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Growth of $La_{2-x}Sr_xCuO_4$ Single Crystals for Device Application

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Abstract

We had succeeded to grow bulk single crystals of $La_{2-x}Sr_xCuO_4$ by the traveling solvent floating zone method (TSFZ), and to prepare $La_{2-x}Sr_xCuO_4$ single-crystalline thick films on the Zn-doped La_2CuO_4 substrate by new liquid phase epitaxial technique using an infrared heating furnace (IR-LPE). In this paper, I review growth of bulk single crystals and single-crystalline thick films of $La_{2-x}Sr_xCuO_4$, and discuss on their device properties to develop high speed integrated electronic devices.

Keywords : crystal growth, LPE, TSFZ, intrinsic Josephson junction bulk single crystals, single-crystalline film

I. Introduction

Since in the crystal structure of $La_{2-x}Sr_xCuO_4$, the CuO_2 conducting layers and the $(La,Sr)_2O_2$ insulating block layers are stacked alternately along the *c*-axis, the Josephson coupling of $CuO_2/(La,Sr)_2O_2/CuO_2$ is formed in the $La_{2-x}Sr_xCuO_4$ lattice. Therefore, $La_{2-x}Sr_xCuO_4$ single crystals are regarded as microelectronics devices consisting of many Josephson junctions. The intrinsic Josephson effects have been observed in $La_{2-x}Sr_xCuO_4$ as well as $Bi_2Sr_2CaCu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$ [1]-[3]. Also the Josephson plasma phenomenon, which is generated by the coupling between the Josephson current flowing along the *c*-axis and the electromagnetic field, has been observed in $La_{2-x}Sr_xCuO_4$ bulk single crystals by infrared reflectivity measurements [4], [5]. The plasma frequency in $La_{2-x}Sr_xCuO_4$ is in THz waveband while that in $Bi_2Sr_2CaCu_2O_8$ is a microwave frequency range [6], [7]. These stacked and coupled Josephson junctions have attracted considerable attention not only as fundamental interest but also for prospects of their practical applications in high frequency devices, high-speed switching devices, THz band oscillators etc. [7]. In this paper, I describe crystal growth of bulk single crystals and single-crystalline thick films of $La_{2-x}Sr_xCuO_4$ superconductor for application of new electronic devices. The bulk single crystals of $La_{2-x}Sr_xCuO_4$ were grown by the traveling solvent floating zone (TSFZ) method, and the single-crystalline films of were prepared by infrared-heating liquid phase epitaxial (IR-LPE) technique, which we had developed [8]. The micro-bridges of intrinsic Josephson junctions were fabricated from the grown crystals, and were characterized by current – voltage measurements.

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II. Growth and Characterization of $Ls_{2-x}Sr_xCuO_4$ Bulk Single Crystals

La_2CuO_4, the host compound of $La_{2-x}Sr_xCuO_4$, melts incongruently above 1600 K and decomposes to La_2O_3 solid and a liquid according to the phase diagram of the La_2O_3 – CuO system [9]. Superconducting $La_{2-x}Sr_xCuO_4$ is also a solid solution in which a part of La ions is substituted to Sr ions in La_2CuO_4. The $La_2\text{-}Sr_xCuO_4$ crystals grown by the flux and top-seeded solution growth (TSSG) methods had been inhomogeneous and low dopant concentration, so that their superconducting properties were a broad transition and a low T_c. In addition, platinum contamination from a platinum crucible during the flux growth was a serious problem on decrease of T_c. By the way, the TSFZ method is useful for crystal growth of incongruent-melting compounds and solid solutions, and also is contamination-free because of no use of a crucible. The details about the TSFZ method had been described in References [9]-[11].

The apparatus for crystal growth was an four-mirror type infrared heating furnace with halogen lamps as a heat source (Crystal Systems Co.). Sr content in the grown crystals could depend on the Sr contents of the feeds and the solvent. The composition of the feed rods was stoichiometric $La_{2-x}Sr_xCuO_4$ with various Sr contents x, and the composition of the solvents was 78 - 80 mol%CuO a nd a Sr content higher than that of the feeds. The feeds and the solvents were prepared by a normal sintering technique. Crystal growth was performed under the oxygen pressure of 0.2 MPa at the growth rate of 1.0 mm/h along the a-axis. The TSFZ growth process is shown in Fig. 1. The solvent was melted and attached on the top of the feed. The feed and seed crystal were set up at the upper and lower shafts respectively, and then the growth was proceeded as same as a normal FZ method.

