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Superconductivity in $(La_{0.9}Sr_{0.1})_2CuO_4$ single-crystal films

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Single-crystal thin films of layered tetragonal-structure $(La_{0.9}Sr_{0.1})_2CuO_4$ have been grown epitaxially on a (100) $SrTiO_3$ substrate by a sputtering technique. The basal plane of the tetragonal structure was parallel to the surface of the substrate. The films showed superconductivity after postannealing. The onset temperature was 34 K with a transition width of 3 K. These properties are similar to those of the single-phase La-Sr-Cu-O ceramics.

Extensive work has been done on high-temperature superconducting ceramics since Bednorz and Müller discovered the La-Ba-Cu-O compound system.[1-4] Most of the ceramic samples have been composed of sintered crystallites with mixed phases. The K_2NiF_4 layered or the ABO_3 perovskite phases were considered to be the major phases.[5] Numerous compositions have been studied in an effort to sharpen the transition and raise the transition temperature T_c. Replacement of Ba ions by smaller Sr ions in the La-Ba-Cu-O compound system has sharpened the transition and elevated T_c.[6] The Y-Ba-Cu-O compound system has a T_c above 77 K,[7] and was found to consist of an oxygen-deficient perovskite structure.[8] The superconductivity observed in these ceramics seems to be governed by the nature both of the crystallites and of the grain boundaries.

A single crystal of the K_2NiF_4 structure will elucidate the detailed nature of the superconductivity in the ceramics. We have prepared single-crystal films of the La-Sr-Cu-O system in the K_2NiF_4 phase. The single-crystal films were prepared by sputtering sintered targets of the La-Sr-Cu-O compounds. Typical sputtering conditions are listed in Table I. The target was stoichiometric $(La_{0.9}Sr_{0.1})_2CuO_4$ and was made by sintering a mixture of La_2O_3 (99.99%), $SrCO_3$ (99.9%), and CuO (99.9%) at 900 °C in air for about 8 h. Perovskite single crystals of (100) $SrTiO_3$ were selected for the substrates. The lattice constant of the $SrTiO_3$ is 3.90 Å, which was close to the lattice constant of basal plane, 3.78 Å, reported for $(La_{0.9}Sr_{0.1})_2CuO_4$.[4] The substrates were kept at 600 °C during the deposition so that the single-crystal films could grow epitaxially on the crystal surface of the substrates similarly to the growth of Pb-La-Ti-O perovskite thin films.[9]

The as-sputtered films were conductive with a black color similar to the target. Electron-probe x-ray microanalysis showed that the concentrations of La, Sr, and Cu were close to the target composition. From x-ray diffraction analyses, the sputtered films were found to have a single-phase K_2NiF_4 structure with the (001) surface parallel to the substrates. The electron diffraction pattern suggested that an excellent single crystal was epitaxially grown on the substrate as indicated in Fig. 1. The epitaxial relations were as follows:

$$(001)(La_{0.9}Sr_{0.1})_2CuO_4 \parallel (100)SrTiO_3$$

and

$$[010](La_{0.9}Sr_{0.1})_2CuO_4 \parallel [010]SrTiO_3 .$$

These sputtered films exhibited superconductivity after postannealing in air at 900 °C for 3 days. To measure the temperature dependence of the resistivity, gold electrodes (2 mm in width) were evaporated on the surface of the films. The standard four-probe technique was used for the resistivity measurements. The samples were fixed to a copper block. The temperature was measured by a chromel-Au(Fe) thermocouple attached to the copper block. Typical results are shown in Fig. 2. The solid line in the figure shows the results for the sputtered films of 1.7-μm thickness measured at 0.05 mA. The onset temperature was 34 K and the zero-resistivity state was ob-

TABLE I. Sputtering conditions.

