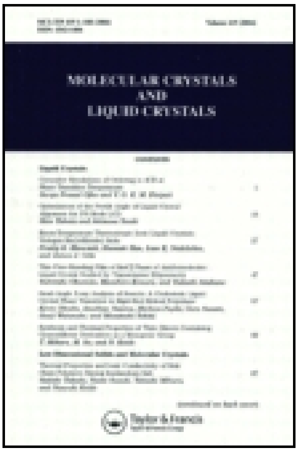

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Oxygen Control and Carrier Property in $Bi_2Sr_2Ca_1Cu_2O_x$ Superconducting Thin Films

Kou Takeuchi [a], Masashi Kawasaki [a], Mamoru Yoshimoto [a], Yasutoshi Saito [a] & Hideomi Koinuma [a]

[a] Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama, 227, Japan

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Oxygen Control and Carrier Property in $Bi_2Sr_2Ca_1Cu_2O_X$ Superconducting Thin Films

Kou TAKEUCHI, Masashi KAWASAKI, Mamoru YOSHIMOTO,
Yasutoshi SAITO, and Hideomi KOINUMA
Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 227, Japan

Abstract Variously activated oxygens were used to control the oxygen stoichiometry in $Bi_2Sr_2Ca_1Cu_2O_X$ superconducting thin films at 400°C. The treatment with an oxygen plasma or ozone decreased the T_C onset of the film by as much as 20K. UV light irradiation of film in atmospheric oxygen resulted similarly. On the other hand, films exposed to UV light irradiation in the presence of N_2O (400Torr) increased their T_C onset by about 20K. These T_C changes accompanied the change in the c-axis lattice constant, suggesting a change in the oxygen content in the film. Hall coefficient measurements verified that the oxygen content or hole concentration in $Bi_2Sr_2Ca_1Cu_2O_X$ films could be controlled by these activated oxygen treatments at a relatively low temperature.

INTRODUCTION

It is well known that the T_C of perovskite related superconductors such as La-Sr-Cu-O or Y-Ba-Cu-O is strongly dependent on their hole concentration1,2). The hole concentration can be controlled by regulating the oxygen nonstoichiometry. In this letter, we generated variously activated oxygens to control the oxygen content in $Bi_2Sr_2Ca_1Cu_2O_X$ films and examined their effect on the hole concentration and superconductivity.

EXPERIMENTALS

An ac sputtering apparatus of our original design was used for both film synthesis and oxygen treatment3). The reaction chamber is a quartz cylinder to which two copper rods are inserted from the both ends. A pair of disc $Bi_2Sr_2Ca_2Cu_3O_Y$ targets mounted on the rods were placed face to face at a distance of 3.5 cm. The targets were sputtered by the application of 50 Hz ac high voltage to deposit thin films of about 0.8μm on 2.5% yttria stabilized zirconia (YSZ) substrates$^{3)}$.

As-deposited films were annealed at 850°C for 30 min to show XRD patterns almost identical to that of c-axis oriented $Bi_2Sr_2Ca_1Cu_2O_x$ phase (abbreviated as 2212 phase hereafter). The film specimens thus prepared have T_C onset of about 80K. Oxygen, ozone and nitrous oxide with or without UV light irradiation and oxygen plasma were employed for oxygen treatments. The oxygen plasma was generated at 0.4 Torr of O_2 by the application of ac 3.6 kV between a pair of stainless-steel electrodes, with which the targets were replaced after the film deposition, facing each other 6 cm apart$^{4)}$. Ozone gas was generated by using a micro ozonizer (Erstat Laboratory AOC-05) and introduced in the apparatus. Every activated oxygen treatment of the film was carried out at 400°C for 30 min and at decreasing temperatures to about 50°C for additional 30 min. Some of the specimens were retreated in differently activated oxygens.

The resistivity of the films was measured by the dc four probe method. The crystal structure of the films was analyzed using an X-ray diffractometer (XRD, Mac Science MXP-3, CuK_α).

Hall coefficients of the films were measured by standard van der Pauw technique at room temperature under a magnetic field of 1 T. The film specimens for this measurement were prepared on MgO substrates using $Bi_{2.5}Sr_2Ca_1Cu_{2.4}O_Y$ targets and annealed at 900°C for 30 min. Contacts were confirmed to be Ohmic from I-V characteristics.

RESULTS and DISCUSSION

Figure 1 shows the temperature dependence of resistivity for some of the specimens after activated oxygen treatments. The application of ozone (C) or oxygen plasma (D) decreased the T_C onset of the film from 80K to about 60K. Activated oxygen treatments did not produce a new XRD peak but gave small shifts towards higher diffraction angles in the c lattice constants. The T_C values of these films returned to about 80K when the films were subjected to further heat treatment in atmospheric oxygen without the light irradiation. All these results were essentially the same as in the case of UV light irradiation in the presence of atmospheric oxygen (B) and prompted us to consider that these activated oxygen treatments should increase the oxygen content in the films and induce the decrease of c lattice constant and critical temperature. The decrease of c lattice constant induced by the oxygen incorporation into the lattice was reported for Y-Ba-Cu-O2).

