Journal of the Korean Crystal Growth and Crystal Technology
Vol. 13, No. 4 (2003) 172-175

Lattice strain effects on superconductivity in $La_{2-x}Sr_xCuO_4$ single-crystalline films grown by IR-LPE technique

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(Received March 13, 2003)
(Accepted July 2, 2003)

Abstract We have investigated effects of the lattice mismatch between the LPE films and the substrates. We have grown $La_{2-x}Sr_xCuO_4$ ($x = 0.1$ to 0.15) single crystalline films on single crystalline substrates having different lattice parameter ratio *c/a* e.g., $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$, $La_{2-x}Ba_xCuO_4$, $LaSrAlO_4$ and $La_{2-x}Sr_xCu_{1-y}Al_yO_4$ etc., using the IR-LPE technique. The superconducting properties of the grown films were found to vary significantly depending on the lattice mismatch with different substrates.

Key words Epitaxial strain, Superconductors, LPE, Film growth, 214 System oxide

1. Introduction

The choice of the substrate for example crystallographic structure, lattice mismatch etc., is very important factor to consider for film growth. Such parameters of the substrate can have a considerable effect on the properties of the film grown on it. The critical temperatures, T_c of most of the high-T_c superconductors are found to be sensitive to application of uniaxial pressure along the different crystallographic axes. For most systems the in-plane and out-of-plane T_c derivatives have opposite signs. So under hydrostatic pressure, the effect is nearly cancelled out and the resultant change in T_c is rather small [1]. On the other hand, epitaxial strain could affect a high anisotropic pressure state. An epitaxial growth causing compressive strain in the a-direction and tensile along the c-axis could add up to increase of T_c and vice-versa. Most notable example is the report by Locquet *et al.* [2], who deposited thin films of $La_{1.9}Sr_{0.1}CuO_4$, on a suitable substrate $LaSrAlO_4$ (LSAO) having a smaller a-axis lattice parameter, by Molecular Beam Epitaxy (MBE) technique. The T_c found at 49.1 K in the strained film is twice of that observed in the bulk compound ($T_c = 25$ K) having the same Sr content. In the same process growth on $SrTiO_3$ (STO) substrate having a larger a-axis had an opposite effect on $La_{1.9}Sr_{0.1}CuO_4$ film. Strain tensile along the a- (or b-) axial direction caused T_c to drop to 10 K from 25 K. The reason for the suppression of T_c is due to the compression of the c-axis (or the expansion of the a-axis) can be explained as similar to the T_c suppression by substitution of Nd in $La_{2-x-y}Sr_xNd_yCuO_4$ [3]. The substitution of Nd for La causes the compression along the c-axis followed by the rotation of the tilt axis of CuO_6 octahedra and decrease in T_c. The tilt of CuO_6 octahedra beyond a critical value leads to a structural phase transition to low temperature tetragonal (LTT) phase, which is a metallic and magnetically ordered ground state. Epitaxial strain along the c-axis could also lead to the similar phase transition and the suppression of T_c.

Therefore, the choice of substrate has an important role to play since it may cause the increase or suppression of T_c. Appropriate substrates having suitable lattice parameters can induce the desired strain. Film growth with optimal strain can be achieved by a compromise between the lattice mismatch and thickness of the grown film. Too large lattice mismatch doesn't always mean the stronger stress, as it could easily lead to misfit dislocations and make the strain ineffective. The optimum thickness using LSAO and STO substrates by MBE technique reported by Locquet *et al.* was about 10~15 nm.

In some electronic device applications e.g., intrinsic Josephsons junctions of $La_{2-x}Sr_xCuO_4$ (LSCO) in low electric power and high speed switching devices, the film-thicknesses of about micrometer order are desired. In our previous work, we reported the preparation of single crystalline films of $La_{2-x}Sr_xCuO_4$ on Zn (or Ni) doped La_2CuO_4 substrates by infrared heated liquid phase epitaxy (IR-LPE) technique [4]. The advantage of this process was the aluminum contamination from crucible, as it often happens in conventional LPE techniques [5], could be avoided.

