Phase control of La$_2$CuO$_4$ in thin-film synthesis

A. Tsukada
Department of Physics, Science University of Tokyo,
1-3, Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

T. Greibe
NTT Basic Research Laboratories, NTT Corporation,
3-1, Morinosato-Wakamiya, Atsugi-shi, Kanagawa 243-0198, Japan

M. Naito
NTT Basic Research Laboratories, NTT Corporation,
3-1, Morinosato-Wakamiya, Atsugi-shi, Kanagawa 243-0198, Japan

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The lanthanum copper oxide, La$_2$CuO$_4$, which is an end member of the prototype high-$T_c$ superconductors (La,Sr)$_2$CuO$_4$ and (La,Ba)$_2$CuO$_4$, crystallizes in the “K$_2$NiF$_4$” structure in high-temperature bulk synthesis. The crystal chemistry, however, predicts that La$_2$CuO$_4$ is at the borderline of the K$_2$NiF$_4$ stability and that it can crystallize in the Nd$_2$CuO$_4$ structure at low synthesis temperatures. In this article we demonstrate that low-temperature thin-film synthesis actually crystallizes La$_2$CuO$_4$ in the Nd$_2$CuO$_4$ structure. We also show that the phase control of “K$_2$NiF$_4$”-type La$_2$CuO$_4$ versus “Nd$_2$CuO$_4$”-type La$_2$CuO$_4$ can be achieved by varying the synthesis temperature and using different substrates.

I. INTRODUCTION

The rare earth copper oxides of the general chemical formula RE$_2$CuO$_4$ take two different crystal structures: K$_2$NiF$_4$ (abbreviated as “T”) and Nd$_2$CuO$_4$ (“T’”). The structural difference between T and T’ can be viewed simply as the difference in the RE-O arrangements: rock-salt-like versus fluorite-like. With regard to the Cu-O coordination, however, there is a significant difference: T has octahedral CuO$_6$, whereas T’ has two-dimensional square-planar CuO$_4$. Empirically, the former accepts only hole doping, the latter only electron doping. The T structure is formed with large La$^{3+}$ ions, while the T’ structure is formed with smaller RE$^{3+}$ ions, such as RE = Pr, Nd, Sm, Eu, and Gd. The T-T’ boundary lies between La$^{3+}$ and Pr$^{3+}$. Namely, La$_2$CuO$_4$ is at the borderline of the T-phase stability.

The crystal chemistry of the rare earth copper oxides has been explained in terms of the crystallographic tolerance factor (\(t\)) which is defined as

\[
t = \frac{r_i(\text{RE}^{3+}) + r_i(\text{O}^{2-})}{\sqrt{2 \times \{r_i(\text{Cu}^{2+}) + r_i(\text{O}^{2-})\}}}
\]

where \(r_i(\text{RE}^{3+})\), \(r_i(\text{Cu}^{2+})\), and \(r_i(\text{O}^{2-})\) are the ionic radii for RE$^{3+}$, Cu$^{2+}$, and O$^{2-}$ ions. The \(t\) values for La$_2$CuO$_4$ and Pr$_2$CuO$_4$ are evaluated as 0.8685 and 0.8562 using the room-temperature ionic radii by Shannon and Prewitt. From the extensive data collected for a variety of RE$_2$CuO$_4$-type cuprates, the critical (room-temperature) value for the T → T’ transition is presumed to be \(t_c = 0.865\), below which T is unstable.

The different thermal expansion (“thermal-expansion mismatch”) between the RE-O and Cu-O bond lengths plays an important role in the T-versus-T’ stability as pointed out initially by Manthiram and Goodenough. The “ionic” RE-O bond has a larger thermal expansion than the “covalent” Cu-O bond, which leads to the increase in \(t\) with increasing temperature. Hence the T phase is stable at high temperatures whereas the T’ phase is stable at low temperatures. In the case of La$_2$CuO$_4$, the transition from T to T’ is predicted to occur at around 700 K (427°C), where \(t(700\ K) \sim 0.88\). There have been a few attempts to stabilize the T’ phase of La$_2$CuO$_4$ in the past. However, a conventional solid-state reaction method requires firing temperature of at least 500°C even with coprecipitated fine powders, so it could not produce single-phase T’-La$_2$CuO$_4$. Bulk synthesis of T’-La$_2$CuO$_4$ has been achieved only by a very special recipe as given by Chou \textit{et al.} Their recipe consists of the following two steps. The first step is to reduce T-La$_2$CuO$_4$ with hydrogen around 300°C and obtain the Sr$_2$CuO$_3$-like phase. The second step is to convert the Sr$_2$CuO$_3$-like phase to T’-La$_2$CuO$_4$ by reoxygenation below 400°C. The resultant product was the single-phase T’, although x-ray peaks were broadened due to the considerable lattice disorder and defects.

