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BRIEF COMMUNICATION

Growth of Thin Films of the Defect Perovskite $LaCuO_{3-\delta}$ by Pulsed Laser Deposition

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Oriented thin films of the defect perovskite $LaCuO_{3-\delta}$ (LCO) have been grown on (100) $SrTiO_3$ substrates by pulsed laser deposition. The orthorhombic, oxygen-deficient $La_2Cu_2O_5$ ($\delta = 0.5$) phase, which is the end-member of the perovskite series, is formed at a growth temperature of 700°C under 200 mTorr background O_2 pressure. With additional oxygen uptake during cooldown, the orthorhombic phase can be easily converted to the monoclinic modification ($\delta \leq 0.4$). The more highly oxygenated tetragonal phase ($\delta \leq 0.2$) is, however, not obtained for background O_2 pressures up to 760 Torr. Partial conversion to the tetragonal phase has been achieved by postannealing the films at 600–650°C under high oxygen pressure (450 bar). From resistivity measurements, a distinct insulator-metal transition is observed in going from the orthorhombic to the monoclinic structure, with postannealed films containing the mixed tetragonal and monoclinic phases showing the lowest resistivity. However, no evidence of superconductivity has been detected in any of the films down to 5 K.

1. INTRODUCTION

In recent years, the pulsed laser deposition (PLD) technique has been receiving much attention as a viable method for the deposition of thin films of a wide variety of materials (1). The stoichiometric ablation of constituent species from the target, as well as the process simplicity, makes the PLD technique particularly attractive for the synthesis of complex multicomponent phases like the high T_c copper oxide superconductors. Furthermore, the nonequilibrium nature of the ablation process offers the opportunity to synthesize interesting metastable copper oxide structures at low growth temperatures, which would be difficult or impossible to synthesize by conventional solid-state methods. For example, Fincher and Blanchet (2) have recently succeeded in growing phase-pure Ce and Tb-substituted $YBa_2Cu_3O_{7-\delta}$ superconducting thin film by PLD. Bulk synthesis of these phases by conventional solid-state reactions have not been successful. Similarly, epitaxial films of the tetragonal infinite-layer compounds, $Ca_{1-x}Sr_xCuO_2$ ($0.18 \leq x \leq 1$), have been grown at low temperatures using PLD (3). Although these compounds have also been prepared in the bulk, they require extreme temperature and pressure conditions for synthesis.

Herein, we report on the synthesis of oriented thin films of the defect perovskite series $LaCuO_{3-\delta}$ (LCO) on $SrTiO_3$ substrates by PLD under subatmospheric pressure conditions. This series of compounds is closely related to the superconducting cuprates, with a wide oxygen stoichiometry range ($0.0 \leq \delta \leq 0.5$) (4). Thus, by controlling the oxygen content, the formal oxidation state of copper can be continuously varied from +2 to +3 while maintaining the basic perovskite framework. The bulk synthesis of the oxygen-deficient perovskite series was recently reported by Bringley *et al.* under O_2 pressures of 0.2–1 kbar using coprecipitated La and Cu hydroxide precursors (4). Earlier Demazeau *et al.* (5), and Webb *et al.* (6), had reported on the preparation of a rhomohedrally distorted perovskite, $LaCuO_3$, at elevated temperatures (900–1500°C) and pressures (65 kbar), using oxide precursors and $KClO_3$ as an oxygen buffer. We have taken advantage of the epitaxial lattice match of LCO ($\delta \sim 0.5$) with the cubic perovskite $SrTiO_3$ substrate (3.905 Å) to enforce growth of this metastable phase under a low pressure O_2 ambient.

2. EXPERIMENTAL

The basic experimental system for pulsed laser deposition has been described in detail previously (7). Briefly, a high-density, sintered pellet with La : Cu stoichiometry of 1 : 1 was used as a target for ablation. The pellet was prepared by compaction and sintering of the powder obtained by decomposing and reacting the precursor nitrates at 1050°C in air. This preparative route does not produce the LCO phase, and the pellet consisted predominantly of a homogeneous mixture of La_2CuO_4 and CuO. For the

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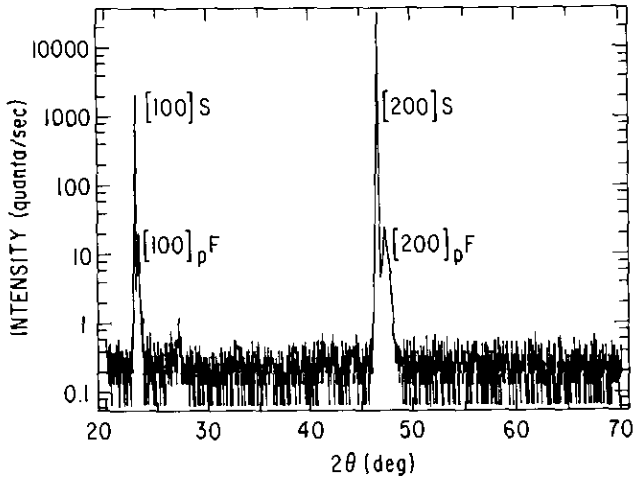

