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Preparation of High T_c Oxide Superconducting Films by Laser Annealing

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Superconducting Ba-Y-Cu-O films were prepared by using a pulsed laser evaporation and a pulsed laser irradiation for annealing techniques. Superconducting film with Tc(end)=67K was obtained by a CO_2 pulsed laser annealing of as-deposited amorphous films on (100)$SrTiO_3$ followed by low-temperature annealing. The films on various substrate materials prepared by the excimer laser evaporation without the laser annealing exhibits superconductivities. Especially, the film (0.8-2μm) without a buffer-layer on crystalline Si exhibits superconductivity with Tc(end)=82K. In addition we recognized some indication that an excimer laser annealing during the laser evaporation improves the superconducting properties of the films.

INTRODUCTION

In early stage most oxide superconducting films were prepared by a subsequent long-term high-temperature annealing after the film deposition. It is well known that such a high temperature process degrades the film and the substrate, and deteriorates surface smoothness. To surmount the difficulties, alternative technologies such as a low-temperature preparation technique[1] and/or an insertion of a buffer-layer between the film and substrate,[2] have been developed so far. In the case of the preparation by sputtering, the effect of plasma might be essential for reducing the nominal preparation temperature. Based on that point of view, a laser beam irradiation during the film deposition attracts our interest for reducing the preparation temperature. For the film deposition the pulsed laser evaporation technique was employed because of the easy control of the film composition.[3] First we investigated the crystallization of as-deposited amorphous $Ba_2YCu_3O_X$ films caused by a CO_2 pulsed laser or an excimer laser annealing, resulting in a successful preparation of superconducting films by the CO_2 laser annealing followed by 450°C furnace annealing in flowing O_2.[4] Second we proceeded to an investigation on an in-situ preparation, without a high-temperature process after the film deposition. This report presents our preliminary results on preparations of superconducting thin films by the following three methods; (1)preparation by CO_2 pulsed laser irradiation for annealing after the deposition of amorphous films, (2)preparation by the excimer laser evaporation alone, and (3)preparation by an excimer laser irradiation for annealing onto the growing surface during the laser evaporation.

EXPERIMENTAL AND RESULTS

+ On leave from Shibuya Kogyo Co.,Ltd.

1) Preparation by CO_2 pulsed laser annealing after deposition of amorphous films

The film deposition was carried out by evaporation of a target material in a vacuum chamber with O_2 environment of 13Pa using an ArF excimer laser (SHIBUYA SQL2240, 193nm wavelength, 10ns pulse width, 5Hz repetition rate, 120mJ/shot). The target was the pellet of $Ba_2YCu_3O_x$, which was prepared by the conventional powder method. Various kinds of substrates, (100)$SrTiO_3$, crystalline Si(c-Si), fused quartz(SiO_2) and alumina(Al_2O_3) were used, and kept at 400°C during deposition. A CO_2 pulsed laser beam (KOMATSU KLM2048, 10.6um wavelength) was scanned on the substrates for crystallization of as-deposited amorphous films. Subsequently the film was further annealed by a furnace at 450°C with O_2 flow for 6 hours and then cooled slowly to 300°C so as to compensate the oxygen deficiency. For investigation of the structure of the films, X-ray diffraction measurements were performed with CuKα at room temperature. The temperature dependence of the resistivity was measured using the conventional four-probe technique. Although the resistivity of films deposited on all kinds of the substrate starts to decrease around 90K, only film on $SrTiO_3$ substrate exhibits superconductivity. Under the condition that the CO_2 pulsed laser beam (1ms pulse width, 91Hz repetition rate) was scanned at a speed of 2mm/s in air, the film on $SrTiO_3$ substrate with a zero resistance at 67K was obtained. This superconducting property is largely improved compared with our previous one.[4] However it has become clear that the CO_2 laser beam deeply penetrates the film because of a low absorption coefficient, resulting in a heating of the substrate. This might be the reason why films on the other substrates do not exhibit a superconductivity. Annealing with an excimer laser beam after the evaporation is not effective for crystallization because of a too high absorption coefficient. Therefore we tried an in-situ excimer annealing during the laser evaporation.

(2) Preparation by excimer laser evaporation without laser annealing

The evaporation technique was similar to that described above. The main differences in the evaporation condition are as follows; the O_2 pressure was maintained at 26Pa, the nominal substrate temperature was varied over 600°C-800°C, and the laser power was 125 or 30 mJ/shot. After the evaporation, the films were cooled to a nominal temperature of 490°C within several minutes and kept for 2 hours at that temperature. During the cooling the chamber was filled with O_2 to 1.3KPa in order to increase the oxygen content in the film.

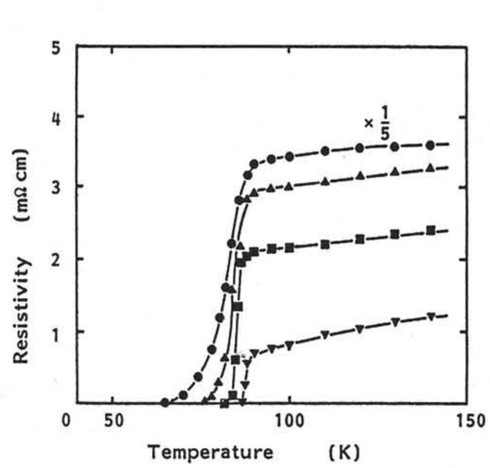

Fig.1 Typical temperature dependences of resistivities for films grown on (110) $SrTiO_3$(▼), c-Si(■),SiO_2(●) and Al_2O_3(▲) substrates. All the films were prepared by excimer laser evaporation without laser annealing. The plotted resistivity for the film on SiO_2 is reduced by a factor of 1/5 in this figure.

