Superconductivity and Cu valence of Bi-Sr-Ca-Cu-O thin films

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Bi-Sr-Ca-Cu-O superconducting films were prepared by rf magnetron sputtering using a target with modulated composition and successive annealing in oxygen. The resistivity and Cu valence of the films varied before and after annealing. The zero-resistance temperature of the films was 10 K before the annealing, and rose up to 96 K (midpoint 105 K) after annealing. Essentially no change in the characteristic layer spacing (d value) of ≈ 18 Å, corresponding to $c/2$, was observed before and after annealing as seen by x-ray diffraction. The Cu valence of the films was investigated by x-ray photoemission before and after annealing. The photoemission core-level spectra and LMM Auger emission spectra revealed that the Cu valence after annealing became larger than that obtained before annealing. The superconductivity obviously is correlated with the Cu valence of the films.

It is well known that a high-temperture superconducting transition takes place in cuprate-based systems.[1−6] Bednorz and Müller[1] first reported high-temperature ($T_c \sim 30$ K) superconductivity in the La-Ba-Cu-O system. Other workers[2,3] recorded higher T_c's (~ 40 K) in the La-Sr-Cu-O systems. Wu et al.[4] discovered 90-K superconductivity in the Y-Ba-Cu-O system. Recently, Maeda, Tanaka, Fukutomi, and Asano[5] reported that Bi-Sr-Ca-Cu$_2$O$_x$ has a T_c ranging from 105 to 70 K. Following the discovery of the Bi-Sr-Ca-Cu-O system, Sheng and Hermann[6] have reported superconducting transitions in a Tl-Ba-Ca-Cu-O system ($T_c \sim 107$ K).

Thin-film studies of these materials are important for fundamental research and electronic-device applications.[7,8] It is of great interest to elucidate the origin of the high-T_c superconductivity. In this experiment we study the change in electronic state of Bi-Sr-Ca-Cu-O thin films before and after annealing in flowing oxygen, using x-ray photoemission, as a step toward understanding the mechanism of high-T_c superconductivity.

Bi-Sr-Ca-Cu-O thin films were prepared by rf planar magnetron sputtering. Sputtering conditions are listed in Table I. The target was a complex oxide of Bi-Sr-Ca-Cu which was made by sintering a mixture of Bi$_2$O$_3$ (99.999%), SrCO$_3$ (99.9%), CaCO$_3$ (99%), and CuO (99.9%) at 880 °C for 8 h in air. The thickness of the films was 2000 Å. Annealing of the films was done as follows: the as-deposited films were annealed at 900 °C for 20 min and subsequently kept at 865 °C for 5 h in an oxygen gas flow.

TABLE I. Sputtering conditions.

Target	Bi-Sr-Ca-Cu-O (diam 100 mm)
Substrate	MgO (100)
Sputtering gas	Ar/O$_2$ = 1.5
Gas pressure	0.5 Pa
rf power	150 W
Substrate temperature	800 °C
Growth rate	80 Å/min

The composition of the films was determined by inductively coupled plasma-emission spectroscopy and electron microprobe analysis. The ratio of Bi:Sr:Ca:Cu was found to be about 2:2:2:3.

The Bi-Sr-Ca-Cu-O system is known to have two (higher-T_c and lower-T_c) phases exhibiting T_c of 105 and 80 K, respectively. The crystal structure of Bi$_2$ (Sr,Ca)$_3$Cu$_2$O$_x$ with orthorhombic cell $a \sim 5.4$, $b \sim 27$, and $c \sim 30$ Å has been reported.[9−12] The lower-T_c phase in the Bi-Sr-Ca-Cu-O system was identified as Bi$_2$(Sr,Ca)$_3$Cu$_2$O$_x$ and its structure comprises pairs of Cu-O sheets, interleaved by Ca (Sr), alternating with double Bi-O sheets.[9] It was reported that the characteristic layer spacing (d value) of the higher-T_c phase was ~ 18 Å and the composition should correspond to Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$.[13,14] The higher-T_c phase should be constructed by inserting a supplementary Cu-O layer and a Ca layer between double Bi-O layers.