The as-grown crystals of $La_{2-x}Sr_xCuO_4$ were black with a metallic luster, and their typical size was 5 mm in diameter and about 40 mm in length, as shown in Fig. 2. The composition of the grown crystals was uniform along the growth and radius directions, as results of the electron probe microanalysis.

We have measured device properties of the La_2-Sr_xCuO_4 bulk single crystals as follows. The intrinsic Josephson effect was observed in the mesas of La_2-Sr_xCuO_4 single crystal with the typical size of 50μm x 50mm x 0.1μm [12]. Also shapiro steps were induced by microwave irradiation of 9.0 GHz on the current – voltage characteristic. Josephson vortices flow was measured in micro-bridge with 1mm length along the c-axis, which is corresponding to about 1500 stacks of the intrinsic Josephson junctions in La_2-Sr_xCuO_4 [13]. The velocity of the vortices was estimated to be the range from 90. x 10^4 m/s at the external magnetic field of 1.0 T to 1.6 x 10^5 m/s at 0.1 T. The vortex velocity of 1.6 x 10^5 m/s is corresponding to the radiation frequency of 370 GHz, and this result suggests possibility of application for submillimeter wave generator. However, the vortex velocity in the La_2-Sr_xCuO_4 grown crystals was 10 times lower than the value calculated from some parameter in La_2-Sr_xCuO_4. The point-like defects such as oxygen vacancies and the twinning formation due to a ferroelastic transition between orthorhombic and tetragonal phases may influence the vortex motion in the crystals.

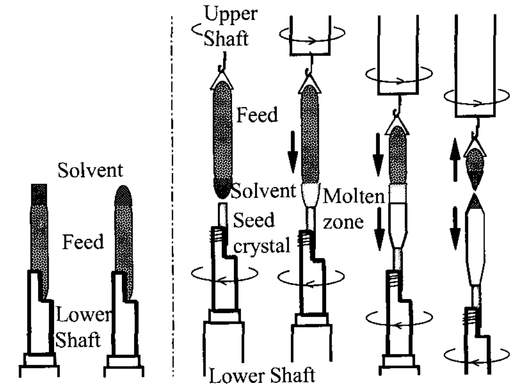

Fig. 1. Operation process in the TSFZ growth.

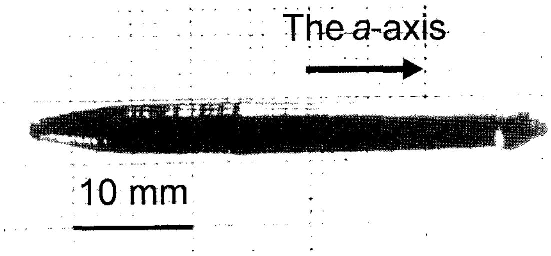

Fig. 2. As-grown crystal of $La_{2-x}Sr_xCuO_4$.

III. Preparation and Characterization of $Ls_{2-x}Sr_xCuO_4$ Single-Crystalline Films

Device processing of bulk single crystals proved complicated as described above in the measurements of the device properties. The a-axis oriented single crystalline films of thickness of micro-meter order would be more suitable for processing and development of electronic devices of intrinsic Josephson junctions. Liquid phase epitaxial (LPE) technique is considered to be useful for growing single-crystalline films under a low supersaturation, while the vapor deposition methods are suitable for the growth of orientated films of thickness in angstrom-order but not for single-crystalline films, since Volmer-Weber and Stranski-Krastanov models are dominant for growth under a high supersaturation such as vapor deposition method [15]. We have succeeded to prepare single-crystalline films of $La_{2-x}Sr_xCuO_4$ on Zn (Ni) -doped La_2CuO_4 substrates by a conventional LPE technique using an alumina crucible, but aluminum contamination from the crucible destroyed the superconductivity in the films [16].

We have designed a new LPE technique, infrared heated LPE (IR-LPE) technique using no crucible, where the TSFZ method used for bulk crystal growth was applied to film preparation, and prepared single crystalline films of $La_{2-x}Sr_xCuO_4$ on Zn-doped La_2CuO_4 substrates [17]. In this paper, I discuss film preparation of the $La_{2-x}Sr_xCuO_4$ single-crystalline films by IR-LPE growth and current-voltage (I-V) characteristics of the LPE films. Furthermore, the problems on IR-LPE growth of $La_{2-x}Sr_xCuO_4$ single-crystalline films are pointed out.

