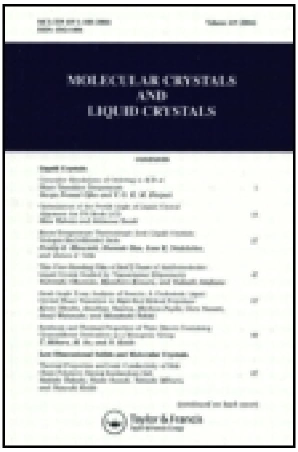

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PREPARATION OF Ce-DOPED THIN FILMS OF Ln–Cu–O SYSTEMS BY SPUTTERING

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Abstract A 50Hz ac sputtering method was applied to the preparation of thin films of n-type Nd-Ce-Cu-O superconductor. Films were deposited on $SrTiO_3(100)$ at a temperature of 600°C in Ar gas. An as-sputtered film with a composition of $Nd_{1.85}Ce_{0.15}Cu_{1.06}O_x$ had T' crystal structure with strong (110) and (001) orientations after it was annealed at 1000°C for 4h. It showed the onset and zero-resistivity temperatures at 17K and 12K, respectively. Films of Eu-La-Ce-Cu-O superconductor were also prepared by the same method to give an X-ray diffraction patterns primarily composed of T' structure.

INTRODUCTION

The n-type superconductors of Ln-Ce-Cu-O discovered by Tokura et al. have T' crystal structure[1]. T'-structure is distinguished from T* and T-structures, which are known for p-type superconductors of $(Nd,Ce,Sr)_2CuO_4$ and $(La,Sr)_2CuO_4$, respectively, with respect to the coordination state around the Cu. Thin film preparation of these systems is an interesting research subject since thin films are basic material for the device fabrication as well as useful specimens for elucidating anisotropic physical properties. We already reported the preparation of thin films of various oxide superconductors by using our original ac sputtering system.[2-4] Corresponding to the difference in the preparation conditions of bulk superconductors, the preparation conditions of n-type superconducting Nd-Ce-Cu-O thin films were reported to be significantly different from these of p-type La-Sr-Cu-O films.[5,6]

In this paper, we report on the superconducting Nd-Ce-Cu-O films with a focus placed on the optimization of preparation conditions.

Also reported here are our preliminary results of film preparation of Eu-La-Ce-Cu-O system which we believe is a new n-type superconductor.[7] This system was designed under the assumption that Nd in $(Nd,Ce)_2CuO_4$ could be replaced by a mixture of Eu and La, since its average ionic radius could be adjusted to be equal to the ionic radius of Nd. The bulk material of this system was confirmed to have T'-structure and negative Hall coefficient.

EXPERIMENTAL

(Nd-Ce-Cu-O FILM)

The 50Hz ac sputtering apparatus used in the present study is essentially the same as the one used in the previous studies.[2-4] It consists of a quartz cylinder (50mmϕ,50cm long) to which two copper rods are inserted from the both ends, a vacuum pump, and a neon sign transformer (50Hz, 9kV). On top of the copper rods, a pair of sintered targets with a 20mm diameter are fixed by Ag paste. The substrate can be heated up to 600°C by a focused IR lamp (Thermo RIKI IR-1000) placed under the cylinder.

The composition of both targets used for Nd-Ce-Cu-O films was $Nd_{1.82-1.86}Ce_{0.14-0.18}Cu_{1.2}O_x$. These targets were prepared from a mixture of Nd_2O_3(99.9%), CeO_2 (99.9%), and CuO(99.9%). The mixture was calcined at 1000°C for 10h in air and pressed into pellets. The pellets were then sintered at 1000°C for 10h in air.

Sputtering was carried out under 100mTorr Ar by applying a 7.2kV ac 50Hz voltage between the targets. The $SrTiO_3$(100) substrate was heated at 600°C. After the deposition, films were annealed at 800-1050°C for 0.5- 18h in Ar. The film thickness was measured by the stylus method using a Hobson's Talystep. The composition and crystal structure of the films were determined by inductively coupled plasma chemical analysis (ICP, Seiko SPS-1200) and X-ray diffractometry (XRD, MAC Science model MXP3 with monochrometer), respectively. The surface morphology of the annealed films was observed by a scanning electron microscope(SEM, Hitachi model S450). The film resistivity was measured by the standard four probe method with a current range of 25μA.

(Eu-La-Ce-Cu-O FILM)

$(Eu,La)_{1.85}Ce_{0.15}Cu_{1.20}O_x$ (Eu/La=1/2) sintered targets were prepared from a mixture of Eu_2O_3(99.9%), La_2O_3(99.9%), CeO_2(99.9%), and CuO(99.9%). The mixture calcined at 1000°C for 10h in air was pressed into pellets and sintered at 1000°C for 10h in air. The sputtering conditions were the same as those in the Nd-Ce-Cu-O film preparation except for the application of 9kV ac voltage. The deposited films were annealed at 1070°C for 1-2h in air and then at 980°C for 1min to 60min in Ar.

