

## Effect of annealing in oxygen on the structure formation of Bi-Sr-Ca-Cu-O thin films

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The structure, bonding, and  $T_c$  of Bi-Sr-Ca-Cu-O superconducting films, prepared by rf magnetron sputtering, changed systematically upon varying the annealing conditions in oxygen. The spacing between the double Bi-O layers decreased from 22 to 18 Å and the degree of  $c$ -axis orientation became higher with the annealing. No change in the Bi core-level electron spectra with the annealing was observed. The Cu core-level electron spectra indicated an increase of the Cu valence with the annealing. The core-level electron spectra of Sr and Ca showed the possibilities of random distribution of the Ca and Sr atoms between the double Bi-O layers prior to annealing and exchanging their lattice sites in the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  crystal structure after annealing. The zero-resistance temperature of the films was 10 K before annealing, and rose up to 96 K (midpoint 105 K) after annealing. The annealing favors both oxidation of Cu and ordering of Sr and Ca atoms within the unit cell of the 2:2:2:3 crystal structure.

Recently, Maeda, Tanaka, Fukutomi, and Asano<sup>1</sup> have reported that  $\text{BiSrCaCu}_2\text{O}_x$  is a high- $T_c$  superconductor. The Bi-Sr-Ca-Cu-O system is known to have two (higher- $T_c$  and lower- $T_c$ ) phases exhibiting  $T_c$ 's of 105 and 80 K. It was reported that the characteristic layer spacing ( $d$  value corresponding to  $c/2$ ,  $c$  is the lattice parameter) of the higher- $T_c$  phase is 18 Å and the composition should correspond to  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ .<sup>2,3</sup> The higher- $T_c$  phase should be constructed by inserting a supplementary Cu-O layer and a Ca layer between double Bi-O layers of the lower- $T_c$  phase.

The studies of high- $T_c$  superconducting thin films are important for fundamental research and electronic device applications.<sup>4,5</sup> It is necessary to anneal the sputter deposited films on the substrates in flowing oxygen for obtaining the high- $T_c$  superconductivity. In this experiment we study the effect of annealing in oxygen on the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  (2:2:2:3) crystal structure formation of Bi-Sr-Ca-Cu-O thin films.

Bi-Sr-Ca-Cu-O thin films were prepared by rf-planar magnetron sputtering. Sputtering conditions are described elsewhere in detail.<sup>6</sup> The target was a complex oxide of Bi-Sr-Ca-Cu which was made by sintering a mixture of  $\text{Bi}_2\text{O}_3$  (99.999% pure),  $\text{SrCO}_3$  (99.9% pure),  $\text{CaCO}_3$  (99% pure), and  $\text{CuO}$  (99.9% pure). The thickness of the films was 2000 Å. The composition of the films was determined by electron probe microanalysis (EPMA).

TABLE I. Annealing conditions of the sputter-deposited films.

Sample	Time (min)	Temperature (°C)	
a	...	...	As deposited
b	12	845	One step
c	60	845	One step
d	300	845	One step
e	20+300	900+865	Two step

The result of the EPMA analysis of the thin films is subject to some uncertainty (15%). The ratio of Bi:Sr:Ca:Cu was found to be about 2:2:2:3. Annealing conditions of the films are listed in Table I.

The crystal structure of the films was examined by x-ray diffraction with a Rigaku RU-200 using Cu  $K\alpha$  radiation. X-ray diffraction patterns are shown in Fig. 1. The peak position of the (002) reflection, represented by the arrow in Fig. 1, shifted from 4.0° (sample a) to 5.2° (sample e). The  $d$  value decreased from 22 Å (sample a) to 18 Å (sample e) and the degree of  $c$ -axis orientation became higher with the annealing. In this experiment the