In thin-film synthesis, the reaction temperature can be lowered significantly, since reactants are much smaller in size and also more reactive than in bulk synthesis. The reactants in thin-film synthesis are atoms or molecules
or ions or clusters, depending on the technique employed. The limiting case is achieved by reactive coevaporation from metal sources, in which the reactants are atoms and the oxidation reaction is initiated on a substrate. Using this reactive coevaporation technique, we have learned from our ten-year experience that cuprate films crystallize at temperatures as low as 400°C. This enabled us to synthesize single-phase T'-La$_2$CuO$_4$. In this article we describe the phase control of “K$_2$NiF$_4$”-type La$_2$CuO$_4$ versus “Nd$_2$CuO$_4$”-type La$_2$CuO$_4$ by varying the synthesis temperature and using different substrates.

II. EXPERIMENT

We grew La$_2$CuO$_4$ thin films in a customer-designed MBE chamber from metal sources using multiple electron-gun evaporators with accurate stoichiometry control of the atomic beam fluxes. During growth, RF activated atomic oxygen was used for oxidation. The chamber pressure during growth was 6 × 10$^{-6}$ Torr. The substrate temperature was varied from 425°C to 725°C. The growth rate was ∼ 1.5 Å/s, and the film thickness was typically 450 Å. After the evaporation, most of the films were cooled to temperatures lower than 200°C at a rate lower than 20°C/min in 1 × 10$^{-5}$ Torr molecular oxygen to avoid phase decomposition. Some of the films were cooled in vacuum or in ozone to investigate the change of the transport properties by excess oxygen.

In order to examine the substrate influence on the selective phase stabilization, we used various substrates as listed in Table 1. The in-plane lattice constant ($a_0$) covers from 3.6 Å to 4.2 Å, which should be compared to $a_0$ = 3.803 Å for T-La$_2$CuO$_4$ and $a_0$ = 4.000 - 4.010 Å for T'-La$_2$CuO$_4$ (T-La$_2$CuO$_4$ has orthorhombic structure with $a' = 5.3574$ Å and $b' = 5.4005$ Å, and $a_0$ is calculated as $\sqrt{(a' \times b')/2}$). The crystal structures include perovskite, K$_2$NiF$_4$, NaCl, and CaF$_2$ (fluorite). We deposited films simultaneously on all the substrates listed in Table 1, which were pasted to one substrate holder by Ag paint. This avoids run-to-run variations.

The lattice parameters and crystal structures of the films were determined using a standard x-ray diffractometer. Resistivity was measured by the standard four-probe method using electrodes formed by Ag evaporation.

III. RESULTS AND DISCUSSION

A. Effect of synthesis temperature on the selective phase stabilization

Figure 1 shows the x-ray diffraction (XRD) patterns of La$_2$CuO$_4$ films grown on NdCaAlO$_4$ (NCAO) substrates with different synthesis temperatures ($T_s$). Since the c-axis lattice constant ($c_0$) is distinct between T and T' ($c_0(T) = 13.15$ Å versus $c_0(T') = 12.55$ Å), the phase identification is rather straightforward. The calculated patterns for T and T' are also included in Fig. 1. The films grown at $T_s > 625°C$ are single-phase T, while the films grown at $T_s = 500 - 550°C$ are single-phase T'. The films grown at $T_s = 575 - 600°C$ are a two-phase mixture of T and T' with T' more dominant for lower $T_s$. The films grown below $T_s = 475°C$ show unidentified peaks at 2θ $\sim$ 31.4° and 65.5°. From this result, we can see the following trend for synthesis temperature on the selective phase stabilization. High $T_s$ stabilizes T and low $T_s$ stabilizes T'.

B. Effect of substrates on the selective phase stabilization

Figure 2 shows the XRD patterns of La$_2$CuO$_4$ films grown at $T_s = 525°C$ on different substrates. Of these films in this figure, the films on KTaO$_3$ (KTO), NCAO, and ZrO$_2$(Y) (YSZ) are single-phase T, while the films on LaSrGaO$_4$ (LSGO), LaAlO$_3$ (LAO), LaSrAlO$_4$ (LSAO), PrSrAlO$_4$ (PSAO), and NdSrAlO$_4$ (NSAO) are single-phase T. On YAlO$_3$, the film is dominantly T' with a trace amount of T. On SrTiO$_3$ (STO) and NdGaO$_3$ (NGO), the films are clearly a mixture of T and T'. The film on STO contains some amount of the T'-like (!) phase. On MgO (MGO), no clear peak is observed. The $c_0$ values of these films together with films on other substrates are summarized in Fig. 3. Because of epitaxial strain, $c_0$ of the T structure is noticeably substrate-dependent: the longest ($c_0 = 13.25$ Å) for LSAO and the shortest ($c_0 = 13.05$ Å) for LSGO. From these results, we can see the following trend for a substrate lattice parameter on the selective phase stabilization. Substrates with $a_0$ of 3.70 - 3.85 Å stabilize T, and substrates with $a_0$ of > 3.90 Å or < 3.70 Å stabilize T' (or destabilize T).

