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Low-Temperature Oxidation Process for High-T_c Ba-Y-Cu-O Thin Films

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We have developed a selective plasma oxidation technique to prepare superconducting patterns in oxygen deficient $Ba_2YCu_3O_{7-x}$ thin films. The rate of oxygen diffusion into deoxygenated Ba-Y-Cu-O films during plasma oxidation was studied by measuring the weight and X-ray diffraction pattern of the film. The change in composition variable x calculated from the weight gain during 20 minutes of plasma oxidation was about 0.6. Preliminary experiments showed that superconducting patterns were formed in oxygen deficient Ba-Y-Cu-O films.

1. Introduction

The electrical properties of $Ba_2YCu_3O_{7-x}$ films change from superconducting to semiconductor-like depending on the oxygen stoichiometry. Plasma oxidation¹⁻³ can control the oxidation state of Ba-Y-Cu-Ocompounds at low temperatures, thus it might enable the fabrication of superconducting patterns embedded in semiconductor-like regions. The rate of oxygen in-diffusion during plasma oxidation must be determined before the application of such a process.

We measured the weight and X-ray diffraction pattern of these films to determine how fast and to what extent oxygen diffuses into oxygen-deficient Ba-Y-Cu-O films during plasma oxidation. After that, we made a preliminary experiment to delineate superconducting patterns in oxygen deficient Ba-Y-Cu-O films.

Oxygen diffusion into oxygen deficient Ba-Y-Cu-O films during plasma oxidation

Ba-Y-Cu-O films were (thickness: 460 nm) prepared on single-crystal (100) MgO by

evaporating Y, Ba, and Cu from electron-beamheated metal sources $^{4-6}$, and then annealing them in an oxygen flow at a maximum temperature of 900°C. The zero-resistivity temperature was 50 K to 70 K. X-ray diffraction peaks were obtained by using Cu K_{α} radiation, and these peaks suggested that the c axes of crystal domains in the films tend to align perpendicular to plane of the film. Scanning electron photomicrographs revealed that these films consist of grains with sizes between 200 nm and 1200 nm.

Ba-Y-Cu-O films were deoxygenated by an anneal in a N_2 flow after their weight and Xray diffraction patterns were measured. The weight of films and the substrate was measured for films deposited on one side of a 3-cm-square, 0.5-mm-thick MgO substrate. The N₂ anneal was for 1 hour at 600°C. The films were then cooled to room temperature in a furnace. Annealing the films in an Ar flow gave the same results as for those treated in N2. The deoxygenated films were plasma-oxidized in a barrel reactor at an oxygen pressure of 133 Pa and an rf power of 200 W. The rf power supply frequency was

13.56 MHz. The sample temperature was below 230°C during plasma oxidation. The weight and X-ray diffraction patterns were also measured after deoxygenation and plasma oxidation. The weight of the MgO substrate alone was not changed by either the N_2 anneal or the 1 hour plasma oxidation processes.

Figure 1 graphs the resistivity versus temperature characteristics of Ba-Y-Cu-Ofilms, for as-prepared, deoxygenated by an N_2 anneal, and plasma-oxidized films after deoxygenation. Plasma oxidation was uninterrupted for 1 hour in this case. The deoxgenated film showed a semiconductor-like temperature dependence with a resistivity two to three orders of magnitude higher than that of virgin films. The plasma oxidation restored superconductivity and metallic behavior of the oxygen deficient film.

Figure 2 shows the X-ray diffraction patterns for as-prepared, deoxygenated, and films that were plasma oxygenated for 1 hour after first being deoxygenated, for values of 20 between 45.5 degrees and 48.0 degrees. Lattice constants for the a, b and c axes were obtained from 2θ values of the (00L), (020), and (200) peaks for Cu $K_{\alpha 1}$, where L values were 5, 6, and 7. The as-prepared films were orthorhombic, and the (006) and (200) peaks overlap. Annealing in No changed the diffraction peaks to those for a The (006) peak shifted to tetragonal phase. a lower angle value after the deoxygenation, indicating that the c axis length increases due to an oxygen loss. The X-ray







Fig.2 X-ray diffraction peaks for Ba-Y-Cu-O films.

diffraction patterns once again depicted the original orthorhombic structure after plasma oxidation. These results clearly show that plasma oxidation supplied enough oxygen into the oxygen-deficient Ba-Y-Cu-O films to permit the orthorhombic-to-tetragonal phase transformation.

The weight loss and gain of a 3-cmsquare film during a N_2 anneal and plasma oxidation for 1 hour was about 30 µg. The change in the films oxygen stoichiometry was estimated from the film area, the thickness of the evaporated metal, and the weight gain assuming that the oxygen entered the film uniformly. The estimated change in the composition variable x for $Ba_2YCu_3O_{7-x}$ films was 0.6. The change in x estimated from the change in the c-axis length (about 0.1 Å) was 0.5, from the empirical linear relation between x and the c-axis length⁷.

We measured the changes in film weight and lattice parameters versus plasma oxidation time to determine how fast oxygen diffused into the film. The weight of deoxygenated films and their c-axis length were measured after each 5-min plasma oxidation. The sample temperature was below 160°C during 5-min oxidations. Figure 3 graphs the change in film weight and c-axis length versus the accumulated plasma treatment time. The weight and length of the c axis returned to their original values in 10 min to 20 min.

The diffusion equation was solved assuming isotropic oxygen diffusion from the film surface into the 460-nm-thick film, using boundary conditions where the oxygen content at the film surface was constant. The result matched to the experimental values within a total weight gain error of 5 % when the diffusion constant was $2.2 \times 10^{-12} \text{ cm}^2/\text{s}$.



Fig.3 Change in film weight and c-axis length versus plasma treatment time.

3. Patterning by plasma oxidation

Deoxygenated, semiconducting Ba-Y-Cu-O films were selectively plasma-oxidized by using metal masks to form the superconducting patterns. We simply put a metal mask on a deoxygenated Ba-Y-Cu-O film, as shown in Fig. 4(a), and plasma-oxidized it. The plasma oxidation was performed at an oxygen pressure of 133 Pa, and an rf power of 200 W for 30 min. The film under the opening of the metal mask was selectively oxidized. The resulted pattern was visible, and also observable by scanning electron microscope. Figure 4(b) shows the scanning electron photomicrograph of the patterned film. We confirmed that the bright part in the figure, which corresponded to oxidized region, was superconducting.



(a)



Fig.4 (a) Selective oxidation using metal mask. (b) Scanning electron photomicrograph of selectively plasma-oxidized Ba-Y-Cu-O thin films.

4. Summary

We demonstrated that plasma oxidation introduces appreciable amounts of oxygen, about 0.5 oxygen atoms per unit cell, into deoxygenated, 460-nm-thick Ba-Y-Cu-O films in about 20 min, as determined by weight gain measurements of the films during plasma oxidation. Plasma oxidation also restores superconductivity and metallic behavior in deoxygenated films, and changes their crystal structure from tetragonal to orthorhombic. Superconducting patterns can be embedded in deoxygenated, semiconducting Ba-Y-Cu-O films by selective plasma oxidation.

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