The substrate used for film growth was obtained from 2%Zn-doped La_2CuO_4 single crystal grown by the TSFZ method along the a_{tetra}-axis. Each substrate was about 1 mm in thickness perpendicular to the a_{tetra}-axis with its surface polished mechanically. The solvents with composition of 80 ~ 86 mol%CuO and Sr content x, 0.3 ~ 0.6, were prepared by a normal sintered method. The apparatus for the IR-LPE growth was the same infrared heating furnace as for TSFZ growth. The IR-LPE process is illustrated in Fig. 3. The substrate was attached on an alumina rod using alumina cement, and the alumina rod was fixed to the upper shaft. A La_2CuO_4 crystal rod to support a molten zone was fixed to the lower shaft, and a tip of solvent less than 0.2 g was put on the La_2CuO_4 crystal rod. After the solvent was melt in oxygen ambient, a molten zone was formed by moving up the lower shaft. The molten zone was stirred by rotating the substrate and the crystal rod at 10 ~ 30 rpm in counter direction. The growth was performed by pulling up the substrate at 1.0 mm/h for 0 ~ 120 sec. After the growth, the molten zone was separated from the substrate by moving down the lower shaft. Fig. 4 shows an optical microphotograph of the growth section of the $La_{2-x}Sr_xCuO_4$ films on the Zn-doped La_2CuO_4 substrate. The interface between the films and the substrate was almost flat, but some cracks were included in the films. As the analysis results by EPMA, it was found that the Sr content in films was about 0.136(4), and that Zn contamination to film from substrate was negligibly small. The electron diffraction patterns of the film agreed with that of the substrate, so it was confirmed that the $La_{2-x}Sr_xCuO_4$ film was grown epitaxially on the La_2CuO_4 substrate.

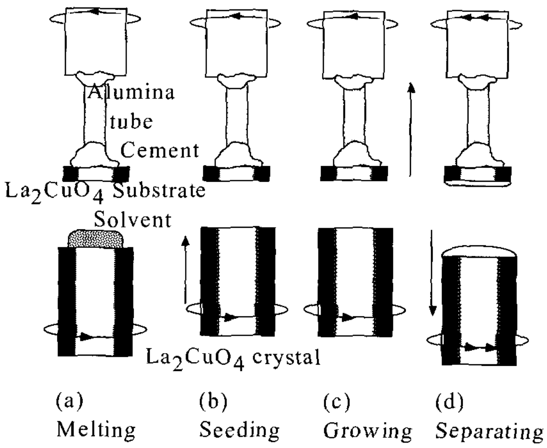

Fig. 3. Operation process of IR-LPE growth.

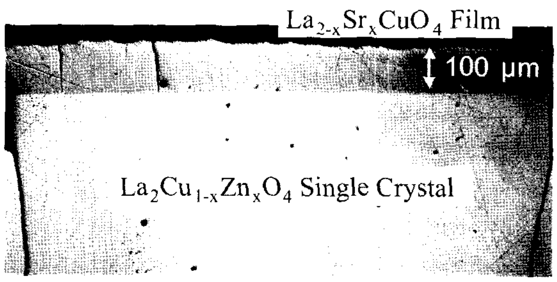

Fig. 4. Optical microphotograph of growth section of $La_{2-x}Sr_xCuO_4$ LPE film on Zn-doped La_2CuO_4 substrate.

Figure 5 shows the magnetization in the $La_{2-x}Sr_xCuO_4$ films (x=0.11) annealed in oxygen at 1073 K for 48 h. The superconducting properties in the $La_{2-x}Sr_xCuO_4$ films prepared by IR-LPE technique indicate higher T_c and narrower ΔT_c as compared with conventional LPE technique [16]. Further, the $La_{2-x}Sr_xCuO_4$ (x=0.11) films prepared by IR-LPE technique were superconducting with $T_{c,onset} \sim 36$ K, which is 10 K higher than that in the bulk single crystals. However, the superconducting properties of the films depend on the thickness of the films. Fig. 6 shows the results of resistance (normalized) versus temperature measurement done on LPE films along the c-axis, with different thickness. We observe that all LPE films shows $T_{c,onset}$, but the films thinner than 80 μm do not show zero resistance current at temperature down to 4.2 K. The $T_{c,onset}$ was also found to decrease with decreasing film thickness. 80 μm film shows $T_{c,onset}$ ~24K and $T_{c,end}$ ~7K for 10 mA current flow. The secondary y-axis in Fig. 6 shows the property of the substrate along the same direction. The R(T) measurement on substrate shows semiconductor-like characteristic.

