

LPE growth of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single-crystalline films

Isao Tanaka^{*,**}, Hideyoshi Tanabe^{*}, Satoshi Watauchi^{*,**} and Hironao Kojima^{*,**}

^{*}*Institute of Inorganic Synthesis, Yamanashi University, 7, Kofu 400-8511, Japan*

^{**}*CREST Project, Japan Science and Technology Corporation (JST), Japan*

(Received June 9, 1999)

Abstract $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single-crystalline films were prepared on bulk single crystals of Zn-doped La_2CuO_4 as the substrates by LPE technique using two different methods. When prepared using an alumina crucible in normal electrical furnace, the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films were contaminated with less than 3 at% aluminum from the alumina crucibles. Aluminum contamination either reduced or completely destroyed the superconductivity of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films. For LPE growth by modified TSFZ method using an infrared heating furnace without crucibles, the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films of $x = 0.11$ showed superconducting with $T_{\text{onset}} \approx 36$ K, which is 10 K higher than that in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ bulk single crystals.

1. Introduction

The intrinsic Josephson junctions of CuO_2 conducting layer - $(\text{La,Sr})_2\text{O}_2$ insulating layer - CuO_2 conducting layer are formed along the c -axis in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ lattice. The Josephson plasma is generated by the coupling between the Josephson current flowing along the c -axis and the electromagnetic field [1]. Table 1 shows the characteristics of the intrinsic Josephson junctions in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single crystals as compared with those of Nb SIS Josephson junctions [2]. The plasma frequency is in the terahertz band, and is hundred times higher than that in the SIS Josephson junctions, and the size of the vortex quantum is a hundred times smaller than that in the SIS junctions. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single crystals are expected to be applicable in THz oscillators, high-speed microelectronics switching and large current switches [2]. Bulk single crystals of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ have previously been grown by the TSFZ method [3, 4], but the device processing using the bulk single crystals is complicated. Therefore, a -axis-

orientated single-crystalline films of micron-order size thickness are desired for the processing and development of electronics devices and a -axis-oriented single-crystalline films cause the carriers of the Josephson plasma to vibrate in-plane of the film. Liquid phase epitaxial (LPE) technique are considered to be useful techniques for growing single-crystalline films, while the vapor deposition methods are suitable for the growth of orientated films of angstrom-order thickness but not single-crystalline films.

In this study, homoepitaxial growth of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ thin films was performed on bulk single crystals of Zn-doped La_2CuO_4 as the nonsuperconducting substrates by the LPE technique.

2. Experimental

The substrates were made into semiconductors by substitution of Zn for a part of Cu in La_2CuO_4 . The single crystals of Zn-doped La_2CuO_4 were grown along the a -axis by the TSFZ method with an infrared heating furnace. The as-grown boules, typically 5 mm in diameter and 40 mm in length, were sliced into sections of 1 mm thickness perpendicular to the a -axis, and then used as the substrates. The LPE growth was performed by two methods. One was a normal method with an alumina crucible in the electrical furnace as shown in Fig. 1a, and the another new method was a modified TSFZ method using the infrared heating furnace with no crucibles as shown in Fig. 1b. Table 2 indicates the typical growth conditions. For the normal

Table 1
Comparison between intrinsic Josephson junctions in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single crystals and Nb Josephson junctions

	Intrinsic Josephson junctions	Nb Josephson junctions
Plasma frequency	≈ 5 THz	≈ 50 GHz
Magnetic penetration depth	< 1 μm	≈ 100 μm
Critical current density	$\approx 10^{11}$ A/m ²	$\approx 10^8$ A/m ²

method, the solvent of about 150 g was melted in an alumina crucible by heating up to 1215°C at the rate of 30°C/h, and cooled to 1125~1160°C at the rate of 80°C/h. Then, the substrate was moved down into the molten solvent and rotated at the speed of 30~200 rpm for 30~60 sec, and then pulled up and rotated at a speed higher than 1000 rpm to remove the molten

solvent. For the new method, an infrared heating furnace with halogen lamps as heat source was used. The solvent was melted down on the substrate fixed in the lower shaft. The substrate was fixed under the upper shaft, and the sintered or single-crystalline La_2CuO_4 was fixed on the lower shaft. The molten zone was formed after the solvent was melted, and the substrate was pulled up at 1 mm/h for 36~60 sec. The lower shaft was moved down with cooling down, and then, the molten zone was separated.

The films were characterized by polarizing optical microscopy and electron probe microanalysis (JEOL Co., model JXA-8600M). The samples for microscopic observations were prepared by cutting and polishing parallel to the growth direction. The superconducting properties of the grown films were investigated by magnetization measurements using a SQUID magnetometer (QUANTUM DESIGN Co., model MPMS-5S). The solvent remaining on the surface of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films was removed by mechanical polishing.