The crystal structure of the films before and after annealing was examined by x-ray diffraction using Cu $K\alpha$ radiation. X-ray diffraction patterns of the films before and after annealing are shown in Figs. 1(a) and 1(b), respectively. A broad peak at $2\theta = 4.8°$, characterizing the higher-T_c phase, is observed in both films. This fact indicates that most of the cation layered structure in the higher-T_c phase is constructed in the films before annealing. In the films after annealing the higher-T_c phase coexists with the lower-T_c phase, since a small sharp peak at $2\theta = 5.8°$, characterizing the lower-T_c phase, is also observed. By analogy with the lower-T_c phase with $d \sim 15$ Å, the peak at $2\theta = 4.8°$ was assigned to the (002) reflection of the higher-T_c phase, and then the characteristic layer spacing corresponds to ~ 18 Å. The broadening of the (00n) reflection of the higher-T_c phase may be due to coexistence of the ~ 15, ~ 18, and ~ 21 Å layers. Lattice images of the films before and after annealing were observed with a Japan Electron Optics Lab (JEOL) JEM400FX transmission electron microscope operated at 400 kV. Three types of layered structure with ~ 15, ~ 18, and ~ 21 Å spacing were observed for both films.
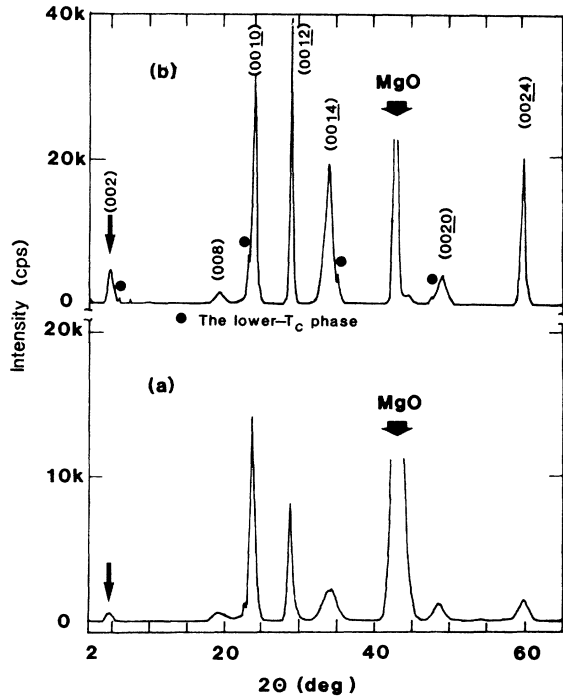
FIG. 1. X-ray diffraction patterns over the 2θ range from $2°$ to $65°$ for the Bi-Sr-Ca-Cu-O films (a) before and (b) after annealing. Reflections with the Miller indices are for the higher-T_c phase.

The resistivity measurement of the films was performed using a standard four-probe method with gold electrodes deposited on the film surface. The temperature dependence of the resistivity of the films before and after annealing, shown in Fig. 2, clearly reveals the effect of annealing in oxygen. The superconductivity of the films changed significantly before and after annealing. The zero-resistance temperature varies from 10 to 96 K with the annealing. The films after annealing exhibit a sharper superconducting transition than they do before annealing.

It is a common belief that a Cu valence greater than 2 is required to have superconductivity in the cuprate-based systems. The dominant charge carriers are holes, which are supplied in the Cu-O plane by the substitution of La for Sr in La_2CuO_4 or by adding oxygen to $YBa_2Cu_3O_6$.
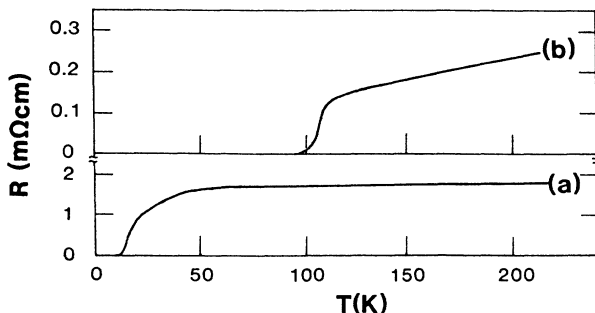

FIG. 2. Resistance vs temperature curves for the films (a) before and (b) after annealing.

In $Bi_2(Sr,Ca)_3Cu_2O_x$ the conduction is dominated by holes and the mean Cu valence is 2.35.[15] Therefore, the Cu valence must be correlated with the superconductivity in cuprate superconductors.