The suppression of T_c in the $La_{2-x}Sr_xCuO_4$ films thinner than 80 μm may be caused by an epitaxial strain between the film and the substrate as shown in Fig. 7. It is known that the reasons of T_c enhancement in $La_{2-x}Sr_xCuO_4$ are orthorhombic distortion, anisotropy of uniaxial strain coefficients and lattice mismatch between the films and substrates [18]-[20]. The lattice parameters of $La_{2-x}Sr_xCuO_4$ (x=0.10) are a= 0.53260 nm, b= 0.53713 nm and c= 1.31641 nm at 60 K while those of La_2CuO_4 are a= 0.53352 nm, b= 0.54160 nm and c= 1.31058 nm at 60 K. The a-axis oriented $La_{2-x}Sr_xCuO_4$ films on the La_2CuO_4 substrate could be expended along the b-axis and compressed along the c-axis at the same time. The T_c tends to decrease as the lattices of $La_{2-x}Sr_xCuO_4$ are compressed along the c-axis

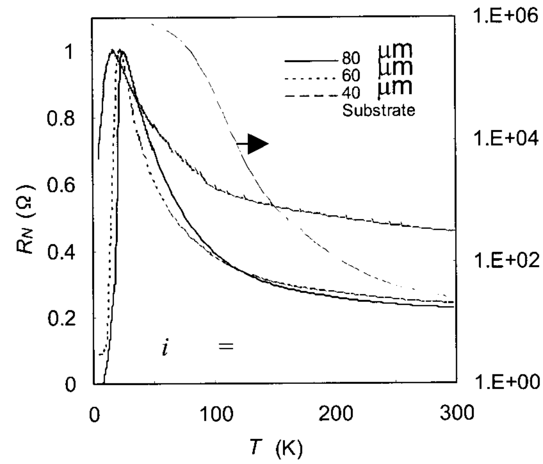

Fig. 6. Temperature dependence of normalized resistance (R(T)) of LPE films of different thickness Secondary y-axis shows R(T) of substrate in the same temperature range.

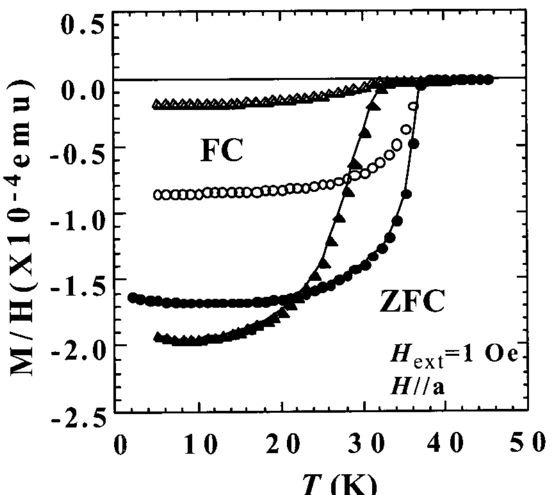

Fig. 5. Magnetization of $La_{2-x}Sr_xCuO_4$ films prepared by IR-LPE (circles) and by conventional LPE (triangles) (Ref. 16). The samples were annealed in oxygen at 1073 K for 48 h.

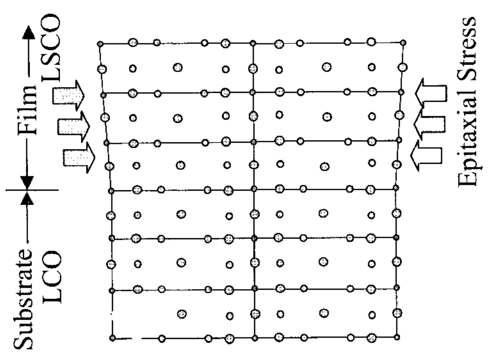

Fig. 7. Illustration of Epitaxial strain in $La_{2-x}Sr_xCuO_4$ films on Zn-doped La_2CuO_4 substrate.

[18]-[20]. Therefore, the superconducting properties in the *a*-axis oriented $La_{2-x}Sr_xCuO_4$ films on the La_2CuO_4 substrate may be suppressed with decreasing the thickness of the $La_{2-x}Sr_xCuO_4$ films. We are looking for substrate materials which induce the $La_{2-x}Sr_xCuO_4$ films expanded along the *c*-axis.

IV. Conclusion

I described on growth of $La_{2-x}Sr_xCuO_4$ bulk single crystals by the TSFZ method and $La_{2-x}Sr_xCuO_4$ single-crystalline films by IR-LPE method. We obtained the bulk single crystals and the single-crystalline films of high quality with uniform composition and crystallographic arrangement. However, point-like defects and epitaxial strain may be significant for the superconducting properties and device properties.

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