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Composition Range Exhibiting 110K-T_c in Bi-Sr-Ca-Cu-O Superconducting Oxide Films Prepared by Sequential Deposition

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Bi-Sr-Ca-Cu-O superconducting oxide films were prepared by a sequential electron beam deposition technique. The deposited films were annealed at around 875°C. Only films thinner than 250 nm with appropriate composition showed zero resistance transition above 100K. This composition range lays from 1112 (Bi:Sr:Ca:Cu= 1:1:1:2) to 1312 with a constant ratio of Ca:(Bi+Cu)=1:3. Outside this region showed either low-Tc (60-80K) only or characteristics mixed with high- and low-Tc phases. X-ray analysis revealed that the peaks related to the high-Tc phase were largest around the composition of 1312, but a volume fraction of the high-Tc phase was revealed to be less than 10% by magnetization measurements.

1. Introduction

The Bi-Sr-Ca-Cu-O superconducting oxide system, first discovered by Maeda et al.,[1] has a higher transition temperature than the $YBa_2Cu_3O_x$ system. This system does not include the rare earth materials and is reportedly resistant to water or humid atmosphere, in contrast to the $YBa_2Cu_3O_{7-y}$ family. This oxide system has three kinds of superconductors: $Bi_2Sr_2Ca_2Cu_3O_x$ (T_c=105K, 2223 abbreviated hereafter),[2] $Bi_2Sr_2CaCu_2O_x$ (T_c=75K, 2212),[3] and $Bi_2Sr_2Cu_1O_x$ (T_c=22K, 2201).[4] In Maeda et al.'s first report, their specimen included at least two phases, the 105K phase (high-T_c phase) and the 75K phase (low-T_c phase) for 1112. In fact, the films of this system fabricated by sequential deposition showed multi-phase characteristics.[5] Many efforts have been focused on film formation applying such methods as codeposition, sputtering, chemical vapor deposition, and laser deposition. Some reports described epitaxial film growth,[6] but most of the reports suggest the difficulty of single high-T_c phase formation. The sequential deposition technique using a single electron beam gun is simple and convenient for varying composition in the high-T_c superconducting oxide films. This paper will describe the composition range with a full resistance transition above 100K in Bi-Sr-Ca-Cu-O films.

2. Film preparation

Cu, Bi, CaF_2, and SrF_2 were used as starting materials. The fluorides of Sr and Ca can be easily evaporated by a conventional evaporation system and they stabilize the as-deposited films, while the films containing metallic Ca and Sr are easily corroded in air. These materials were evaporated in a vacuum of 10^{-4} Pa by a four-hearth electron beam gun deposition system in the order Cu, Bi, CaF_2, and SrF_2 with the substrate maintained at ambient temperature. Substrates used were (100) MgO, (100) $SrTiO_3$, Al_2O_3, YSZ, and oxidized Si. Among the various substrates, MgO and $SrTiO_3$ were found to be suitable for obtaining superconducting films, but only films on MgO substrates showed full superconducting transition above 100K. Thus, the following experiments were carried out using MgO substrates.

Only a single deposition cycle was used for each film and the composition was changed by adjusting the thicknesses of the constituents. A typical total thickness was about 200 nm. The composition was determined by x-ray fluorescence analysis (XFA) calibrated by inductive coupled plasma (ICP) for pre-annealed films. Comparing the same sample before and after annealing, no composition deviation due to annealing was detected.

The as-deposited films were annealed in oxygen flow at a temperature of 250°C for 3 hours and then 850 -890 °C for 1 hour to obtain the superconducting film. The first stage annealing was carried out for oxidation of Bi at a temperature lower than the melting point of Bi, 271°C. The heating and cooling rates were 300 °C/hour.

The optimum annealing temperature for obtaining high-T_c (T_{cend}>100K) films was around 875°C. It was only at this temperature that T_{cend}>100K was achieved. Annealing at 5°C higher or lower than this temperature resulted in high- and low-T_c mixed phased resistance-temperature (R-T) characteristics.