Figure 1 also shows the temperature dependence of resistivity for a film after 400 Torr N_2O treatment with UV light irradiation (E). This treatment increased the T_C onset from 80K to about 100K. The XRD peaks showing (00c) shifted towards lower diffraction angles. This tendency was contrary to the tendency resulted from the above cases. When the N_2O pressure was reduced to 4Torr, the T_C onset of the film increased again to 100 K. At an N_2O pressure below 0.4 Torr, the films turned to be semiconductive without showing a clear T_C onset. This semiconductive film recovered the T_C onset of about 60K after the treatment of atmospheric oxygen with UV light irradiation. All these T_C changes were reversible, which means the T_C changes were induced only by the change of oxygen content in the film. Although the other oxygen treatments activated by UV light and plasma worked to incorporate the oxygen into the films, N_2O treatment with UV light irradiation apparently worked to reduce the oxygen content in the film. This effect of N_2O/UV treatment was rather contrary to our expectation, since atomic oxygen should also be formed from N_2O by the UV light irradiation5). Annealing the film in vacuum ($<10^{-3}$ Torr) at 400°C made the film semiconductive with a broad T_C onset remained at about 80K.

Figure 2 summarizes the relationship between T_C onset and c lattice constant calculated from the (00<u>10</u>) peak of 2212 phase for the film specimens subjected to various oxygen treatments at 400 C. The T_C onset and c lattice constant are linearly correlated up to $c < 3.072$ nm. However, films with too longer c parameter (> 3.075 nm) became semiconductive as shown in #1 and #2 in Fig.2. The activated oxygen treatments at room temperature gave almost no change in T_C.

Hall coefficient (R_H) measurements were carried out for the specimens treated under three typical activated oxygen treatments listed in Tab. 1. The signs of the R_H were positive, suggesting the charge carriers are holes. Table 1 also shows the relationship between hole concentration ($1/eR_H$) and T_C. The hole concentration is clearly indicated to have a strong correlation with the oxygen content in the films as well as with the change in the T_C of the film.

CONCLUSION

The T_C of $Bi_2Sr_2Ca_1Cu_2O_X$ superconducting thin films were changed by variously activated oxygen treatments at 400°C. The treatments accompanied systematic changes in c-lattice constant and hole concentration, providing a new method for controlling the oxygen content in superconducting oxide films at a relatively low temperature. N_2O behaved substantially different from O_2 when the films were exposed to UV light in their presence. By this procedure, we can control the hole concentration and T_C without changing a metallic composition.

Acknowledgments

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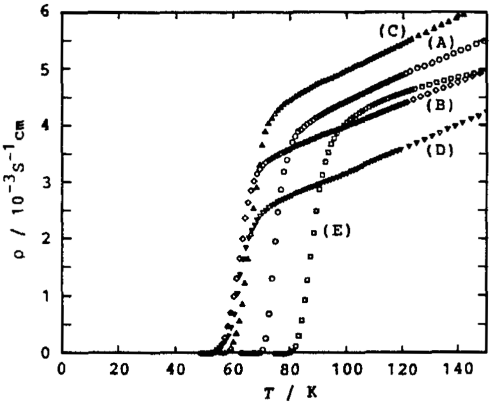

FIGURE 1 Temperature dependence of resistivity for $Bi_2Sr_2Ca_1Cu_2O_X$ films treated by some activated oxygens.
(A) O_2 1 atm, (B) O_2 1 atm / UV, (C) O_3 1atm,
(D) Oxygen plasma, (E) N_2O 400 Torr / UV

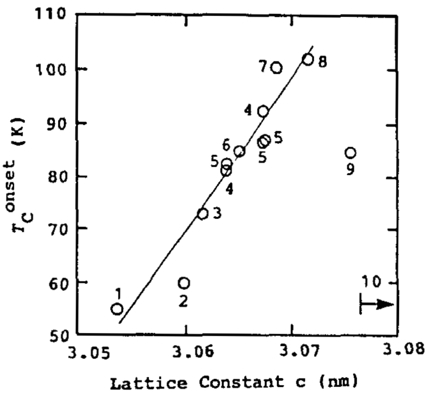

FIGURE 2 T_C^{onset} vs. lattice constant c of the films subjected to various activated oxygen treatments at 400°C.
(1)O_2 1atm / UV, (2)O_2 1atm / UV indirect,
(3)O_2 1atm / UV with quartz filter, (4)O_2 1atm,
(5)air 1atm, (6)O_2 1atm / UV with glass filter,
(7)N_2O 4Torr / UV, (8)N_2O 400Torr / UV,
(9)vacuum (<1mTorr), (10)N_2O 0.4Torr / UV; no T_C

Table 1. Activated oxygen treatment conditions, T_C onset, Hall coefficients and carrier concentrations.

specimen	activated oxygen treatment condition	T_C^{onset} (K)	R_H ($10^{-3}cm^3/C$)	$N_H(=1/eR_H)$ ($10^{21}cm^{-3}$)
F	O_2 1 atm / UV	69	4.0	1.6
G	O_2 1 atm	91	6.0	1.0
H	N_2O 4 Torr / UV	103	7.2	0.87