August 1987

Superconducting Y-Ba-Cu-O oxide films by sputtering

M. Hong
AT&T Bell Laboratories, Murray Hill, New Jersey

Sy_Hwang Liou
University of Nebraska-Lincoln, sliou@unl.edu

J. Kwo
AT&T Bell Laboratories, Murray Hill, New Jersey

B.A. Davidson
AT&T Bell Laboratories, Murray Hill, New Jersey

Hong, M.; Liou, Sy_Hwang; Kwo, J.; and Davidson, B.A., "Superconducting Y-Ba-Cu-O oxide films by sputtering" (1987). *Si-Hwang Liou Publications*. 17.
https://digitalcommons.unl.edu/physicsliou/17

Superconducting Y-Ba-Cu-O oxide films by sputtering

M. Hong, S. H. Liou, J. Kwo, and B. A. Davidson
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 5 June 1987; accepted for publication 13 July 1987)

We have prepared superconducting thin films of Y-Ba-Cu-O with T_c onsets above 95 K by both diode and magnetron sputtering. Films with full superconductivity ($R = 0$) at 85 K have been produced by dc magnetron sputtering. The compositions of the films are fairly uniform across an area 50 mm in diameter and through the film thickness. Structural properties of the films were studied by x-ray diffraction. Critical current densities in the range of 3000 to 10^4 A/cm^2 have been measured at 4.2 K.

The recent discovery of the new class of high critical temperature superconducting oxides, particularly the Y-Ba-Cu-O system[1] with T_c's in excess of 90 K, has caused extraordinary interest and intensive activity in scientific and technological research. The possibility of operating superconducting devices and magnets at or above liquid-nitrogen temperature is regarded as an unprecedented technological development. There are potential applications in microelectronics and computers, sensors, energy storage, power transmission, magnets for high-energy physics accelerators, fusion reactors, and nuclear magnetic resonance (NMR) imaging systems. Besides the practical applications, the discovery of these very high T_c metallic oxides has raised many fundamental questions about the nature of the superconductivity in this class of materials. These questions include the origins of the high T_c's, whether a new mechanism of superconductivity is present, or whether the Bardeen–Cooper–Schrieffer (BCS) theory, including its extensions to strong coupling, can describe the superconductivity in these materials.

Currently most of the research activity has focused on bulk samples obtained from powder processes.[2-5] Of equal interest for practical applications, as well as providing more quantitative mesurements on basic superconducting parameters, is the preparation and study of high T_c oxide films. In this letter we report our work in fabricating Y-Ba-Cu-O films by both diode and magnetron sputtering techniques from composite oxide targets. Superconducting films (50 mm × 50 mm) with T_c onsets of 95 K have been successfully and reproducibly obtained.

The diode and magnetron sputtering systems used here, although not elaborately designed or constructed, are not commercially available. The detailed description of the systems and the operating parameters have been published earlier.[6,7] Films 0.4–2.0 μm thick were deposited on substrates of sapphire and Al_2O_3 with deposition rates of 0.05–0.3 nm/s. The argon pressure during deposition was 5 mTorr for magnetron sputtering and 30 mTorr for diode sputtering. The substrate holder temperatures could be varied from room temperature to 500 °C. The results reported here are from the films deposited at room temperature. Compacted and sintered Y-Ba-Cu-O oxide powders with various compositions were used as sputtering targets. The film composition was examined by Rutherford backscattering spectrometry (RBS). The structure of the films was studied using x-ray diffraction analysis.

The as-deposited films are amorphous from both x-ray and electron diffraction, and are generally insulating. Post-deposition oxygen annealing treatments at temperature above 800 °C are necessary to transform the films to become superconducting at low temperatures. Inadequate heat treatments such as annealing at temperatures below 750 °C usually give films a semiconducting behavior before the superconducting transitions. The critical transition temperatures were measured using both ac and dc resistance versus temperature data. The ac method employed four-point pressure contacts usually with a small applied current of 0.05 to 0.25 μA. The dc method also uses the four-point technique but switching the polarization of the applied current during the measurements. The applied current in the dc method is larger, typically around 10–100 μA. Therefore, the T_c's obtained in the dc method, particularly at the complete superconducting state ($R = 0$), are slightly lower than the values by the ac method.