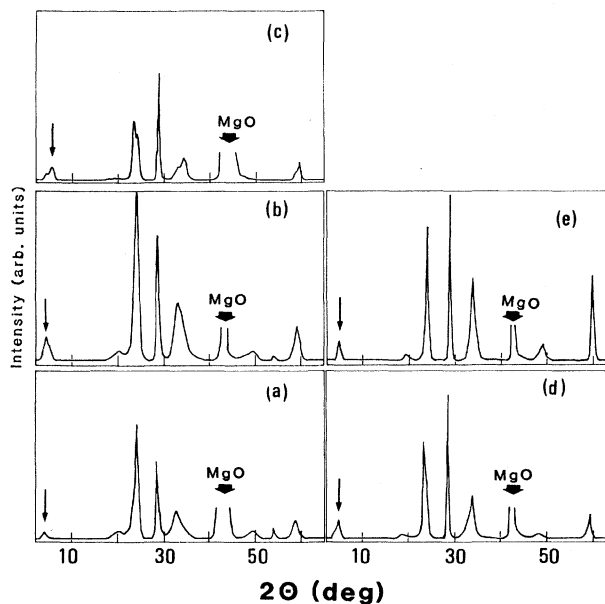


FIG. 1. X-ray diffraction patterns over the  $2\theta$  range from 2° to 65° for samples a, b, c, d, and e. The arrow represents the (002) reflection.

content of the 2:2:1:2 phase with a  $T_c$  of 80 K and a  $d$  value of 15 Å was smaller than a few percent in the films judging from these x-ray diffraction patterns. However, we can prepare highly  $c$ -axis oriented films of the 2:2:1:2 phase of the bismuth cuprate superconductor by annealing at lower temperature (800 °C, 300 min).<sup>7</sup>

The resistivity measurement was performed using the standard four-probe method with gold electrodes deposited on the film surface. The samples annealed with longer time and higher temperature exhibited sharper superconducting transitions than those with shorter time and lower temperature anneals. From sample a to e the zero-resistance temperature varied from 10 to 96 K. The temperature dependence of the resistivity of samples a to e are shown in Fig. 2. Figure 2 clearly reveals a significant change of  $T_c$  of the films by the annealing. This fact shows that the high- $T_c$  superconductivity can be obtained by the proper annealing.

Lattice images of the samples a and e, shown in Fig. 3, were observed with JEOL JEM400FX transmission electron microscope operated at 400 kV. Many dark or bright blobs are observed with diffused and bold lines corresponding to  $c$ -plane layers in sample a. This may reflect the disordering of the Sr, Ca, and Cu atoms between the double Bi-O layers. The complete Bi-layered structure ( $d=18$  Å) is formed in sample e. The spacing of 21 Å was also observed in sample e. The broadening of the ( $00n$ ) reflection in the x-ray diffraction pattern of sample e may be due to coexistence of the 21 and 18 Å layers.

The material with  $d=21$  Å should have an extra Cu-O and a Ca layer between the double Bi-O layers of the 2:2:3 phase and its composition should be 2:2:3:4 in analogy with the thallium cuprate superconductor.<sup>8,9</sup> In Ref. 9 the  $T_c$  for the 2:2:3:4 phase of the thallium system was estimated to 150 K and it is expected that the  $T_c$  for the 2:2:3:4 phase of the bismuth system should become higher than that for the 2:2:2:3 phase. However, no sign of superconductivity above 110 K has been observed on sample e as shown in Fig. 2. Recently, Adachi *et al.*<sup>10</sup> have found out that the  $T_c$  of the 2:2:3:4 phase of the bismuth system was 90 K. So the result in Fig. 2 is consistent with that in Ref. 10.

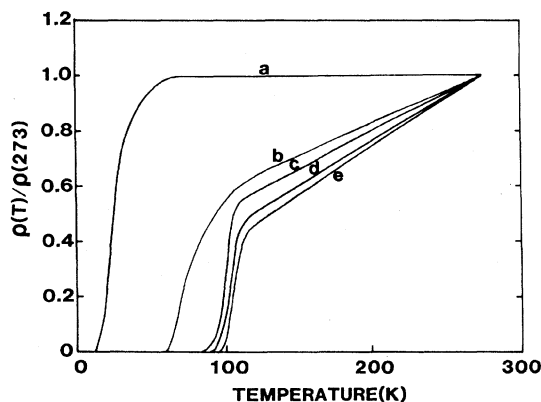


FIG. 2. Normalized resistance vs temperature curves for samples a to e.