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In this work, we present some results of characterizations of the electric properties of the films grown on the different substrates. We have grown single crystalline films of LSCO on the different substrates e.g., $La_2Cu_{1-y}Zn_yO_4$ (LCZO, y = 0.05), $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ (LSCZO, x = 0.15, y = 0.05), $La_{2-x}Ba_xCuO_4$ (LBCO, x = 0.113), $La_{2-x}Sr_xCuO_4$ (LSCO, x = 0.186), $LaSrAlO_4$, $La_{2-x}Sr_xCu_{1-y}Al_yO_4$ (LSCAO, x = 0.25, y = 0.03) etc., having different lattice parameters, using the IR-LPE technique. The effects of the different substrates on the composition and superconducting transition temperature T_c of the grown films were investigated by electron probe microanalysis and temperature dependence of resistivity [R(T)] measurements, respectively.

2. Experimental Process

The substrates for LSCO film growth were grown by the Travelling Solvent Floating Zone method along the crystallographic c-axis. The as-grown single crystals were cylindrical shaped with 5 to 5.5 mm in diameter and 40 to 55 mm in length. The as-grown crystals were sliced to the ac-plane and polished mechanically to mirror-like surface. The substrates were then cleaned using alcohol and ultrasound cleaner.

The film growths were performed on the different substrates by IR-LPE method [4]. The flux used for film growth was $La_{2-x}Sr_xCuO_4$ with 80~85 mol% CuO with x = 0.3 to 0.65 and were prepared by normal sintering method. After growth, the crystallinity of the grown LPE films on the different substrates were checked by Laue X-ray diffraction photograph and polarizing optical microscopy. Electron probe micro analysis (EPMA) was done to examine the composition of the grown film and substrate quantitatively and to check for the possible contamination from the substrate. The top surface of the films was polished mechanically to remove any residual flux on the film. Resistance versus temperature measurements were done on the LPE film surface by conventional four point probe method using a cryostat.

3. Results and Discussion

Figure 1 shows the results of resistance versus temperature measurement done on LPE films along the c-axis, with different thicknesses. 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 $T_{c,\,onset}$ ~24 K and $T_{c,\,end}$ ~7 K for 10 μA current flow. This may also imply that the actual superconducting part is only the top thin layer for an 80mm thick $La_{2-x}Sr_xCuO_4$ film. And between this superconducting part and the substrate there might be a non-superconducting layer, most likely metallic LSCO film part. The secondary y-axis shows the property of the substrate along the same direction. The R(T) measurement on substrate shows semiconductor-like characteristics.

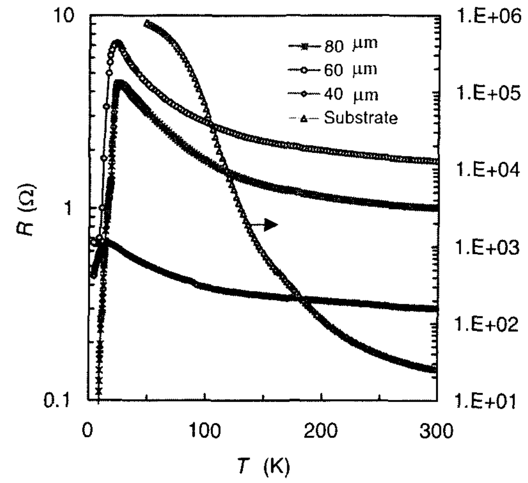

Fig. 1. Temperature dependence of resistance [R(T)] of LPE films of the different thicknesses. Secondary y-axis shows R(T) of substrate in the same temperature range.