Figures 1(a) and 1(c) are the x-ray diffractometer traces of the post-deposition oxygen annealed Y-Ba-Cu-O films 0.7 μm thick deposited on sapphire and Al_2O_3 substrates, respectively. The majority phase of the films is similar to the orthorhombic structure observed for high T_c sin-

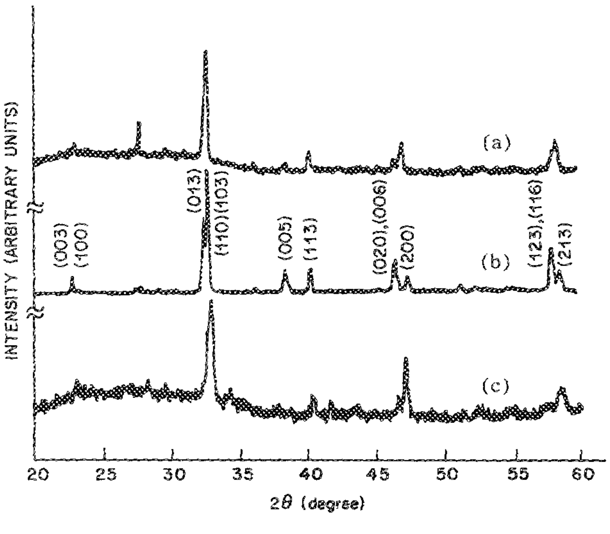

FIG. 1. X-ray diffraction traces of post-oxygen-annealed Y-Ba-Cu-O films on a sapphire substrate and (c) on randomly oriented Al_2O_3 substrate. The x-ray diffraction data in (b) was taken on a sintered powder sample with a composition of $Y_1Ba_2Cu_3O_{7-x}$.

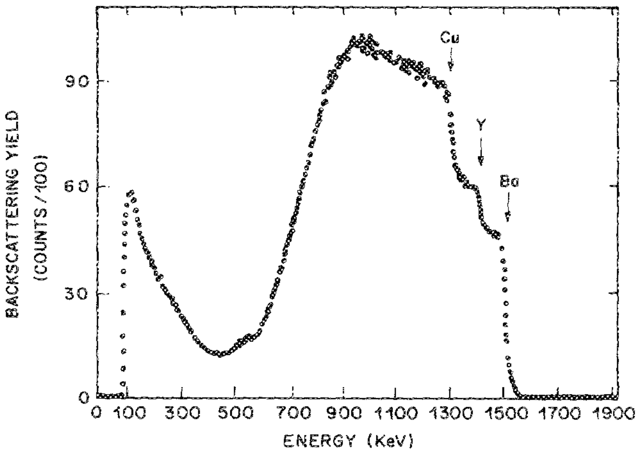

FIG. 2. Rutherford backscattering yield for a dc magnetron sputtered Y-Ba-Cu-O film.

