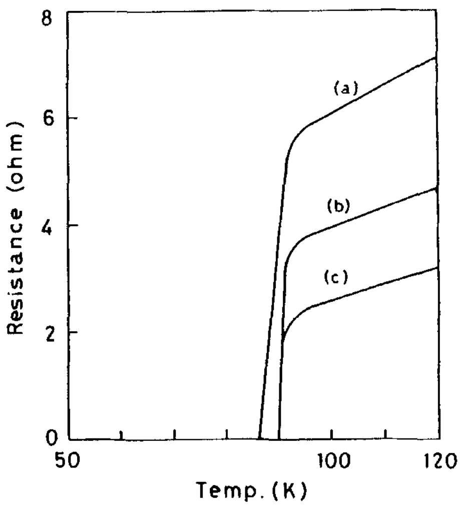

FIGURE 3 Resistance vs temperature of annealed films (a),(b) and (c)

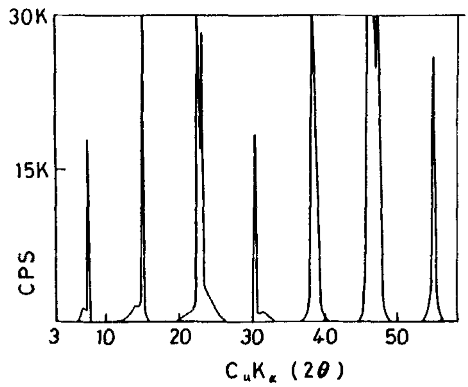

FIGURE 4 X-ray diffraction pattern of film (c) annealed at 850°C

CONCLUSION

We have produced highly c-axis oriented YBCO films by the ECR sputtering. The insulating films in as-deposited state were annealed in an oxygen folw. The Tc(R=0) of the annealed films was as high as 90K. We also provide the evidence based on the X-ray diffraction pattern that the 124 phase appears during the annealing process, and predominates at 800°C while the 123 phase predominates at the temperature above 850°C. SEM observation showed the phase change clearly.

REFERENCES

1. M.K.Wu, J.R.Ashburn, C.J.Torng, P.H.Hor, R.L.Meng, L.Gao, Y.Q.Wang and C.W.Chu, Phys. Rev. Lett., 58(9) 908 (1987)
2. T.Kamada, K.Setsune, T.Hirao and K.Wasa, Appl. Phys. Lett. 52(20) 1726 (1988)
3. S.H.Liou, M.Hong, J.Kwo, B.A.Davidson, H.S.Chen, S.Nakahara, T.Boone and R.J.Felder, Appl. Phys. lett. 52(20) 1735 (1988)
4. H.Asano, M.Asahi and O.Michikami, Jpn. J. Appl. Phys.28(6) L981 (1989)
5. M. Matsuoka and K. Ono, J. Appl. Phys. 65(11) 4403 (1989)
6. T.Goto, H.Matsumoto and T.Hirai Jap. J. Appl. Phys. 28(1) L88 (1989)