A VG Scientific ESCALAB-5 electron spectrometer was used to collect photoemission spectra with Al $K\alpha$ radiation. The spectrometer was calibrated by utilizing the Au $4f_{7/2}$ (84.0 eV), Pd $3d_{5/2}$ (335.4 eV), and Ag $3d_{5/2}$ (368.3 eV) electrons. The probable electron energy uncertainty amounted to 0.1 eV. The normal operating vacuum pressure was less than 3×10^{-8} Pa. The measurement of the electron spectra was carried out after in situ scraping of the film surface with a diamond file until no further change in the photoemission spectra was observed and the composition ratio fell within 10% of the expected value of 2(Bi):2(Sr):2(Ca):3(Cu). The electron binding energies were referred to the C $1s$ line of impurity carbon, which had a value of 284.6 eV.

The Cu $2p_{3/2}$ electron spectra are shown in Fig. 3. The Cu $2p_{3/2}$ electron binding energy of the films before the annealing is 932.5 eV and that after the annealing is 932.9 eV, which are larger than that of Cu_2O (932.1 eV).[16] The greater electron binding energy corresponds to the greater Cu valence in these oxides. Consequently, the mean Cu valence of the films before the annealing is smaller than that after the annealing. A shoulder peak around 934.5 eV, observed clearly in Fig. 3(b), corresponds to the Cu^{3+} species.[17] From the deconvolution and peak fitting with a 100% Gaussian with a 2.0-eV full width at half maxima, the Cu^{3+} species is seen to contain approximately 20% of the total Cu, so the mean Cu valence corresponds to 2.2. Moreover, the satellite structure of the spectra due to d^9 electronic states[18] is observed in the films after annealing. This confirms the presence of dominantly Cu^{2+} species and the charge transfer between Cu and O atoms in the films. The intensity ratios of the satellite peak to the main peak of the films before and after annealing are 0.16 and 0.44, respectively. The value is larger for the films after
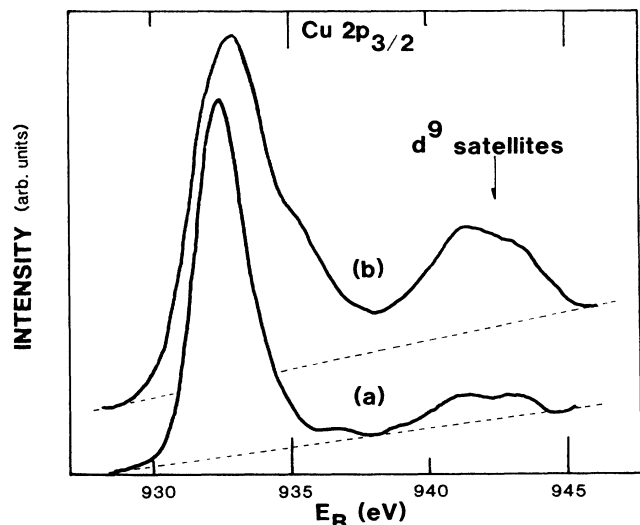

FIG. 3. The Cu $2p_{3/2}$ electron spectra of the Bi-Sr-Ca-Cu-O films in the higher-T_c phase (a) before and (b) after annealing.
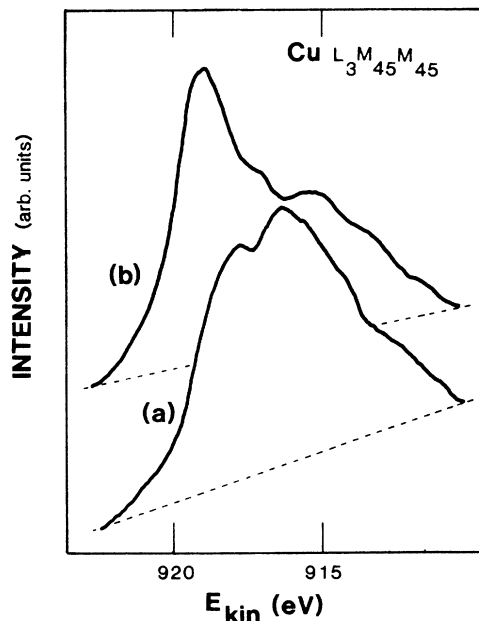
FIG. 4. The Cu $L_3M_{45}M_{45}$ Auger electron spectra of the Bi-Sr-Ca-Cu-O films in the higher-T_c phase (a) before and (b) after annealing.