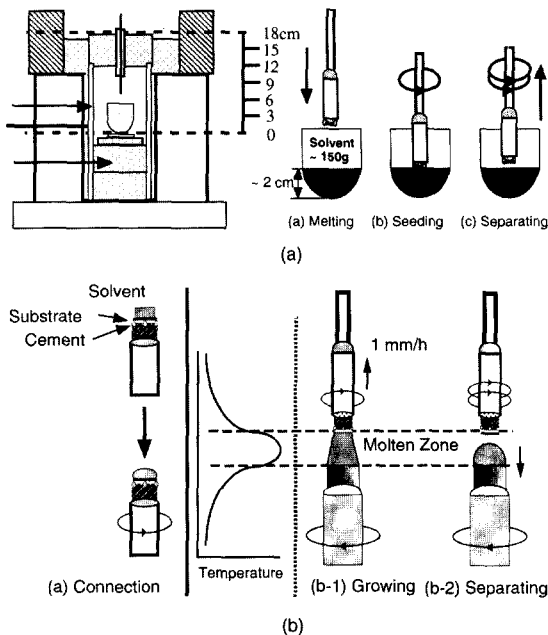


Fig. 1. LPE processes using normal electrical furnace (a) and using infrared heating furnace (b).

Table 2
Growth conditions for using normal electrical furnace and infrared heating furnace

Growth conditions	Normal electrical furnace	Infrared heating furnace
Solvent composition	87~88 mol%CuO	80~85 mol%CuO
Sr content x in Solvent	0.40	0.30~0.40
Weight of solvents	150 g	~0.2 g
Growth atmosphere	Oxygen	Oxygen
Growth time	30~60 sec.	36~60 sec.
Shaft rotation rate	30~200 rpm	10~30 rpm
Growth temperature	1125~1160°C	-----
Crucible material	Alumina	-----
Growth speed	-----	1.0 mm/h

3. Results and discussion

The growth results were shown in Table 3. When prepared using the normal electrical furnace, the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films with the thickness of 5~50 μm were obtained. Figure 2 shows the profiles of the X-ray intensities along the growth direction in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ film on $\text{LaCu}_{1-y}\text{Zn}_y\text{O}_4$ substrate. The thickness of the films was determined to be about 20 μm from the width of the Sr-contained region. The Sr distribution in each $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ film was uniform, but the Sr concentration (x) of the films varied between 0.07 and 0.11 even though all the films were prepared under the same conditions. The $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films were Zn-free, but were contaminated with less than 3 at% aluminum from the alumina crucible. The aluminum contamination destroyed the superconductivity in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

Table 3
Growth results for using normal electrical furnace and infrared heating furnace

	Normal electrical furnace	Infrared heating furnace
Thickness	5~50 μm	35~250 μm
Orientation	the a -axis	the a -axis
Sr content x	0.07~0.11	0.08~0.11
Zn content	Not detected	Not detected
Al content	~3 at%Al	Not detected

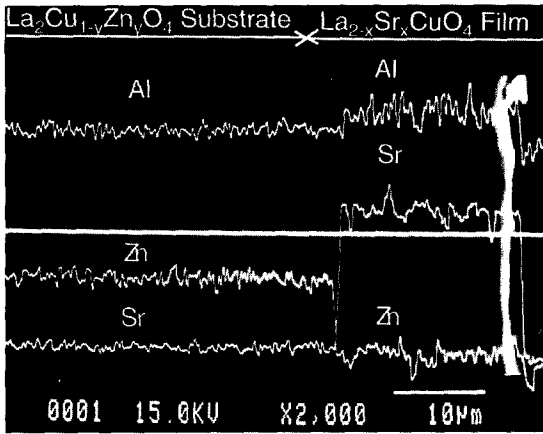


Fig. 2. SEM photograph and X-ray profiles in the cross section of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films prepared using an alumina crucible.

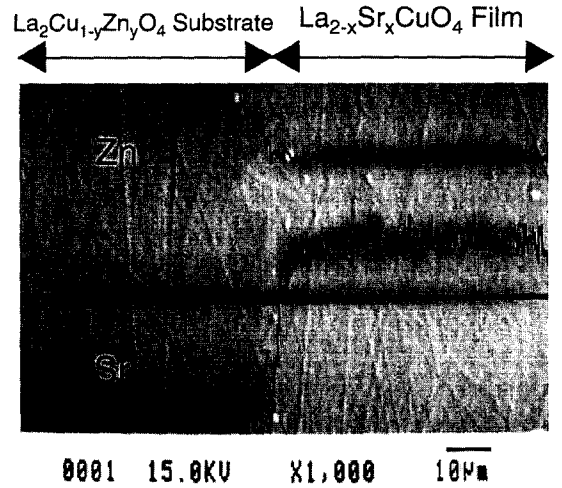


Fig. 4. SEM photograph and X-ray profiles in the cross section of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films prepared using infrared heating furnace.