Next we mention the effect of substrate crystalline structure on the selective phase stabilization. If, in Fig. 2, one compares the films grown on perovskite and K$_2$NiF$_4$-type substrates with almost the same $a_0$, for example, NGO ($a_0 = 3.838$ Å) vs LSGO ($a_0 = 3.843$ Å) or YAO ($a_0 = 3.715$ Å) vs NSAO ($a_0 = 3.712$ Å), one can notice the trend that K$_2$NiF$_4$-type substrates have a tendency to stabilize the T structure rather than the T' structure.
C. Phase diagram in the $T_s$-$a_s$ plane

Our survey was performed at $T_s$ from 425$^\circ$C to 725$^\circ$C on all substrates in Table 1. Figure 4 summarizes the results, which show the phase diagram on the selective stabilization of $T$ versus $T'$ in the $T_s$-$a_s$ plane.

High $T_s$ ($625 \sim 725^\circ$C)

The films on most of the substrates are single-phase $T$. There are three exceptional substrates: KTO, YAO, and YSZ. The films on KTO and YSZ do not show any definite x-ray peak. The film on YAO is a mixture of $T$ and $T'$ even at the highest temperature investigated. This can be explained by interdiffusion of Y from YAO substrates into La$_2$CuO$_4$ since Y substitution for La is known to stabilize the $T'$ structure.

Low $T_s$ ($450 \sim 600^\circ$C)

The films on the $T$-lattice matched substrates (LSGO, LAO, LSAO, PSAO, and NSAO) are single-phase $T$. The films on $T'$-lattice matched KTO and on fluorite YSZ are single-phase $T'$. The films on other substrates (STO, NGO, YAO, and NCAO) are a two-phase mixture of $T$ and $T'$ with $T'$ more dominant for lower $T_s$.

D. Comparison of $T$-La$_2$CuO$_4$ and $T'$-La$_2$CuO$_4$

Next, we make a brief comparison of the physical properties of $T$-La$_2$CuO$_4$ and $T'$-La$_2$CuO$_4$, which have the same chemical formula but different crystal structures. Figure 5 shows the temperature dependences of resistivity for both the phases. The solid lines represent the $\rho$-$T$ curves for the films cooled in vacuum to ambient temperature, which do not have excess oxygen but might have slight oxygen deficiencies (La$_2$CuO$_{4+\delta}$ with $\delta \sim 0$). The broken lines represent those for the films cooled in ozone, which have interstitial excess oxygen ($\delta > 0$). The excess oxygen occupies the tetrahedral site in $T$, and the apical site in $T'$. The vacuum-cooled $T$ film has much higher resistivity (by several orders of magnitudes at low temperatures) than the vacuum-cooled $T'$ film. In fact, $T'$-La$_2$CuO$_4$ is metallic down to 180 K. The ozone cooling causes a totally opposite effect on $T$ and $T'$. The resistivity of the $T$ film gets lowered by five orders of magnitudes at room temperature from $\sim 50 \, \Omega \cdot \text{cm}$ to $\sim 5 \times 10^{-4} \, \Omega \cdot \text{cm}$, indicating that holes doped by excess oxygen are itinerant. Furthermore the film becomes superconducting. In contrast, the resistivity of the $T'$ film increases, indicating that holes doped by excess oxygen are localized.

IV. SUMMARY

In summary, we have demonstrated that La$_2$CuO$_4$ can crystallize in the Nd$_2$CuO$_4$ structure using low-temperature thin-film synthesis. Furthermore the phase control of “K$_2$NiF$_4$”-type La$_2$CuO$_4$ versus “Nd$_2$CuO$_4$”-type La$_2$CuO$_4$ can be achieved by varying the synthesis temperature and also the substrate. The general trends are as follows: (i) high $T_s$ stabilizes $T$ and low $T_s$ stabilizes $T'$, (ii) substrates with $a_s \sim 3.70 - 3.85 \, \text{Å}$ stabilize $T$ and substrates with $a_s > 3.90 \, \text{Å}$ or $a_s < 3.70 \, \text{Å}$ stabilize $T'$ (or destabilize $T$), and (iii) K$_2$NiF$_4$-type substrates stabilize $T$.