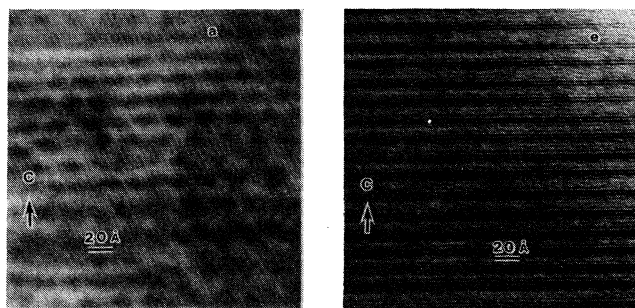


FIG. 3. Lattice images of samples a and e.

Highly ordered films can be obtained by annealing with sufficient time and temperature to form the 2:2:2:3 crystal structure ranging over the 2000 Å film thickness.

A VG Scientific ESCALAB-5 electron spectrometer was used to collect photoemission spectra with Al  $K\alpha$  radiation. The normal operating vacuum pressure was less than  $3 \times 10^{-8}$  Pa. The measurement of the electron spectra was carried out after *in situ* scraping the film surface with a diamond file until no further change in the photoemission spectra was observed and the composition ratio fell within  $\pm 10\%$  of the expected value of 2(Bi):2(Sr):2(Ca):3(Cu).

The Bi  $4f_{7/2}$  electron binding energy of the films before and after annealing was 158.1 eV which is almost identical to that of  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_x$  (158.0 eV).<sup>11</sup> Since the annealing gives no effect for Bi, the Bi-O bond should be formed even in the as-deposited films.

The Cu  $2p_{3/2}$  electron spectra are shown in Fig. 4. The

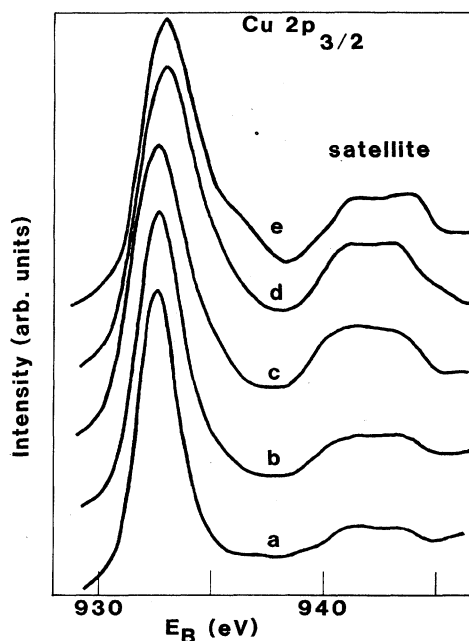


FIG. 4. The Cu  $2p_{3/2}$  electron spectra of samples a, b, c, d, and e.

Cu  $2p_{3/2}$  electron binding energies were 932.5 (sample a), 932.7 (samples b, c, and d), and 932.9 eV (sample e). The linewidth of the main peak gradually increased from samples a to e. Since the greater electron binding energy corresponds to the greater valence in x-ray photoemission, the mean Cu valence of sample a is smallest among the samples and that increases with the annealing of the films. A shoulder peak around 934.5 eV, observed clearly in spectrum e, corresponds to the  $\text{Cu}^{3+}$  species.<sup>12</sup> From the deconvolution and peak fitting with 100% Gaussian and 2.0 eV full width at half maxima the  $\text{Cu}^{3+}$  species is contained in approximately 20% of the total Cu, so the mean valence for Cu corresponds to +2.2 in sample e. Moreover, the satellite structure of the spectra due to the  $d^9$  final state<sup>13</sup> was observed significantly in the annealed samples. This confirms the presence of dominantly  $\text{Cu}^{2+}$  species and the charge transfer between Cu and O atoms. The intensity ratios of the satellite peak to the main peak of the samples a and e were 0.16 and 0.44, respectively. The satellite to main peak ratio of CuO is 0.54, so sample e contains the  $\text{Cu}^{3+}$  species in approximately 20% of the total Cu. Thus, the mean valence for Cu of +2.2 was reconfirmed in sample e. The Cu  $2p_{3/2}$  electron binding energy, the main peak width, and the satellite peak intensity are smallest in sample a. The sample a should contain predominantly the  $\text{Cu}^{1+}$  species judging from these features. The  $\text{Cu}^{2+}$  content in the sample a was approximately 30% of the total Cu, and the mean valence for Cu corresponds to +1.3.

