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Light Irradiation Effect on the Preparation of High T_c Superconducting Oxide Films

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By using a simple ac sputtering apparatus in which the Yb-Ba-Cu-O and Bi-Sr-Ca-Cu-O thin films have been prepared under the irradiation with light from a low pressure mercury lamp at various steps of film preparation. The light irradiation was found to be effective for improving the superconductivity of the Yb-Ba-Cu-O films, providing a promising method for decreasing the processing temperature of high T_c superconducting oxide films. For Bi-Sr-Ca-Cu-O films, reproducible and reversible T_c onset change was observed between T_c onset of 60K measured after annealing under light irradiation and 80K after annealing without light irradiation.

1. INTRODUCTION

Preparation of high T_c superconducting thin films has been extensively studied[1,2] with a primary expectation of their application to electronic devices. In order to fabricate tunnel type Josephson Junction, the films should have smooth surface and chemical stability not to be deteriorated at the interface with the insulating layer. Although the post-annealing of deposited films at high temperatures is quite effective for increasing T_c, it usually accompanies the surface roughness and chemical reaction at the interface of the films. Thus, the decrease of film preparation temperature is an important problem to be solved.[3]

Light irradiation is known to be effective for the epitaxial growth of semiconductor films at temperatures far lower than the temperatures required for thermally activated growth. Recently, we found that T_c of sputter-deposited Y-Ba-Cu-O films could be increased by the irradiation of low pressure mercury light during the sputtering step and/or the post annealing step in oxygen atmosphere. Irradiation of UV light at the preparation of superconducting oxide films may be useful for both facilitating the crystallization at a low temperature and the control of oxygen stoichiometry as well. In the present study, we have further investigated the UV light irradiation effect on the preparation of Yb-Ba-Cu-O (abbreviated as YbBCO here) films, together with the effect on the preparation of Bi-Sr-Ca-Cu-O (BSCCO) films.

2. EXPERIMENTAL

The ac sputtering apparatus used is schematically represented in Fig.1. Through the synthetic quartz window which is mounted in the center of quartz cylinder (5cm ϕ x 50cm), UV light from a low pressure mercury lamp (SEN Tokushu Kogen SUV-110V, 110W) can irradiate a substrate (yttria stabilized zirconia) placed on the bottom of the cylinder. A focused IR lamp (Thermo RIKO IR-1000) was used to heat the substrate up to 850°C. The substrate temperature was confirmed not to rise (<1°C) by the light irradiation. A pair of disc targets, which also worked as electrodes, were supported by the horizontally inserted copper rods, and the sputtering was initiated by the application of 50Hz ac high voltage. The distance between the lamp and the substrate was about 13cm. The targets were prepared by mixing the prescribed amounts of commercial powders of Yb_2O_3, $BaCO_3$ and CuO for YbBCO system and Bi_2O_3, $BaCO_3$, $CaCO_3$ and CuO for BSCCO, calcining the mixture, pressing the calcined powders into discs of 20mm diameter and 3mm thick, and then sintering. The nominal target compositions were $Yb_1Ba_2Cu_{3.6}O_x$ for YbBCO system and $Bi_2Sr_2Ca_2Cu_3O_y$ for BSCCO system, respectively.

The preparation process of superconducting thin films is composed of two main steps: the sputtering step and the in-situ post annealing step in oxygen atmosphere. For the preparation of YbBCO films, the sputtering was performed at a pressure of 100mTorr of 10% oxygen and 90% argon mixture by applying 9kV 50Hz ac voltage between a pair of targets. For the preparation of BSCCO films, conditions employed include the sputtering gas pressure of 100 mTorr using 50% oxygen and 50% argon gas mixture and the voltage of 6.3 kV applied between the targets. Following the sputtering process, oxygen was introduced into the reactor to increase oxygen content in the film.

The resistivity of the films was measured by the dc four probe method by depositing four striped gold electrodes on the specimens. Metal compositions and crystal structures of the films were analyzed by an ICP emission spectroscopy(Jerrell-Ash Atom-Comp or Seiko SPS-1200) and an X-ray diffraction(Mac Science MX-3, CuKα), respectively.

3. RESULTS AND DISCUSSION

(1) Yb-Ba-Cu-O

The compositions of the films deposited at a temperature of 650° C were close to $YbBa_2Cu_3O_x$ and the deposition rates were about 0.8μm/4h. The effect of UV light irradiation at the various step of the film preparation is summarized in Table 1. The temperature dependences of resistivity for some of the films prepared are shown in Fig.2 and Fig.3. In Fig.2 is shown the result for the films annealed in oxygen atmosphere at 650°C, the same temperature as the substrate temperature during the sputtering step, for half an hour and subsequently at 400°C for another half an hour. Critical temperature (T_c^{zero}) of a film, prepared without the irradiation of UV light, was 53K. The superconductivity of films was improved by the preparation under the irradiation of UV light at either the sputtering step or the post annealing step in oxygen atmosphere : T_c^{zero} values increased to 61, 68 and 63K for specimens b, c and d in Table 1, respectively. For the specimens e and f annealed at 700°C, UV light irradiation was effective for improving superconductivity.