FIG. 5. The Bi $4f$ electron spectra of the Bi-Sr-Ca-Cu-O films in the higher-T_c phase (a) before and (b) after annealing.

annealing. The satellite-to-main-peak ratio of CuO is 0.54, so the films after annealing contain Cu^{3+}, comprising approximately 20% of the total Cu. Thus, the mean Cu valence (2.2) is reconfirmed. The Cu^{2+} content in the films before the annealing is approximately 30% of the total Cu, and the mean Cu valence corresponds to 1.3.

We can observe the Cu $L_3M_{45}M_{45}$ Auger electron emission accompanying the Cu $2p$ hole relaxation. The Cu LMM Auger spectra of the films before and after annealing are shown in Fig. 4. The Auger parameter, which is defined as the sum of the Cu $2p_{3/2}$ electron binding energy and the Cu $L_3M_{45}M_{45}$ Auger electron kinetic energy, changed from 1848.9 to 1851.8 eV with the annealing. The Auger parameters reported for Cu_2O and CuO are 1849.2 and 1851.7 eV, respectively.[19] From both the core-level and Auger electron emissions of the films before and after annealing we conclude that the Cu oxidation of the as-deposited films proceeds with the annealing in oxygen.

It is unlikely that Bi plays a direct role in any conduction mechanism for the Bi-Sr-Ca-Cu-O system unless some of the Bi is oxidized to Bi^{4+}. The Bi $4f_{7/2}$ electron binding energy of the films before and after annealing is 158.1 eV as shown in Fig. 5, which is almost identical to that of $Bi_2(Sr,Ca)_3Cu_2O_x$ (158.0 eV).[20] The existence of Bi^{4+} was not observed in this experiment. There is no change in the spectra of the films before and after annealing. Since annealing in oxygen gives no effect for Bi, we can conclude that the Bi valence must not be correlated with the resistivity change of the films with annealing.
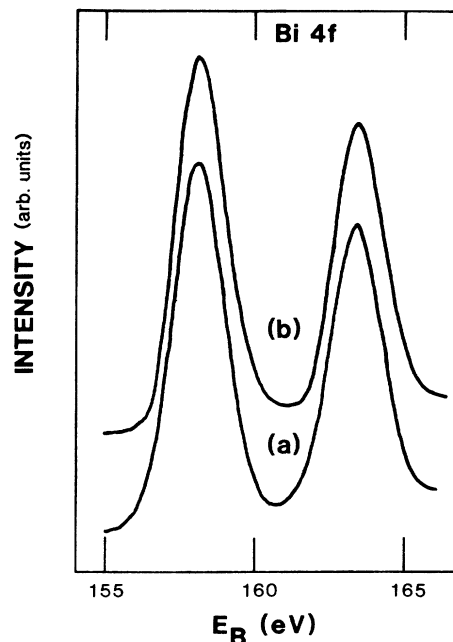
The dominant charge carriers of the Bi-Sr-Ca-Cu-O system are holes[15] which are supplied to the Cu-O plane similarly to the La-Sr-Cu-O and Y-Ba-Cu-O systems. There must be strong Cud-Op interactions resulting in Cu^{2+}-Cu^{3+} charge fluctuations. The possible resonant coupling to, and enhancement of, the natural ground-state Cu^{2+}-Cu^{3+} fluctuations between in-plane Cu atoms may be important for high-T_c superconductivity.[21] The mean Cu valence variation with annealing for the Bi-Sr-Ca-Cu-O films in the higher-T_c phase is reflected in their superconducting transition temperatures.

The present experiment leads to the conclusion that the mean Cu valence increase, by 0.9 with the annealing in oxygen, is responsible for the change in the resistivity of the Bi-Sr-Ca-Cu-O films in the higher-T_c phase. It is possible that strong Cud-O$2p$ interactions bring about Cu^{2+}-Cu^{3+} charge fluctuations. The existence of Bi^{4+} in this system is unlikely. For obtaining high-temperature superconductivity in the cuprate systems, it is necesssary to increase the Cu^{3+} species in the films.

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