The Sr  $3d$  and Ca  $2p$  spectra are shown in Figs. 5 and 6. The chemical states of the Sr and Ca atoms changed systematically from samples a to e. The chemical states of these atoms are complicated. An SSI SSX100 electron spectrometer with monochromatized Al  $K\alpha$  radiation was used to collect the high-resolution (0.6 eV) Sr  $3d$  and Ca  $2p$  spectra of sample e. The Sr  $3d$  and Ca  $2p$  high-resolution spectra are shown in Figs. 7 and 8. As shown in both figures these spectra can be separated into two components. The Sr  $3d_{5/2}$  lower binding energy (L) and higher binding energy (H) peaks positioned at 131.7 and 132.7 eV, respectively. The Ca  $2p_{3/2}$  L and H peaks positioned at 344.8 and 346.1 eV, respectively. The L and H peaks can readily be assigned to the Sr and Ca atoms between the Bi-O and Cu-O sheets and between the adjacent Cu-O sheets, respectively.<sup>11</sup> The electron spectra expected from the proposed crystal structure of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  is not consistent with the observed splitting of the Sr and Ca core-level electron peaks for the Bi-Sr-Ca-Cu-O films.

The difference of the divalent ion radius between Sr and Ca is 0.21 Å. However, in spite of such a difference, the result shown in Figs. 7 and 8 indicates that Sr and Ca atoms can occupy both sites in the proposed  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  structure. The intensity ratios of H to L peaks of the Sr  $3d$  and Ca  $2p$  spectra in the sample e were 0.69 and 0.71, respectively. The H to L ratios of the Sr and Ca spectra expected from the proposed  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  structure is 1, if Sr and Ca are randomly distributed among two possible sites. This result may be due to the

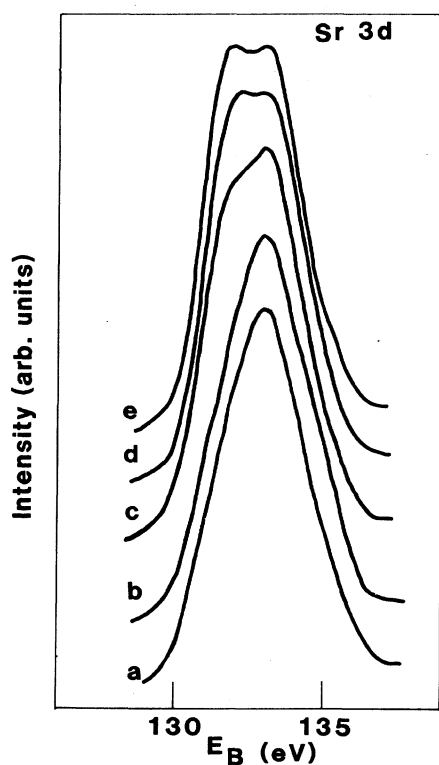


FIG. 5. The Sr  $3d$  electron spectra of samples a, b, c, d, and e.