Figure 2 shows the temperature dependence of resistivity of LSCO films grown on the different substrates. We observe that the T_c suppression from the films (of

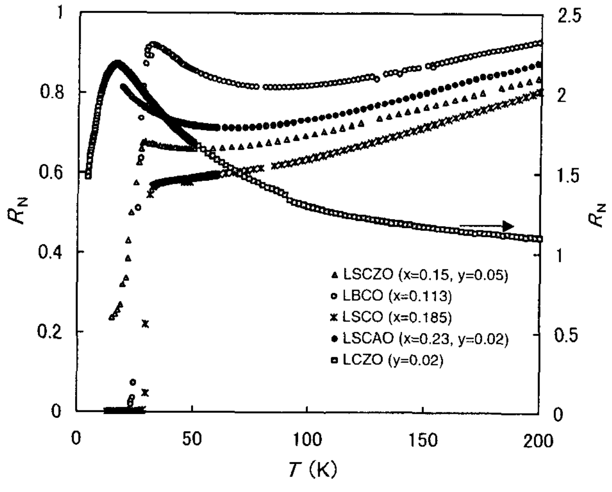

Fig. 2. Temperature dependence of resistance (normalized) for LPE films grown on the different substrates. The film thicknesses of LCZO and LSCZO are about 40 μm. The thicknesses of the other films are about 10~15 μm.

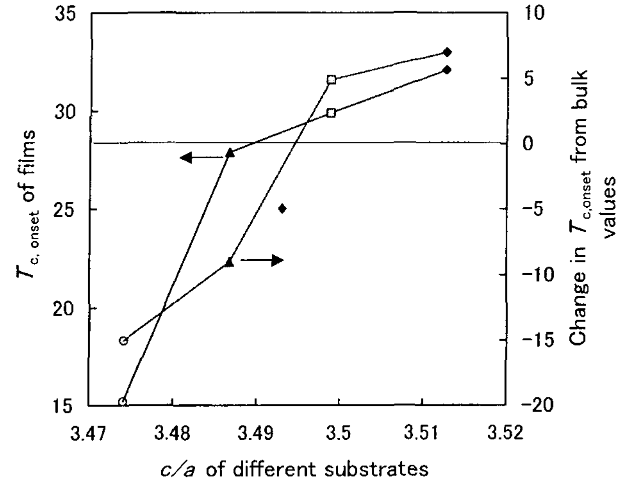

Fig. 3. $T_{c,\,onset}$ of LSCO films grown on the different substrates [○ LCZO, ▲ LSCZO, ■ LBCO, ● LSCO (x = 0.186)] having Sr content x = 0.134, 0.155, 0.105 and 0.11, respectively. ◆ represents values for bulk LSCO (x = 0.1). Secondary y-axis shows change in $T_{c,\,onset}$ from the value of bulk LSCO having the same Sr contents. Lines are drawn to aid the eyes.

thickness ~40 μm) grown on LCZO and LSCZO substrates. Although the R(T) shows $T_{c,\,onset}$ like behavior and metallic characteristics below that, the resistance doesn't go to zero even at low temperatures.

On the other hand, LSCO (~0.1) films grown on LBCO (0.113) and LSCO (~0.186) substrates show the increase of T_c significantly. The results are summarized and explained through Fig. 3. We find that LCZO and LSCZO lattices have small c/a ratio than the films grown on them. This clearly is responsible for the epitaxial strain on the films and the suppression of T_c. LSCO (~0.11) films on LBCO and LSCO (0.186) substrates show T_c to increase by about 4.9 K and 7.1 K, respectively (Fig. 3) compared to the values of their bulk counterpart having the same Sr content. With higher c/a ratio in LSCO (0.186) from LBCO the ΔT_c was also found to decrease to 3.7 K from 6.6 K for films grown on LBCO.

The films grown on LSCAO substrates failed to show the superconducting property (Fig. 3). Compositional analysis by EPMA shows that Al was easily contaminated and a non-supeconducting phase containing Al has developed by the reaction with the film. Contamination of Al from the substrate was common, similar to a previous report showing formation of $La_{1-x}Sr_xAl_{1-y}Cu_yO_3$ phase during LPE growth. Films growth on LSAO substrates was proved to be difficult since LSAO is transparent and difficult to heat up using infrared heaters. LSAO substrate was reported to be the most effective to enhance T_c in LSCO films by MBE technique [2, 6]. But it turned out to be unusable in our IR-LPE technique.