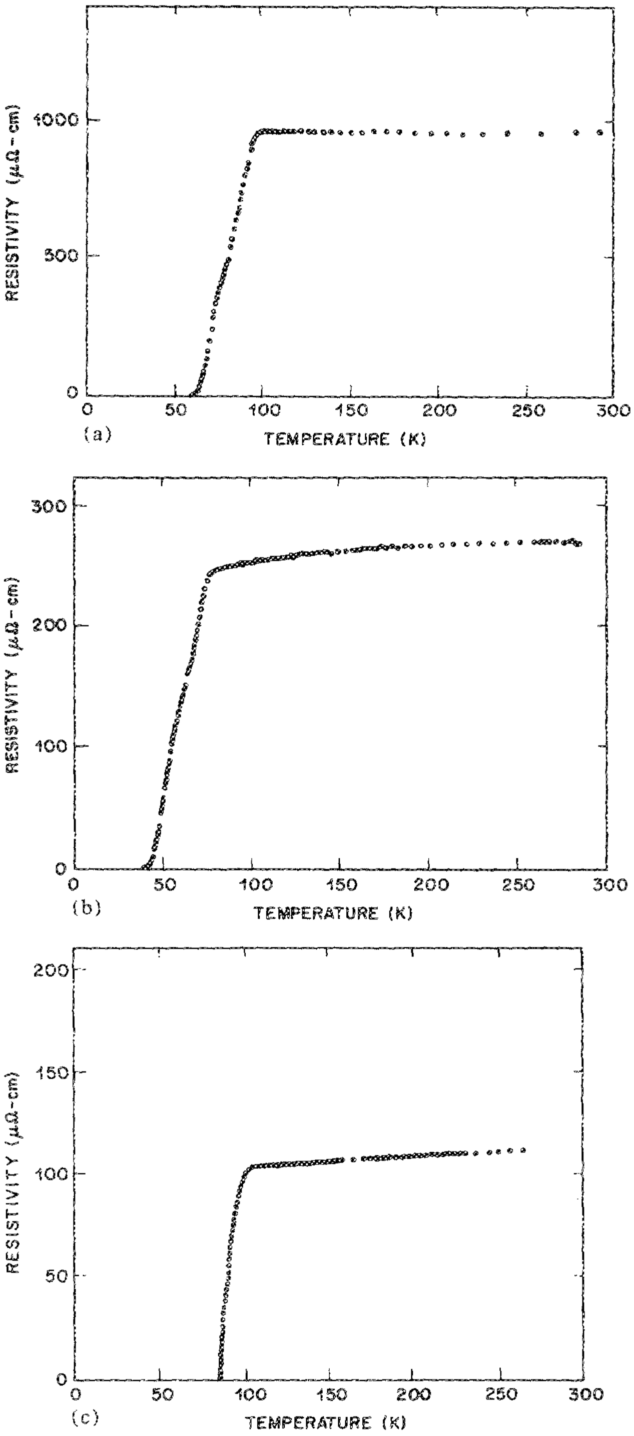

FIG. 3. Resistivity vs temperature for diode and magnetron sputtered Y-Ba-Cu-O films: (a) typical films from diode or magnetron sputtering for annealing at 850–900 °C in oxygen for more than 0.5 h (b) films annealed at 900 °C for a few minutes or annealed below 825 °C, and (c) the highest transition obtained from a magnetron-sputtered film heat treated at 850 °C for ~ 1 h in oxygen.

gle-phase bulk-powder $Y_1Ba_2Cu_3O_{7-x}$ samples [Fig. 1(b)]. This "high T_c" phase, in fact, has always been obtained in films with a somewhat wider range of compositions around the stoichiometry of $Y_1Ba_2Cu_3O_y$. So far the highest T_c's in our sputtered films have been found in the Cu-rich films with compositions approximately of $Y_1Ba_{1.9}Cu_{4.2}O_y$.

A closer examination of the x-ray diffraction data shows that there is a preferred orientation in the heat-treated films with the *c* axis lying in and the *a* axis perpendicular to the film plane. This is evidenced by comparing the intensities of the (006), (020), and (200) peaks in the films with those from the randomly oriented powders. Moreover, the (200) diffraction peak of the films shifts slightly toward the lower angle indicating a larger lattice spacing along the *a* axis. Thus, the difference in lattice spacing between the *a* and *b* axis is smaller in the films. The result may indicate a more random ordering of oxygen in the films than in the powder, and may well explain why the T_c's of the sputtered Y-Ba-Cu-O films are in general lower than those obtained in the bulk powder.

We found that in our sputtered films the superconducting properties do not seem to be directly correlated to the crystallographic structure (or phase). The "right" phase in the sputtered films is only a necessary condition, i.e., may not lead to the full superconductivity because of the lack of the percolating path connecting the superconducting islands. Evidently a significant portion of the heat-treated films is still amorphous as can be seen from the x-ray diffraction data. Prolonged heat treatments at high temperature (>850 °C) in the oxygen atmosphere which have been designed to eliminate the amorphous region as well as to increase the ordering of the oxygen in the right phase were found to increase the intensity of the minority phases. These additional x-ray diffraction peaks in the range between ($2\theta =$) 28° and 32° using copper K_α radiation could be some second phases in the films or may be caused by the film/substrate interaction, and need further identification. The microscopic distribution of the crystalline and amorphous phases in the film now being studied by the transmission electron microscopy in our laboratory is important and may lead to a better understanding of the superconducting properties.

A typical RBS curve of a post-oxygen heat-treated Y-Ba-Cu-O film is shown in Fig. 2 from which the chemical composition of the film was determined to be $Y_1Ba_{1.9}Cu_{4.2}O_y$ (at. %). From the RBS examinations on the entire films we found that the composition variation is no more than 10% across the sputtered film area, 50 mm in diameter for magnetron sputtering. For diode sputtered films, the composition is much more uniform across the film area which is 25 mm in diameter. The size of the uniformity is mainly determined by the size of the targets. The composition is also uniform through the film thickness.

We were able to obtain very consistent superconducting and structural properties in the sputtered films from run to run as long as we used the same target. This is consistent with the observation that the film composition does not vary much from one film to another when the sputtering conditions are kept the same.

In order to determine the oxygen (or other gas impurity such as argon) content, films with thinner thickness less than 0.1 μm are needed. However, in such a thin-film regime the film/substrate interaction can be significant, and the use of the substrates then becomes critical.