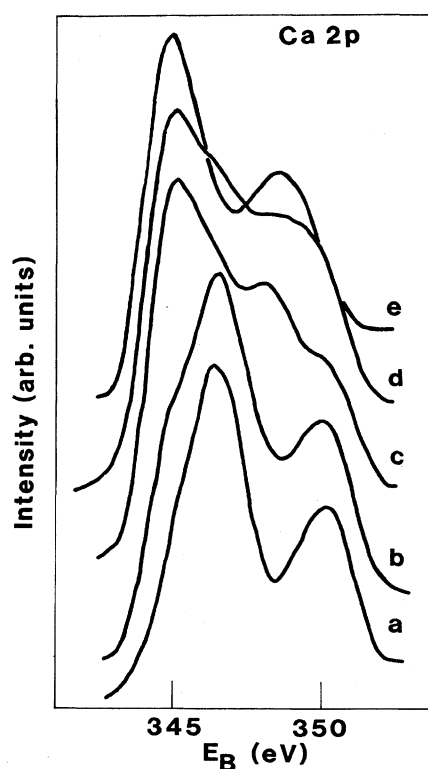


FIG. 6. The Ca  $2p$  electron spectra of samples a, b, c, d, and e.

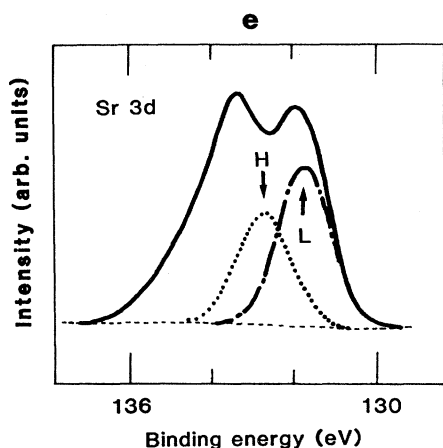


FIG. 7. The high-resolution Sr  $3d$  spectrum of sample e. The  $3d_{5/2}$  spectra of the deconvoluted peaks are only illustrated in this figure.

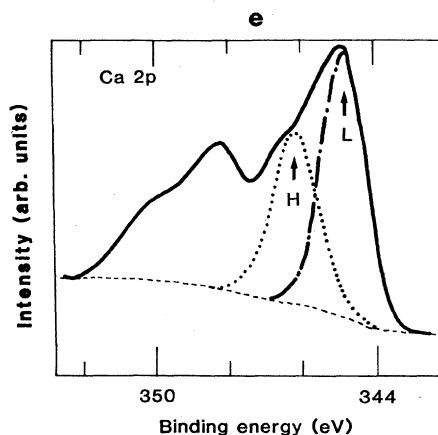


FIG. 8. The high-resolution Ca  $2p$  spectrum of sample e. The  $2p_{3/2}$  spectra of the deconvoluted peaks are only illustrated in this figure.

incompleteness of the cation ordering even in the annealed films as well as observed for ceramics.<sup>14</sup> The Sr, Ca, and Cu atoms in the as-deposited films should randomly distribute between the double Bi-O layers judging from the x-ray diffraction pattern showing weak reflection and the transmission electron microscopy showing many blobs between the bold lines.

These results suggest that the formation of the 2:2:2:3 crystal structure of the Sr, Ca, Cu, and O atoms between the double Bi-O layers can be completed by annealing in oxygen. The annealing favors the ordering of Sr and Ca atoms and the oxidation of Cu atoms within the unit cell. It is unlikely that Bi plays a direct role in any conduction

mechanism for the Bi-Sr-Ca-Cu-O system. The valence for Cu must correlate with the superconductivity in cuprate superconductors. Ordering of the Sr and Ca atoms and oxidation of the Cu atoms within the unit cell are necessary for obtaining the high- $T_c$  superconductivity.

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<sup>1</sup>H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, *Jpn. J. Appl. Phys.* **27**, L209 (1988).

<sup>2</sup>E. T. Muromachi, Y. Uchida, Y. Matsui, M. Onoda, and K. Kato (unpublished); H. W. Zandbergen, Y. K. Huang, M. J. Menken, J. N. Li, K. Kodawaki, A. A. Menovsky, G. van Tendeloo, and S. Amelinckx, *Nature (London)* **332**, 620 (1988).