Further examination of the irradiation effect at the post annealing step was carried out at 400°C. A YbBCO film was deposited and annealed without the irradiation of UV light and then additional annealing was done in oxygen atmosphere at 400 °C for 30 minutes. The resistivity at room temperature of the film decreased a little from $7.1x10^{-3}S^{-1}cm$ to $5.9x10^{-3}S^{-1}cm$ by the second annealing, but T_c^{zero}=52K was almost unchanged from the value (53K) measured after the first annealing step (Fig.3). On the other hand, the third annealing at 400 °C for 30 minutes under the irradiation of UV light not only further decreased the film resistivity to $4.1x10^{-3}S^{-1}cm$, but also increased T_c^{zero} to 60K. Apparently, the light irradiation effect is more pronounced at the post annealing step rather than at the sputtering step. Irradiation of UV light was expected to work in two ways. One is the surface activation to promote the film crystallization at a low temperature and the other is the ozone or atomic oxygen generation to accelerate the oxygen uptake in YbBCO film. A low pressure mercury lamp radiates light having two main wave lengths of 254 and 185nm. The energy of the 185nm light is high enough to produce ozone or atomic oxygen from O_2[6]. The results described above indicates that the latter effect is predominant.

Thus, that the UV light irradiation in the preparation of superconducting YbBCO films can decrease the film resistivity and increase T_c significantly. The effect is presumed to come mainly from the acceleration of oxygen incorporation into the film by the formation of ozone or atomic oxygen in the light irradiated annealing step in oxygen atmosphere.

(2) Bi-Sr-Ca-Cu-O

The films deposited from $Bi_2Sr_2Ca_2Cu_3$ targets without substrate heating were amorphous insulator. These films were annealed under such conditions as shown in Table 2 to give XRD patterns (Fig.4) suggesting the existence of oriented 80K phase alone. All the films annealed without UV light irradiation at temperatures ranging between 680°C and 700°C for 30 min. or 80 min. (see a, c, e and g in Table 2), gave T_c onset of about 80K as shown in Fig. 5 (g). On the other hand, all the films annealed with the UV light irradiation (b, d, f and h in Table 2) showed the T_c onset of about 60K without any trace of resistivity drop at 80K as depicted in Fig. 5 (h). The film annealed at 690°C for 30 min. with UV light irradiation immediately followed by the additional annealing at 690°C for 30min. without UV light (sample m listed in Table 2) gave T_c onset of about 80K as indicated in Tab.2. This result should indicate that the photo annealing turned the T_c onset of 80K to 60K. On the contrary, a film showing T_c onset of 60K by the photo annealing was further annealed at 690°C for 30 min. to show the T_c onset of about 80K (specimen j). This change of T_c onset by the photo annealing and thermal annealing cycle was reproducible and reversible. XRD pattern of the films scarcely changed by the photo annealing. The origin of this reversible T_c onset change is not clear at presents. However, the highly reproducible T_c onset of about 60K suggests the existence of a new phase, which can not be detected by XRD in c-axis oriented films normal to the substrate. Further experimentals are now in progress.

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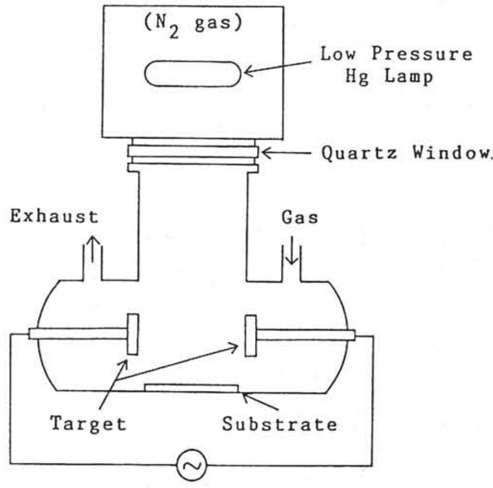

Fig.1 Schematic representation of an ac sputtering apparatus installed with a UV light irradiation system.

Table 1 Conditions of UV light irradiation in the preparation of Yb-Ba-Cu-O films by ac sputtering and T_C values of films prepared.

Specimen	sputtering step	post annealing step[1)]			T_C^{zero}
		650°C+400°C	700°C+400°C	400°C	(K)
a	x	x	—	—	53
b	o	x	—	—	61
c	x	o	—	—	68
d	o	—	—	—	63
e	x	—	x	—	62
f	x	—	o	—	70
g[2)]	—	—	—	x	52
h[3)]	—	—	—	o	60

o : with irradiation of UV light
x : without irradiation of UV light
1) Treatment time : 30min. In oxygen atmosphere.
2) Additional annealing for film a.
3) Additional annealing for film g.