3. Characterization

1) Surface morphology

In-situ microscopic observation at elevated temperatures revealed that the as-deposited film surface slowly changed by partial melting, resulting in the formation of several different features. They are microscopically composed of very thin sheets, platelets, needles and bulky grains. A typical surface of the annealed film is shown in Fig.1. EPMA revealed that the needle-shaped crystals are Ca-rich and the platelet crystals are Sr-rich. The needle crystals were often found in low-T_c films and the thin sheets adhereing on the substrate surface were always found in high-T_c films. The thickness at flat ground was about 20-50 nm, while the size of bulky grains was more than 1 μm across.

2) Tc measurement

Film resistance was measured by the conventional spring contact four-probe method with the probe spacing of 1 mm. Zero-resistance transition was defined as a resistance drop of less than $1/10^5$ of the ambient temperature resistance (sensitivity of 1 μV with 1 mA for 100 Ω).

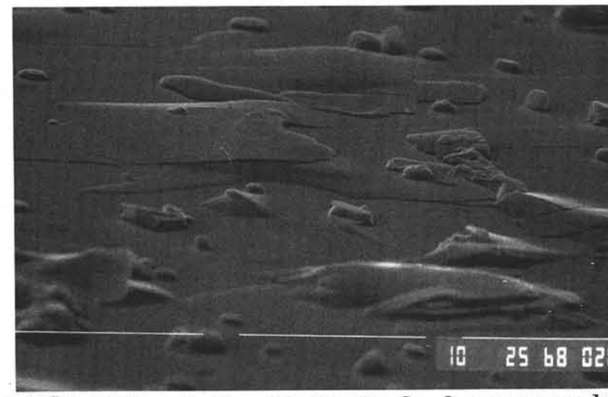


Fig.1 SEM of the Bi-Sr-Ca-Cu-O superconducting film after annealing. (Bar=10 μm)

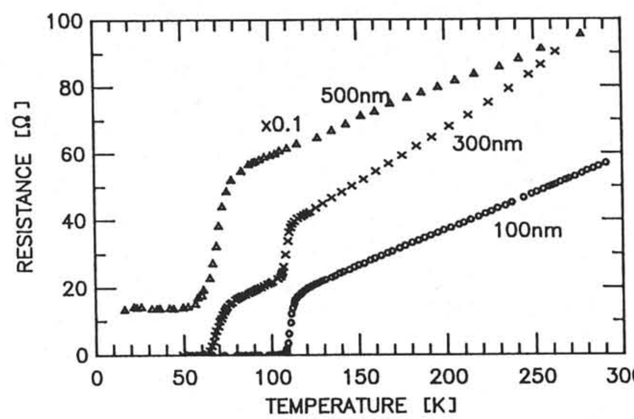


Fig.2 Temperature-resistance relation for various thickness samples of composition of 1212.

The high-Tc transition is as sensitive to film thickness as it is to annealing temperature. The resistances of samples with different thicknesses as a function of temperature is shown in Fig.2. The nominal composition ratio of these samples was 1212. The 100-nm-thick sample shows a full resistance drop above 100K, while the 300-nm-thick film clearly shows multi-phase superconducting characteristics (110K and 75K). The 500-nm-thick sample shows only low-T_c phase and does not exhibit zero resistance in the measured temperature range. In addition, thinner films had lower sheet resistance at the normal conductive temperature range.

3) X-ray diffraction analysis

X-ray diffraction analysis revealed several distinct peaks and that the films are highly oriented for all the films exhibiting superconductivity. Strong peaks can be indexed (00L) corresponding to c=30.6 A, which was reported by Maeda et al. as a low-T_c phase. A few weak broad peaks, such as around 2θ=4.8° and 23.5°, were observed only for high-T_c films, as shown in Fig.3. The peak at 2θ=4.8° can be related to the high-T_c phase (2223),[7] if this peak is indexed to (002) of c=36.8 A. In Addition, the third phase (2201) was identified to the peak at 7.2°. The high-T_c-related peaks were diminished for the thicker films shown in Fig.2. From these results, it can be assumed that the films are multi-phase even when T_c >100K.