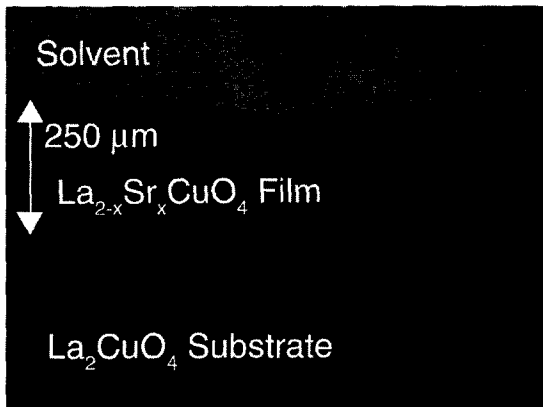


Fig. 3. Optical microphotograph of the cross section in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films prepared using infrared heating furnace.

films as described later. To prevent aluminum contamination from the crucibles, LPE growth was performed by the modified TSFZ method using the infrared heating furnace. Figure 3 shows an optical microphotograph of the cross section of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ film prepared on the $\text{La}_2\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ substrates. The $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ film with the thickness of about $250\ \mu\text{m}$ was single-crystalline with no subgrains, but cracking occurred into the films and the substrate. The interface between the film and the substrate was almost flat and smooth. As shown in Fig. 4, Sr concentration of the film was uniform, and Zn contamination from the substrate was less than the detected limit of the electron probe microanalyzer that we used.

For the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films prepared using the normal electrical furnace, some of the films exhibited

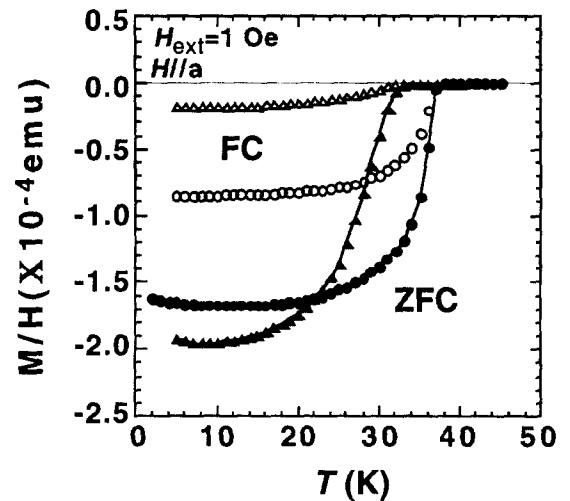


Fig. 5. Magnetization in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films prepared using normal electrical furnace (triangles) and using infrared heating furnace (circles). Their samples were annealed in oxygen at 800°C for 48 h.

superconductivity, while the others were nonsuperconducting. The all of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films prepared using the infrared heating furnace were superconducting. Figure 5 shows the magnetization in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films annealed in oxygen at 800°C for 48 h. The composition of the sample prepared using the normal electrical furnace was Sr concentration (x) of 0.099 and Al content of 2 at%, while the Sr concentration (x) of the sample prepared using the infrared heating furnace was 0.11. The $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films prepared using the

normal electrical furnace were confirmed to be superconductors with $T_{c\text{onset}} = 32$ K and $\Delta T_c = 20$ K. $T_{c\text{onset}}$ in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films was close to that in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ bulk crystals, but the ΔT_c in these films was remarkably broad. On the other hand, the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films prepared by the infrared heating furnace showed superconducting with $T_{c\text{onset}} \approx 36$ K, which is 10 K higher than that in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ bulk single crystals. Aluminum contamination either reduced or completely destroyed the superconductivity of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films.

4. Conclusions

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single-crystalline films were prepared on bulk single crystals of Zn-doped La_2CuO_4 as the substrates by LPE technique using two different methods. When prepared using an alumina crucible in normal electrical furnace, the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single-crystalline films with the thickness of 5~50 μm were obtained. However, the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films were contaminated with less than 3 at% aluminum from the alumina crucibles. Aluminum contamination either reduced or completely destroyed the superconductivity of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films. For LPE growth by modified TSFZ method using the infrared heating furnace without cru-

cibles, the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single-crystalline films with the thickness of 35~250 μm were obtained. The composition of the films was uniform, and had no Zn contamination from the $\text{La}_2\text{Cu}_{1-y}\text{Zn}_y\text{O}_4$ substrates. The all of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films prepared using the infrared heating furnace showed superconducting with $T_{c\text{onset}} \approx 36$ K, which is 10 K higher than that in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ bulk single crystals.

Acknowledgments

This work was supported in part by CREST, Japan Science and Technology Corporation, and also by Grant-in-Aid Scientific Research (B), Japan Society for the Promotion of Science. IT was supported by Murata Science Foundation.

References

- [1] M. Tachiki, T. Koyama and S. Takahashi, Phys. Rev. B 50 (1994) 7065.
- [2] T. Yamashita, Physica C 293 (1997) 31.
- [3] I. Tanaka and H. Kojima, Nature 337 (1989) 21.
- [4] I. Tanaka, K. Yamane and H. Kojima, J. Crystal Growth 96 (1989) 711.