Target	$(La_{0.9}Sr_{0.1})_2CuO_4$, 100$\phi$
Substrate	(100) plane of $SrTiO_3$
Sputtering gas	Ar
Gas pressure	0.4 Pa
rf power	150 W
Substrate temperature	600 °C
Growth rate	100 Å/min

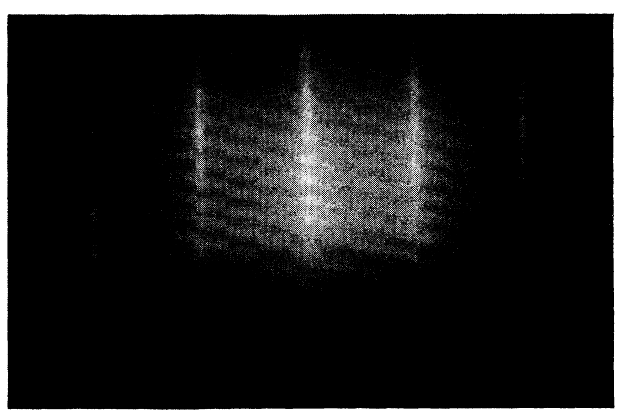

FIG. 1. Reflection high-energy electron diffraction pattern of $(La_{0.9}Sr_{0.1})_2CuO_4$ film epitaxially grown on (100) $SrTiO_3$. The thickness is 0.6 μm.

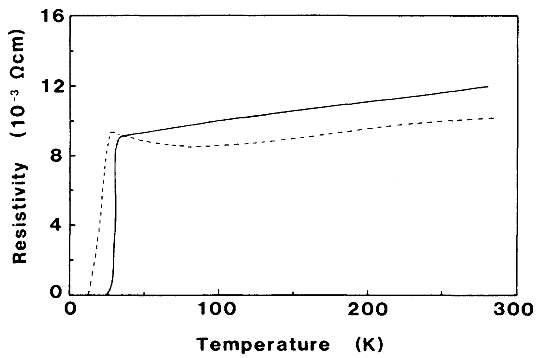

FIG. 2. The temperature dependence of the resistivity for $(La_{0.9}Sr_{0.1})_2CuO_4$ films. The solid line is for an epitaxial film on (100) $SrTiO_3$, and the broken line is for a polycrystal film on (100) MgO.

served below 25 K. The critical current density at 4.2 K was found to be 25 A/cm^2. Similar results were obtained for the sputtered films whose thickness ranged from 0.2 to 6 μm.

The transition width (10% to 90%) was as low as 3 K. In the figure the broken line shows the superconductivity observed for the polycrystal film sputtered onto a (100) MgO substrate. The transition was not as sharp as observed in the epitaxial films. The sharp transition observed in the epitaxial single-crystal films corresponded to the best result for the ceramics. This proves that the transition width is reduced by making the compound with a purer and more homogeneous K_2NiF_4 structure, which was suggested by Hor *et al.*[10]

Although the chemical composition did not change through the annealing, the superconductivity rose after annealing. The lattice constants changed due to the post annealing. The as-sputtered films had a lattice constant of $a = 3.80$ Å. During the postannealing, the lattice constant became 3.78 Å, which was equal to that of the $(La_{0.9}Sr_{0.1})_2CuO_4$ ceramics. The oxidation of Cu^{2+} into Cu^{3+} may not be sufficient during the sputtering deposition. The $[Cu^{3+}/Cu^{2+}]$ ratio is thought to increase during the postannealing process.

The crystallites of the layered tetragonal structure were found to play an important role in the La-Sr-Cu-O compound system. The present single-crystal thin films with no grain boundary could be useful for making Josephson devices. In the thin films, however, there exists thin-film effects, including stress, which will change the superconductive properties. Further study should be done for thin films of the layered tetragonal structure.

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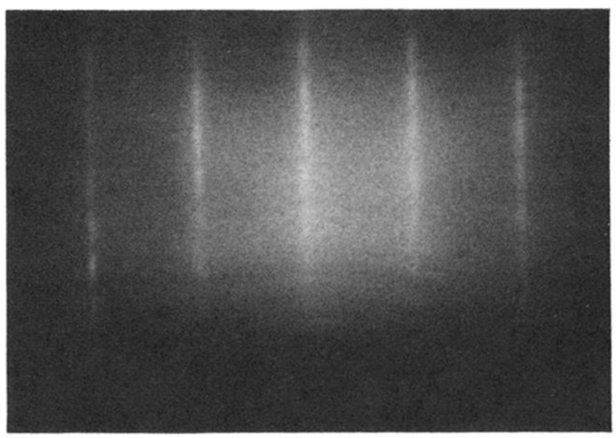

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