In Situ Growth of Bi-Sr-Ca-Cu-O Films by ac Sputtering in Pure Oxygen

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We have carried out the *in situ* growth of Bi-Sr-Ca-Cu-O films in pure O₂ using an ac sputtering technique. The films were grown at different O₂ pressures. We have obtained superconducting Bi-Sr-Ca-Cu-O(2212) films which show T_c (50% resistive)=84 K and a zero resistance at 74 K. The formation and superconductivity of the films prepared in pure O₂ were compared with that prepared in a mixture of Ar and O₂.

KEYWORDS: Bi-Sr-Ca-Cu-O, thin films, sputtering

The first report of the high- T_c superconducting oxide compounds was published in 1986.¹⁾ Since then, a great deal of effort worldwide has been put into the development of thin film technologies.²⁻⁴⁾ The most widely studied has been Y-Ba-Cu-O films, which has now reached the point where the state of the art is mainly produced by *in situ* methods.^{5,6)} The oxide compounds of the Bi-Sr-Ca-Cu-O have so far proved very difficult to make by *in situ* techniques. In this paper we report the *in situ* growth of Bi-Sr-Ca-Cu-O films in pure O₂ by means of an ac sputtering technique.

The films were fabricated by an ac sputtering technique. The system used to prepare the films has the configuration shown in Fig. 1. Two targets with the same composition were mounted on the two electrodes. The targets had a diameter of 1.2 cm and the distance from the substrate to the targets was about 1.0 cm. The substrates were heated to various temperatures by a resistive heater. The sputtering was carried out in pure O₂ at different pressures. The sputtering power was about 90 watts and the sputtering frequency was 60 Hz. The ac voltage was about 6 kV ~ 7 kV. The substrates were MgO(100). After sputtering, the film was rapidly cooled to room temperature in 20-30 minutes without any fur-

ther postannealing. Typical thickness of the films varies from 0.2 to 1 μ m. The data reported here are typical results.

Table I shows the resistive data of the as-grown films in various grown conditions. The resistivity of the as-grown films at room temperature varied from 0.2 to 10 m Ω cm depending on the growth conditions. The resistance of the samples was measured by a conventional four-probe method. Four electrical leads were connected to the samples by silver paints. The current to the sample in the electrical measurements was 3 mA. The temperature of the sample was monitored by a calibrated silicon diode which was placed next to the sample.

Figure 2 contrasts the normalized resistance, $R(T)/R(300)$, for samples grown at 660°C in 0.01 (sample 1-64), 0.02 (sample 1-51), 0.05 (sample 1-60) and 0.07 (sample 1-81) kPa of O₂. The data show that the sputtering pressure affects the growth of the Bi-Sr-Ca-Cu-O films. Sample 1-60, which was grown at 660°C under a pressure of 0.05 kPa, shows the best superconducting properties. Its room temperature resistivity is 0.5 m Ω cm. The resistive transition of that sample is $T_c(50\%)=84$ K and

Fig. 1. Configuration of the ac sputtering system.

Table I. Superconducting properties of the as-grown films under various sputtering conditions. The targets on the two electrodes have the composition of Bi_{1.6}Pb_{0.4}Sr₂Ca₂Cu_{3.6}O_y. The targets were sputtered in O₂ atmosphere except those samples marked by the symbol * which were prepared in a mixture of Ar and O₂ (7:3).

Samples	Temp. (K)	Pressure (kPa)	$T_c(10\%)$ (K)	$T_c(50\%)$ (K)	$T_c(90\%)$ (K)
1-64	660	0.01	91.2	60.9	39.3
1-51	660	0.02	103	80	72
1-60	660	0.05	99.2	84	80.0
1-81	660	0.07	81.4	78.6	76.6
1.75	658	0.1	96	79.3	76.1
1-61	660	0.13	104	81	80
2-67	615	0.05	84.5	67.1	55
2-85	644	0.05	93.8	76.9	67.2
2-78	680	0.05	85.3	81.2	77.3
2-70	702	0.05	semiconducting		
3-10*	630	0.02	60	35	25
3-15*	632	0.02	90	80	72
3-40*	660	0.05	91.9	80.3	72

the zero resistance is $T_{c,zero} = 74$ K.

Figure 3 shows the temperature dependence of $R(T)/R(300)$ for films prepared at four different temperatures: 615°C (sample 2-67), 644°C (sample 2-85), 660°C (sample 1-60) and 680°C (sample 2-78). The targets were sputtered in pure O_2 and the sputtering pressure was 0.05 kPa. The data indicate that the optimum temperature for the growth of superconducting Bi-Sr-Ca-Cu-O films in pure O_2 is about 660°C under 0.05 kPa.

We carried out the X-ray diffraction measurements for most samples on an X-ray diffractometer (Siemens model

Fig. 2. Resistance as a function of temperature for samples grown at 660°C in 0.01 (sample 1-64), 0.02 (sample 1-51), 0.05 (sample 1-60), and 0.07 (sample 1-81) kPa of O_2 .

Fig. 3. Temperature dependence of $R(T)/R(300)$ for samples grown at 615°C (sample 2-67), 644°C (sample 2-85), 660°C (sample 1-60), and 680°C (sample 2-78).

Fig. 4. X-ray diffraction pattern for samples grown at 660°C in 0.05 kPa of O_2 .