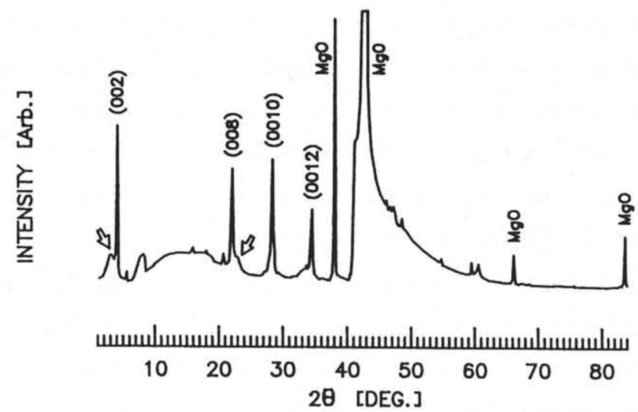
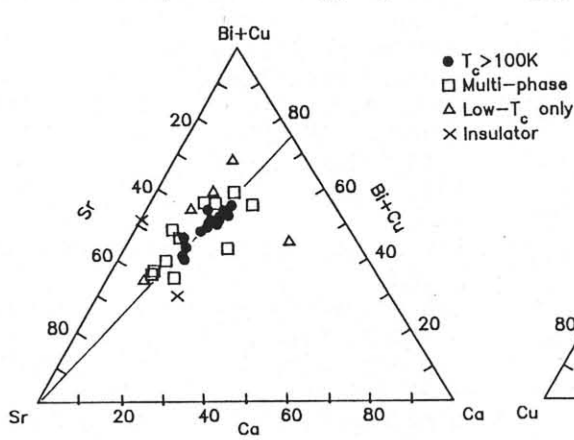


Fig.3 X-ray diffraction pattern of a typical high-T_c film. The peaks indicated by arrows are unique to high-T_c films.

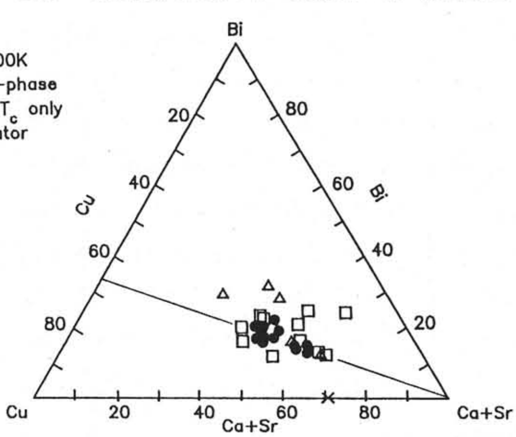
4) Composition dependence

Under the above annealing and thickness conditions (870-880 °C, and a thickness less than 250 nm), we investigated composition dependence of these superconducting oxide films. It was found that the films with zero resistance above 100K can be obtained by a wide variety of nominal compositions, especially in the case of Sr. Such films were obtained by the composition ratio from 1112 to 1312. These results contrast with the $YBa_2Cu_3O_x$ superconducting oxide, in which stoichiometry is very important for obtaining high-T_c films. A composition mapping with respect to transition temperatures, where Bi+Cu, Sr, and Ca are used as three components, is shown in Fig.4(a). Another configuration representing or Bi, Cu, and Sr+Ca is shown as Fig.4(b). In the figures, circles, squares, triangles, and X's represent T_c> 100K, mixed characteristics (2-step R-T), low T_c (60-70K), and insulators, respectively. Note that the high-T_c region lies along the lines of (Bi+Cu):Ca=3:1 and Bi:Cu=1:2, and the outside of this region shows multi-phase resistance properties (2 step R-T curves). This result suggests that Ca plays an important role in high-T_c phase formation.