In general, the resistivity versus temperature behaviors of the superconducting films are classified into two categories and are shown in Figs. 3(a) and 3(b). Freshly deposited films with heat treatments at 850–900 °C in oxygen for over 30 min show a T_c onset of 95 K with $R = 0$ at about 60–70 K. The film in Fig. 3(a) has $R = 0$ at 60 K and a midpoint around 75 K. These films usually do not age over a period of a few days in the dry air. However, for films with improper heat treatments, such as annealing below 825 °C or a few minutes at 900 °C, the T_c ($R = 0$) is reduced substantially, to 36–40 K in a few days even for samples kept in the dry air. The T_c's of all the films are reduced drastically when placed in the surrounding of water or water moisture. The aging phenomenon in the films as well as in the sintered powders certainly causes concern in the practical applications. Although most of the films fall into the above categories, the sharpest transition so far obtained in a dc magnetron-sputtered film annealed at 850 °C for ~ 1 h and then slowly cooled under oxygen is shown in Fig. 3(c), with a T_c onset above 95 K, becoming fully superconducting at 85 K.

For the film with T_c at 85 K ($R = 0$), the critical current at 4.2 K is 66 mA using 1 μV in voltage rise as a criterion. The thickness of the film is 0.7 μm. If the whole cross section of the film were assumed to be uniformly superconducting this implies a critical current density over 3000 A/cm^2. This is very much a lower bound estimate in view of the inhomogeneity of the two-dimensional film, the portion of the amorphous region, and the interaction between the film and the substrate. More recently, a much higher J_c of 10^4 A/cm^2 at 4.2 K has also been obtained in our sputtered films deposited on a different substrate of MgO single crystal with T_c ($R = 0$) around 55 K.

The room-temperature resistivity of the films should be low enough to ensure the occurrence of the superconductivity. The values are generally around 100–1000 $\mu\Omega$ cm. If the values are too high over 5000 $\mu\Omega$ cm films are often semiconducting or even insulating. However, we also found that lowering the resistivity alone would not increase the superconducting transition temperatures. In other words, there seems to be no correlation between the T_c's and the room-temperature resistivities once the latter are low enough.

In conclusion, we have clearly demonstrated that the high T_c oxide superconducting films with T_c onset of 95 K can be grown by simple and common techniques such as sputtering. We have studied the crystallographic phases, the film texture, the composition, and the uniformity in the high T_c films. Reasonably critical currents have been obtained. Future work will be focused on the study of the film microstructure, the increase of the critical currents, and the film/substrate interaction. We will also carry out basic superconductivity measurements and fabricate devices for practical applications.

During the course of this research work, we learned that Laibowitz *et al.* at IBM Yorktown Heights[8] and Hammond *et al.* at Stanford University[9] have used electron beam evaporation to obtain Y-Ba-Cu-O films with T_c ($R = 0$) above 80 K. Somekh *et al.*[10] of the University of Cambridge have also used dc magnetron sputtering to prepare superconducting Y-Ba-Cu-O films.

[1] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[2] R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).

[3] P. M. Grant, R. B. Beyers, E. M. Engler, G. Lim, S. S. P. Parkin, M. L. Ramirez, V. Y. Lee, A. Nazzal, J. E. Vazquez, and R. J. Savoy, Phys. Rev. B **35**, 7242 (1987).

[4] J. Moreland, J. W. Ekin, L. F. Goodrich, T. E. Capobianco, A. F. Clark, J. Kwo, M. Hong, and S. H. Liou, Phys. Rev. B **35**, 8856 (1987).

[5] M. D. Kirk, D. P. E. Smith, D. B. Mitzi, J. Z. Sun, D. J. Webb, K. Char, M. R. Hahn, M. Naito, B. Oh, M. R. Beasley, T. H. Geballe, R. H. Hammond, A. Kapitulnik, and C. F. Quate, Phys. Rev. B **35**, 8850 (1987).

[6] M. Hong, E. M. Gyorgy, and D. D. Bacon, Appl. Phys. Lett. **44**, 706 (1984).

[7] S. H. Liou and C. L. Chien, J. Appl. Phys. **55**, 1820 (1984).

[8] R. B. Laibowitz, R. H. Koch, P. Chaudhari, and R. J. Gambino, Phys. Rev. B **35**, 8821 (1987).

[9] R. H. Hammond, M. Naito, B. Oh, M. Hahn, P. Rosenthal, A. Marshall, N. Missert, M. R. Beasley, A. Kapitulnik, and T. H. Geballe, Materials Research Society Conference Proceedings, Vol. EA-11, on High Temperature Superconductors (Materials Research Society, Pittsburgh, PA, 1987).

[10] R. E. Somekh, M. G. Blamire, Z. H. Barber, K. Butler, J. H. James, G. W. Morris, E. J. Tomlinson, A. P. Schwarzenberger, W. M. Stobbs, and J. E. Evetts, Nature **326**, 857 (1987).