D500). Figure 4 shows a typical X-ray diffraction pattern for sample 1-60. The diffraction peaks of the samples can be mainly identified as the (2212) phase. The films grown at 660°C show clean diffraction peaks and are highly oriented with the c axis perpendicular to the (100) plane of MgO and have the c axis lattice parameter of 3.06 nm. We note that in our original plan of growing Bi-Sr-Ca-Cu-O films, we added Pb impurities to replace Bi in the targets of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{3.6}O_y$ in order to grow superconducting films with a (2223) phase. However, such an attempt was not successful.

Figure 5 shows a typical scanning electron micrograph (SEM) of the films grown at 660°C in 0.05 kPa of O_2 . The scale of the line bar in the SEM picture is one micrometer. The as-grown films are smooth, black and shiny.

It is interesting to compare the films grown in pure O_2 with those grown in a mixture gas of Ar and O_2 . Figure 6 contrasts the temperature dependence of the resistance for samples grown in pure O_2 (sample 1-60) and that grown in a mixture of Ar and O_2 (7:3) (sample 3-40). Both samples were grown at the same temperature and cooled to room temperature at about the same cooling rate after the ac sputtering processes. We found that films grown in pure O_2 show better superconducting prop-

Fig. 5. Scanning electron micrograph of the as-grown films which are smooth and shiny. The sample is the same as that shown in Fig. 4.

Fig. 6. Temperature dependence of resistance for sample 1-60 grown in pure O_2 and sample 3-40 grown in a mixture of Ar and O_2 (7:3).

erties compared with those prepared in a mixture of Ar and O₂ (7:3). We note that the superconductivity of the films grown in a mixture gas of Ar and O₂ (7:3) can be improved if the targets undergo further sputtering in pure O₂. This is illustrated in Figure 7. Samples 3-10 and 3-15 were first prepared in a mixture gas of Ar and O₂ (7:3). Sample 3-15 was then further treated in pure O₂ sputtering, whereas sample 3-10 was not. We found that the extra pure O₂ sputtering process for sample 3-15 improves the superconductivity of the film. The data suggest that the pure O₂ plasma generated in ac sputtering aids the incorporation of oxygen into the films and forms the superconducting phase. We attribute this to the active oxygen available in the sputtering atmosphere, and therefore, the active oxygen aids the incorporation of oxygen into the films.

It is necessary to grow and cool the high- T_c YBa₂Cu₃O_{7-y} films in sufficient oxygen to achieve high-quality films of the correct structure. The cooling rate should be kept as slow as possible as one cools the films. For example, the films can be kept at 500–600°C for one hour and a cooling rate of 5°C per minute can achieve a high-quality film, as reported in our previous work.⁶⁾ We found that the cooling rate is also critical in the growth

of the Bi-Sr-Ca-Cu-O film. In our growth of the Bi-Sr-Ca-Cu-O films, the samples were all subjected to a rapid cooling rate and films of good quality were reproduced. Typically, the films were cooled to room temperature in about 20–30 minutes, as we have mentioned previously.

The ac sputtering technique used to prepare high- T_c superconducting films was first reported by Koinuma *et al.*⁷⁾ They deposited films at room temperature, and a subsequent O₂ postannealing was required in order to achieve superconductivity. In this investigation, we have grown Bi-Sr-Ca-Cu-O films *in situ* by the same technique using pure O₂. We also found that the superconductivity of the films grown in a mixture gas of Ar and O₂ (7:3) can be improved if the films are further grown in pure O₂.

In conclusion, we have grown superconducting Bi-Sr-Ca-Cu-O films *in situ* in pure O₂ by an ac sputtering technique without any further postannealing. We also found that the superconductivity of the films grown in a mixture gas of Ar and O₂ can be improved if the targets are subjected to further sputtering in pure O₂. We attribute this to the easy incorporation of oxygen into Bi-Sr-Ca-Cu-O films in pure oxygen plasma generated in the sputtering process compared with that prepared in a mixture gas of Ar and O₂ (7:3).

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References

- 1) J. G. Bednorz and K. A. Muller: *Z. Phys. B* **64** (1986) 189.
- 2) Y. Nakayama, H. Ochimizu, A. Maeda, A. Kawazu, K. Uchinokura and S. Tanaka: *Jpn. J. Appl. Phys.* **28** (1989) L1217.
- 3) K. Kuroda, K. Kojima, M. Tanioku, K. Yokoyama and K. Hamanaka: *Jpn. J. Appl. Phys.* **29** (1990) L291.
- 4) H. Masumoto, T. Goto and T. Hirai: *Appl. Phys. Lett.* **55** (1989) 1252.
- 5) R. G. Humphreys, J. S. Satchell, N. G. Chew, J. A. Edwards, S. W. Goodyear, S. E. Blenkinsop, O. D. Dosser and A. G. Gullis: *Supercond. Sci. Technol.* **3** (1990) 38.
- 6) H. C. Yang, H. H. Sung, L. Lee, H. E. Horng and T. R. Yang: *Phys. Rev. B* **43** (1991) 8634.
- 7) H. Koinuma, M. Kawasaki, S. Nagata, K. Takeuchi and K. Fueki: *Jpn. J. Appl. Phys.* **27** (1988) L376.

Fig. 7. Temperature dependence of resistance for samples 3-10 and 3-15. Both samples were prepared in a mixture of Ar and O₂ (7:3). Sample 3-15 was further subjected to an extra O₂ sputtering process whereas sample 3-10 was not.