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* Electronic address: tsukada@with.brl.ntt.co.jp
† On leave from Technical University of Denmark.
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TABLE I: Crystal structure and a-axis lattice constant ($a_s$) for the substrates used in this work. The in-plane lattice constants ($a_0$) for T'-La$_2$CuO$_4$ and T-La$_2$CuO$_4$ are also included.

| Substrate Abbreviation | $a_s$ or $a_0$ (Å) | Crystal structure |
|------------------------|-------------------|-------------------|
| MgO (100)              | MGO               | 4.212             | NaCl             |
| KTaO$_3$ (100)         | KTO               | 3.989             | perovskite       |
| SrTiO$_3$ (100)        | STO               | 3.905             | perovskite       |
| LaSrGaO$_4$ (001)      | LSGO              | 3.843             | K$_2$NiF$_4$     |
| NdGaO$_3$ (100)        | NGO               | 3.838             | perovskite       |
| LaAlO$_3$ (100)        | LAO               | 3.793             | perovskite       |
| LaSrAlO$_4$ (001)      | LSAO              | 3.755             | K$_2$NiF$_4$     |
| PrSrAlO$_4$ (001)      | PSAO              | 3.727             | K$_2$NiF$_4$     |
| YAlO$_3$ (100)         | YAO               | 3.715             | perovskite       |
| NdSrAlO$_4$ (001)      | NSAO              | 3.712             | K$_2$NiF$_4$     |
| NdCaAlO$_4$ (001)      | NCAO              | 3.688             | K$_2$NiF$_4$     |
| ZrO$_2$ (Y) (100)      | YSZ               | 3.616             | fluorite         |
| T'-La$_2$CuO$_4$       |                   | 4.005             | Nd$_2$CuO$_4$    |
| T-La$_2$CuO$_4$        |                   | 3.803             | K$_2$NiF$_4$     |

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FIG. 1: XRD patterns for La$_2$CuO$_4$ films grown on NCAO substrates at $T_s = 725 - 425$°C. The top two patterns are simulations for the T and $T'$ structure. The broken and dotted lines indicate the peak positions of the (008) line for the T and $T'$ structure, respectively. Peak positions of NCAO are indicated in the lowest figure.
FIG. 2: XRD patterns for La$_2$CuO$_4$ films grown on various substrates at $T_s = 525^\circ$C. The top two patterns are simulations for the T and T' structure. Substrate peaks are removed. The broken and dotted lines indicate the peak positions of the (008) line for the T and T' structure, respectively.
FIG. 3: Film’s $c_0$ versus substrates $a_s$ for La$_2$CuO$_4$ films grown at $T_s = 525^\circ$C on different substrates. The lattice constants of bulk T- and T’-La$_2$CuO$_4$ ($a_0 = 3.803$ Å, $c_0 = 13.15$ Å for T and $a_0 = 4.005$ Å, $c_0 = 12.55$ Å for T’) are indicated by arrows together with $a_s$ of the substrates. The circles connected by the vertical dotted lines indicate multi-phase formation. The $c_0$ values of the T structure is noticeably substrate-dependent because of epitaxial strain: the longest ($c_0 = 13.25$ Å) for LSAO and the shortest ($c_0 = 13.05$ Å) for LSGO. The $c_0$ value of 12.8 Å on STO seems to correspond to the T’-like phase.
FIG. 4: Phase diagram on the selective stabilization of T versus T’ in the $T_s - a_s$ plane. The crosses indicate no phase formation. The open circles represent single-phase T while the filled circles represent single-phase T’. The partially filled circles represent a two-phase mixture. The size (area) of the circles is proportional to the XRD peak intensities of the (006) lines. For two-phase mixed films, the ratio of the unshaded and the shaded areas represent the ratio of the T and T’ peak intensity of the (006) line. The results on LSGO and NSAO substrates are not included to avoid overlapping with the results on NGO and YAO. On LSGO and NSAO, the T structure is formed for $725^\circ C > T_s > 475^\circ C$, and the T’ structure is not formed for any $T_s$. The gray area at $a_s = 3.905 \text{ Å} \text{ (STO)}$ indicate the formation of the T*-like phase.
FIG. 5: Comparison of resistivity ($\rho$) - temperature ($T$) curves between T-La$_2$CuO$_{4+\delta}$ and T'-La$_2$CuO$_{4+\delta}$ films. The solid lines are for films cooled in vacuum ($\delta \sim 0$) while the broken lines are for films cooled in ozone ($\delta > 0$). With vacuum cooling, the T film has much higher resistivity than the T' film. Ozone cooling causes a totally opposite effect on T and T': the T film gets metallic and superconducting whereas the T' film gets more insulating.