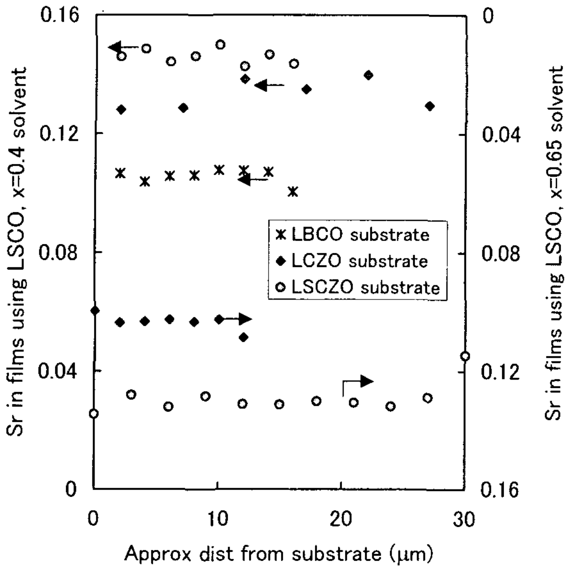

Fig. 4. The Sr content in LSCO film grown on LCZO and LSCZO substrates using solvents of two different compositions: LSCO with x = 0.4 (85 mol%CuO) (primary y-axis) and LSCO with x = 0.65 (85 mol%CuO) (secondary y-axis). Values in secondary y-axis were plotted in reverse order to separate from primary y-axis data.

If we compare the substrates used in our work with those in Locquet *et al.*, we observed that we have successfully suppressed T_c in films using a smaller lattice mismatch [~0.0107 Å for LCZO compare to ~0.1218 Å for STO with LSCO (0.1)]. Strong epitaxial compressive strain along the c-axis (or tensile along the a-axis) is responsible for the buckling of CuO_6 octahedra and consequently suppression of T_c. T_c is completely suppressed when the CuO_6 buckling crosses a critical angle leading to the non-superconducting LTT phase. However other reports show that the LSCO structure having the non-superconducting LTT phase is actually a stable phase [7]. It can be assumed that the suitably smaller lattice mismatch induced during the film growth led to a more stable growth of the LSCO in the LTT phase. So, although the MBE growth of LSCO on LSAO and STO substrates puts an upper limit on the film thickness (10-15nm), in case of IR-LPE growth, the use of substrates having smaller lattice mismatch had extended the effect of epitaxial strain effectively and efficiently to several micrometers.

Figure 4 shows the results of EPMA measurement of the Sr contents in the films grown on LBCO, LCZO and LSCZO substrates. Figure 4 shows the Sr contents in films grown on all substrates using LSCO, x = 0.4 solvent in the primary y-axis and using LSCO, x = 0.65 solvent in the secondary y-axis. In both cases the solvents were high in CuO (85 mol%). We observe that despite the same composition of solvent the Sr content is higher in film on LSCZO substrate. We think that extra Sr in LSCZO had enhanced the lattice matching between the substrates and the film compared to LCZO and LBCO substrates. Higher epitaxial strain by LCZO and LBCO substrates discouraged Sr doping to the film somewhat. This could be the reason for relatively higher Sr contents in films grown on LSCZO substrates under ideal condition.

4. Conclusion

In the present work we have grown LSCO single crystalline films on several different substrates using IR-LPE technique. Using the epitaxial strain due to the lattice mismatch of different substrates we have succeeded to completely suppress T_c (using LCZO substrate) in LSCO (0.135) and enhance T_c by 7 K [using LSCO (0.186) substrate] in LSCO (~0.11) films. We found IR-LPE technique of film growth to be an effective way to apply higher epitaxial strain on LSCO films using small lattice mismatches. Two possible reasons are (1) IR-LPE technique is operated in much higher temperatures near thermoequilibrium conditions and (2) our films are grown on (100) plane of the substrate rather than the (001) plane as done in other works [2, 8], which in turn made the epitaxial stress more effective. We also observed that closer lattice matching between films and substrates enrich the Sr-content in film grown under the identical conditions.

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