RESULTS AND DISCUSSION

(Nd-Ce-Cu-O FILM)

The typical film thickness as-deposited in 0.5h was 2000Å. The composition of the film was $Nd_{1.85}Ce_{0.15}Cu_{1.06}O_x$. Figure 1 shows the XRD pattern of the film that was annealed at 1000°C for 2h in Ar and cooled in the furnace. The obtained film shows strong (110) and (001) orientation. An SEM image of the annealed film is shown in Fig. 2. Needle-like crystals are observed. Figure 3 shows the temperature dependence of resistivity for the films subjected to two different heat treatments. After being annealed at 1000°C for 2h in Ar, Sample(A) was cooled slowly in the furnace, whereas Sample(B) was obtained by annealing Sample(A) at 1000°C for another 2h in Ar and cooled rapidly. The sample(A) was semiconductive, but the sample(B) showed the onset of superconductivity and zero-resistivity at temperatures of 17K and 12K, respectively. Hence, the superconductivity should be quite sensitive to oxygen content.

(Eu-La-Ce-Cu-O FILM)

$(Eu,La)_{1.85}Ce_{0.15}Cu_{1.00}O_x$ (Eu/La=1/2) bulk sample was sintered at 1070°C for 8h in Ar and quenched to show the superconductivity with its onset and zero-resistivity at temperatures of 19K and 9K, respectively.

Using this bulk sample as the targets, several films were prepared by the sputtering for 3h and annealed under various conditions. One of the as-deposited film had a composition of (Eu,La)/Ce/Cu=1.85/0.15/1.00 (Eu/La=1/2) and a thickness of 2000Å. The film was annealed at 1070°C for 1h in air and further at 980°C for 1h in Ar to give the XRD pattern shown in Fig.4. The annealing at temperatures higher than 1030°C was effective to make T'-structure. A resistivity drop suggesting the superconducting, however, has not been obtained yet. T-structure, which is considered to be La_2CuO_4, coexisted with the T'-structure in the films annealed at temperatures lower than 1030°C.

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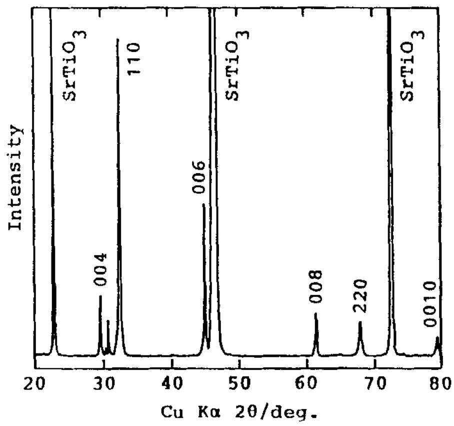

FIGURE 1 X-ray diffraction pattern of the Nd-Ce-Cu-O film annealed at 1000°C for 2h in Ar and cooled in the furnace.

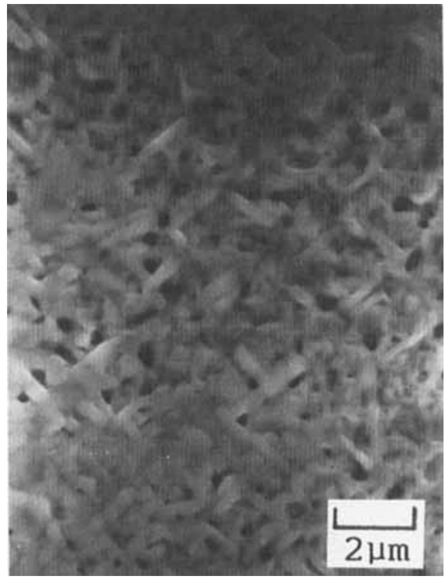

FIGURE 2 An SEM image of $Nd_{1.85}Ce_{0.15}Cu_{1.06}O_x$ film annealed at 1000°C for 4h in Ar.

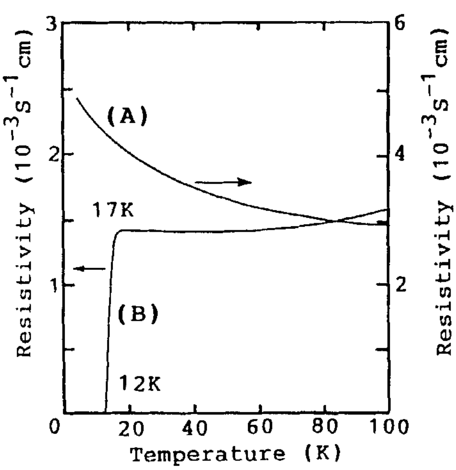

FIGURE 3 Resistivity vs. temperature relationships for the annealed films. (Sample(A):slow cooling, Sample(B):rapid cooling)

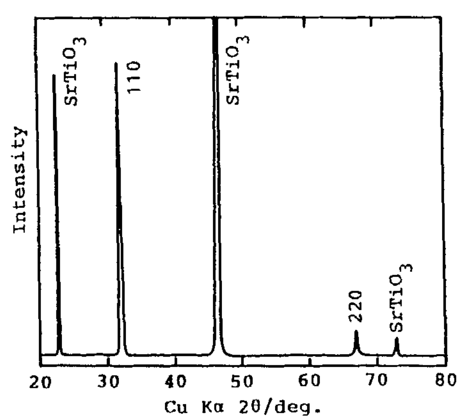

FIGURE 4 X-ray diffraction pattern of the Eu-La-Ce-Cu-O film annealed at 1070°C for 1h in air and further at 980°C for 1h in Ar.