Although the real substrate temperature is not clear, it is roughly estimated to be several tens degrees lower than the nominal temperature, which varies with substrate materials according to a preliminary measurement through a thermocouple and a thermography. The film thicknesses were 0.8-2μm. Figure 1 shows typical temperature dependences of the resistivities for films grown on (110)$SrTiO_3$, c-Si, SiO_2 and Al_2O_3 substrates. Typical Tc values, their preparation conditions and lattice constants derived from X-ray diffraction measurements are listed in Table 1. The film on (110)$SrTiO_3$ substrate shows a sharp superconducting transition in the resistivity measurement, and shows no intense peak except a peak around 2θ=33° in X-ray diffraction spectra, suggesting that the film on $SrTiO_3$ was epitaxially grown. The lattice constants due to the orthorhombic structure for all films except the film on $SrTiO_3$ substrate are determined as shown in Table 1. The origin of such excellent superconducting properties is not clear at present, but the relatively high O_2 pressure of 26Pa during evaporation might be related to it. A further optimization of the preparation condition may improve the superconducting properties. It should be noteworthy that the film on c-Si prepared by this method, in spite of the thin film (0.8-2μm) without a buffer-layer,[5] exhibits the excellent superconductivity with a zero resistance Tc at 82K.

(3) Preparation by excimer laser annealing during laser evaporation

A schematic diagram for our preparation system is shown in Fig.2. The excimer laser beam was split into two beams for the evaporation and the annealing of the growing film on c-Si substrate during the deposition. The evaporation condition was

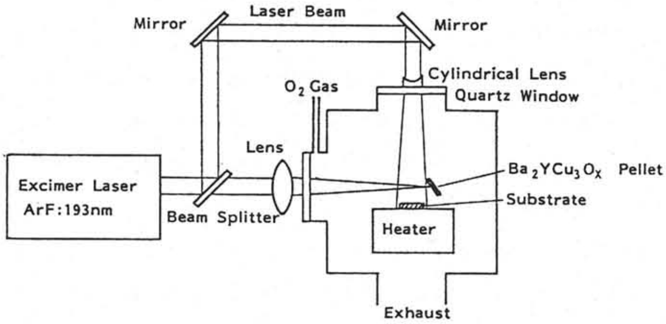

Fig.2 Schematic diagram of preparation system for excimer laser annealing during laser evaporation.

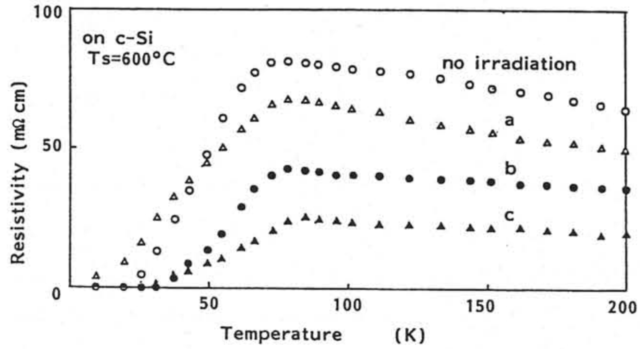

Fig.3 Changes in temperature dependence of resistivity due to laser irradiation for annealing. The intensity of the irradiation increases in the order a, b, c.

Table 1 Typical Tc values, preparation conditions, and lattice constants

Substrate	Tc(onset)	Tc(end)	Laser power	Nominal subst. temp.	a	b	c
(110)$SrTiO_3$	94 K	88 K	125 mJ/shot	800 °C	-	-	-
c-Si	94 K	82 K	30 mJ/shot	650 °C	3.83A	3.89A	11.69A
SiO_2	90 K	75 K	30 mJ/shot	650 °C	3.83A	3.89A	11.66A
Al_2O_3	90 K	75 K	125 mJ/shot	750 °C	3.82A	3.89A	11.70A

similar to that described in (2). Here the nominal substrate temperature was kept at the lowest value of 600°C during the evaporation. The intensity of the irradiation for the annealing was varied into three levels, up to a few tens mJ/shot·cm^2. Figure 3 shows changes in the temperature dependence of the resistivity due to the annealing during the laser evaporation. As shown in Fig.3 the excimer laser annealing improves the superconducting property. This improvement caused by the excimer laser annealing during the laser evaporation was probably ascribed to a temperature increase of the growing surface layer and/or an excitation of oxygen radicals. Anyway, this result suggests that the excimer laser annealing during the deposition is a promising candidate for the low temperature preparation.

CONCLUSION

(1) Superconducting Ba-Y-Cu-O film with a zero resistance at 67K was obtained by a CO_2 pulsed laser annealing of as-deposited amorphous film on $SrTiO_3$ substrate followed by 450°C furnace annealing in O_2 flow.

(2) Superconducting Ba-Y-Cu-O films on various substrates were prepared by the excimer laser evaporation without the laser annealing followed by a low-temperature O_2 annealing. Especially, in spite of the thin film (0.8-2μm) without a buffer-layer, the film on c-Si exhibits superconductivity with a zero resistance at 82K.

(3) It was suggested that an excimer laser annealing during the laser evaporation improves the superconducting properties.

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