<sup>3</sup>R. Ramesh, C. J. D. Hetherington, G. Thomas, S. M. Green, C. Jiang, M. L. Rudee, and H. L. Luo, *Appl. Phys. Lett.* **53**, 615 (1988), J. L. Tallon, R. G. Buckley, P. W. Gilberd, M. R. Presland, I. W. M. Brown, M. E. Bowden, L. A. Christian, and R. Goguel, *Nature (London)* **333**, 153 (1988).

<sup>4</sup>Y. Ichikawa, H. Adachi, K. Hirochi, K. Setsune, S. Hatta, and K. Wasa, *Phys. Rev. B* **38**, 765 (1988).

<sup>5</sup>H. Adachi, K. Wasa, Y. Ichikawa, K. Hirochi, and K. Setsune, *J. Cryst. Growth* **91**, 352 (1988).

<sup>6</sup>Y. Ichikawa, H. Adachi, K. Hirochi, K. Setsune, and K. Wasa, in *Proceedings of the International Meeting on Advanced Materials, 1988*, edited by K. Tachikawa and K. Kitazawa (Materials Research Society, Pittsburgh, in press).

<sup>7</sup>K. Hirochi *et al.*, *Jpn. Soc. Appl. Phys.* (to be published).

<sup>8</sup>S. S. P. Parkin, V. Y. Lee, A. I. Nazzari, R. Savoy, R. Beyers, and S. J. La Placa, *Phys. Rev. Lett.* **61**, 750 (1988).

<sup>9</sup>R. V. Kasowski, W. Y. Hsu, and F. Herman, *Phys. Rev. B* **38**, 6470 (1988).

<sup>10</sup>H. Adachi, S. Kohiki, K. Setsune, T. Mitsuyasu, and K. Wasa, *Jpn. J. Appl. Phys.* **27**, L1883 (1988).

<sup>11</sup>S. Kohiki, T. Wada, S. Kawashima, H. Takagi, S. Uchida, and S. Tanaka, *Phys. Rev. B* **38**, 7051 (1988); the Sr  $3d$  and Ca  $2p$  spectra of the  $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_x$  single crystals, prepared by Takagi *et al.* [H. Takagi, H. Eisaki, S. Uchida, A. Maeda, S. Tajima, K. Uchinokura, and S. Tanaka, *Nature (London)* **332**, 236 (1988)], were partitioned into two components. The Sr and Ca atoms between the Bi-O and Cu-O sheets corresponded to the spectra for 131.7 eV of the Sr  $3d_{5/2}$  and for 344.7 eV of the Ca  $2p_{3/2}$  electrons. Those between the adjacent Cu-O sheets corresponded to the spectra for 132.9 eV of the Sr  $3d_{5/2}$  and 345.9 eV of the Ca  $2p_{3/2}$  electrons.

<sup>12</sup>P. Steiner, V. Kinsinger, I. Sander, B. Siegwart, S. Hufner, C. Politis, R. Hoppe, and H. P. Muller, *Z. Phys.* **67**, 497 (1987).

<sup>13</sup>L. Yin, I. Adler, T. Tsang, L. J. Matienzo, and S. O. Grim, *Chem. Phys. Lett.* **24**, 81 (1974).

<sup>14</sup>S. Horiuchi, H. Maeda, Y. Tanaka, and Y. Matsui (unpublished).

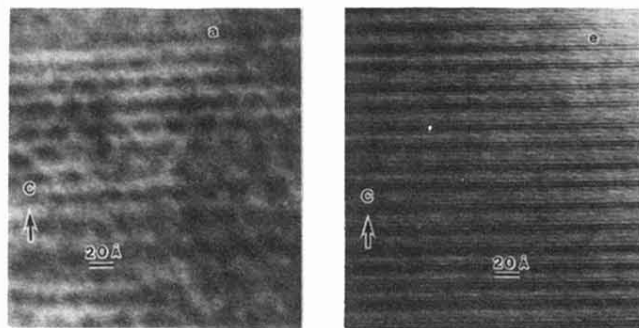


FIG. 3. Lattice images of samples a and e.