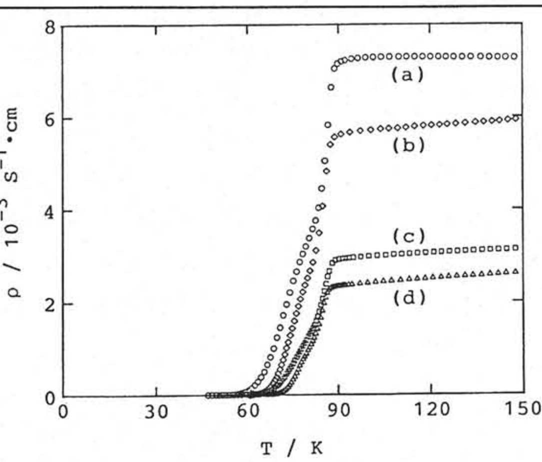

Fig.2 Resistivity vs. temperature relationship for some of the film specimens listed in Table 1.

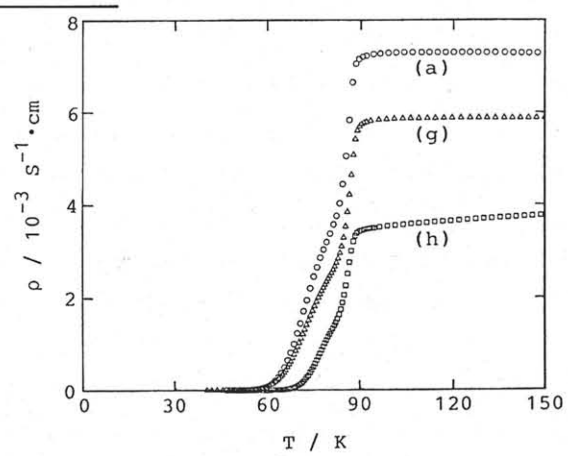

Fig.3 Resistivity vs. temperature relationship for some of the film specimens listed in Table 1.

Table 2 Annealing conditions and T_c's for Bi-Sr-Ca-Cu-O films deposited at room temperature.

Specimen	Post annealing conditions	T_c^{onset}(K)	T_c^{zero}(K)
a	680°C,30min	85	22
b	680°C,30min,UV	58	32
c	690°C,30min	89	30
d	690°C,30min,UV	67	25
e	700°C,30min	86	20
f	700°C,30min,UV	73	40
g	690°C,80min	87	62
h	690°C,80min,UV	69	45
i	690°C,30min,UV+690°C,30min	87	60
j	690°C,30min +690°C,30min,UV	67	40

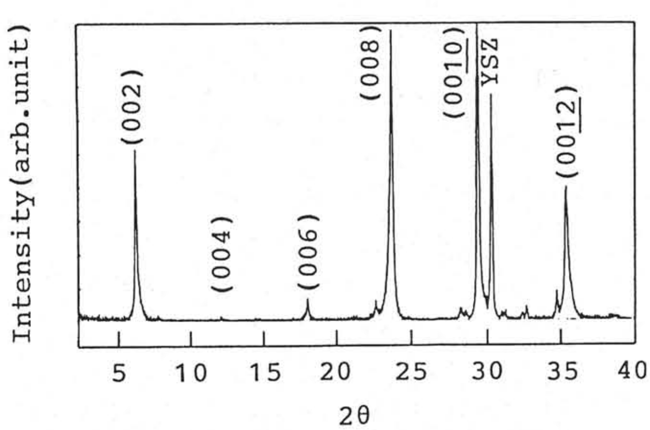

Fig.4 XRD pattern of annealed BSCCO film specimen listed in Table 2.

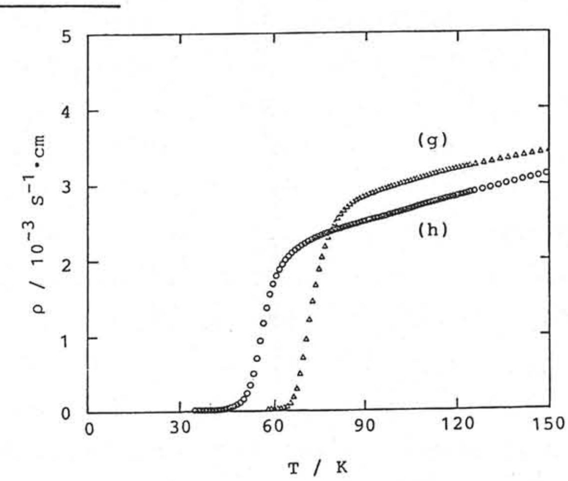

Fig.5 Resistivity vs. temperature relationship for some of the film specimens listed in Table 2.