Figure 5 shows typical R-T curves for the films with different compositions. The T_cs of these samples are almost the same, namely 107K. It should be noted, here, that all extrapolated lines of normal resistance



a) Expression for Bi+Cu, Sr and Ca as three components.



b) Expression for Bi, Cu, and Sr+Ca.

Fig.4 Composition mapping with respect to resistance transition temperature.

to lower temperature for these samples do not go directly to zero but cross the temperature at around 20K. This "characteristic temperature" is also observed for highly oriented films or single crystals.[8] In the case of low-T_c films, on the other hand, the extrapolated lines intersect on the resistance axis on the positive side. This fact suggests that the low-T_c films have larger residual resistance than high-T_c films. Very recently, this point was discussed with respect to the $YBa_2Cu_3O_x$ system but so far the physical meaning has not been clarified.[9]

4. Discussion

Judging from our XD results, volume fraction of high-T_c phase (2223) should be very small even for the films with zero-resistance transition temperature above 100K. The peak intensity ratio at 4.8° and at 5.7° was about 10% at most. In fact, magnetic susceptibility measurement revealed that the high-T_c transition signal is very small, as shown in Fig.6. Zero resistance transition above 100 K suggests that the current path is continuous. A resistivity of 10^{-3} Ωcm at room temperature is derived from the results in Fig.5, assuming a supeconducting path is formed within 20 nm thick sheets. The reason why high-T_c films are easily obtained over a wide composition variation in spite of the small fraction of High-T_c phase is still unclear. The fact that the optimum annealing temperature observed experimentally is close to the melting temperature (850-880 °C) suggests that the formation of the high-T_c phase may be caused by a peritectic or monotectic reaction among the components over a narrow temperature range. Excess components might lower the melting point and play the role of flux for high-T_c phase formation in deviated composition, such as 1312, from the 2223 composition ratio.

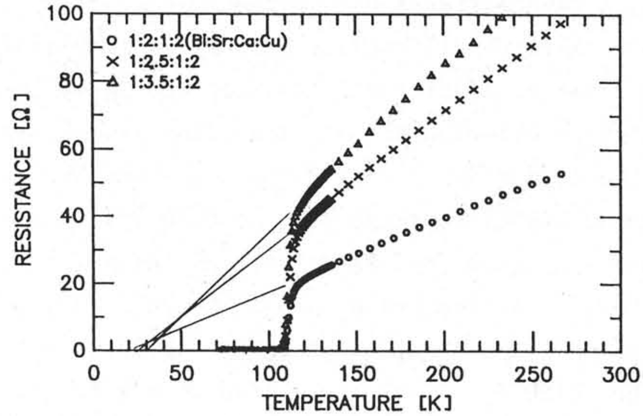


Fig.5 Temperature dependence of various composition ratios.

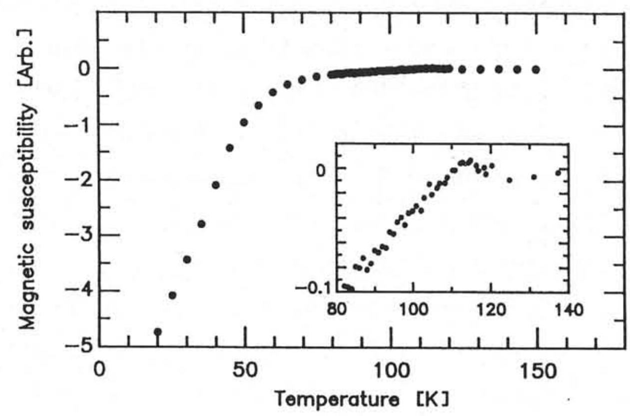


Fig.6 Temperature dependence of the magnetic susceptibility of Bi-Sr-Ca-Cu-O high-T_c film. The detail around T_c is inserted.

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