FIG. 1. X-ray diffraction θ–2θ scan of a LCO film prepared by cooling in 760 Torr O_2, with the probing direction perpendicular to the film surface. The substrate reflections are denoted by S.

deposition process, the third harmonic beam of a Nd-YAG laser (355 nm) was focused onto the target with a fluence of 1.5–2.0 J/cm^2, producing a plume of ablated species perpendicular to the target surface. The films were deposited on optically polished (100) $SrTiO_3$ substrates, which were glued with silver paint to a stainless steel heater block to ensure good thermal contact. The target-to-substrate distance was 5 cm. The heater block temperature was varied between 600–750°C for different runs (henceforth referred to as the deposition temperature), with most of the films being deposited at a temperature of 700°C. All film deposition was performed in an ambient of 200 m Torr of O_2. Following deposition, the films were slowly cooled down to room temperature in different O_2 pressures ($\leq 10^{-6}$–760 Torr) to control the oxygen stoichiometry of the film. The deposition rate under our growth conditions was ~0.35 Å/pulse, with most of the films being ~3000 Å thick. Some of the films were postannealed at temperatures of 600–650°C in a high-pressure oxygen vessel pressurized up to 450 bar. The films were electrically characterized using four-probe dc transport measurements, for which they were patterned using a laser-microscope system to form 50–100 μm wide and 200 μm long microbridges. High resolution X-ray diffraction in the normal Bragg mode using Cu*K*α radiation, and cross-sectional TEM were used for structural characterization of the films.

3. RESULTS AND DISCUSSION

LCO films deposited in the temperature range of 650–750°C were shiny and had a very smooth surface morphology. X-ray diffraction pattern of a film deposited at 750°C and then slow cooled in 760 Torr of O_2 is shown in Fig. 1. Besides the substrate's reflections, the major peaks in the pattern can be indexed as the (100) and (200) reflections of the basic perovskite block with a lattice parameter of 3.845 Å. This indicates a strong preferred orientation, with one or more axes of the perovskite subcell aligned normal to the plane of the film. In order to investigate the structural transformation occurring due to oxygen uptake after deposition, we have monitored the shifts in the positions of the first- and second-order diffraction peaks as a function of the O_2 pressure during cooldown, as shown in Fig. 2. The peak positions for the films cooled under low O_2 pressures ($\lesssim$2 Torr), matches closely with the (120) and (240) supercell reflections of the orthorhombic phase, corresponding to a *d* spacing value of ~3.80 Å. At high O_2 pressures ($\gtrsim$100 Torr), the two peaks shift to lower angles, which match with the closely spaced $(2\bar{1}0)$, (120), and (001) supercell reflections, and the corresponding second-order reflections, respectively, of the monoclinic phase. Note that for intermediate O_2 pressures (~2–100 Torr), peaks corresponding to both the orthorhombic and monoclinic phases are observed. A similar two-phase region has been observed in bulk ceramic samples (4). The preferential growth of the initial orthorhombic phase with the (120)-axis normal to the substrate (corresponding to (100)-normal orientation of the basic perovskite block) is to be expected, since this orientation provides the best in-plane lattice match of the film to the substrate surface.

Figure 3 shows a TEM cross-section of a crystalline LCO film deposited on (100) $SrTiO_3$. The corresponding diffraction pattern is shown below. The film was prepared by cooling in 760 Torr O_2. All the reflections in the diffraction pattern can be indexed on the basis of the monoclinic structure. A large fraction of the film has axes of the

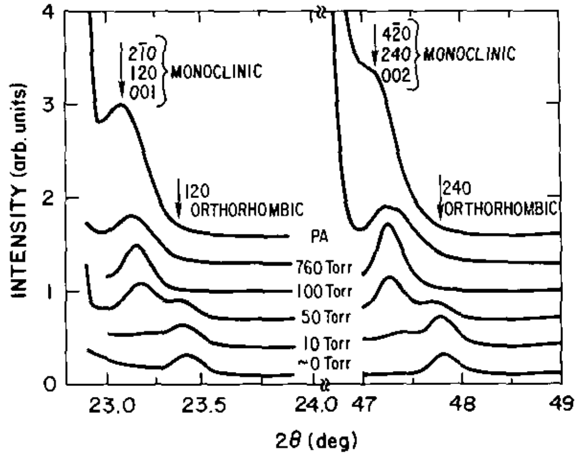

FIG. 2. X-ray diffraction θ–2θ scans in the range of the first- and second-order peaks of LCO films cooled under different oxygen pressures. All the films were deposited at 700°C. The diffraction scan marked PA corresponds to the film cooled under 100 Torr O_2 which has been subsequently postannealed at 650°C for 30 min in 450 bar O_2.

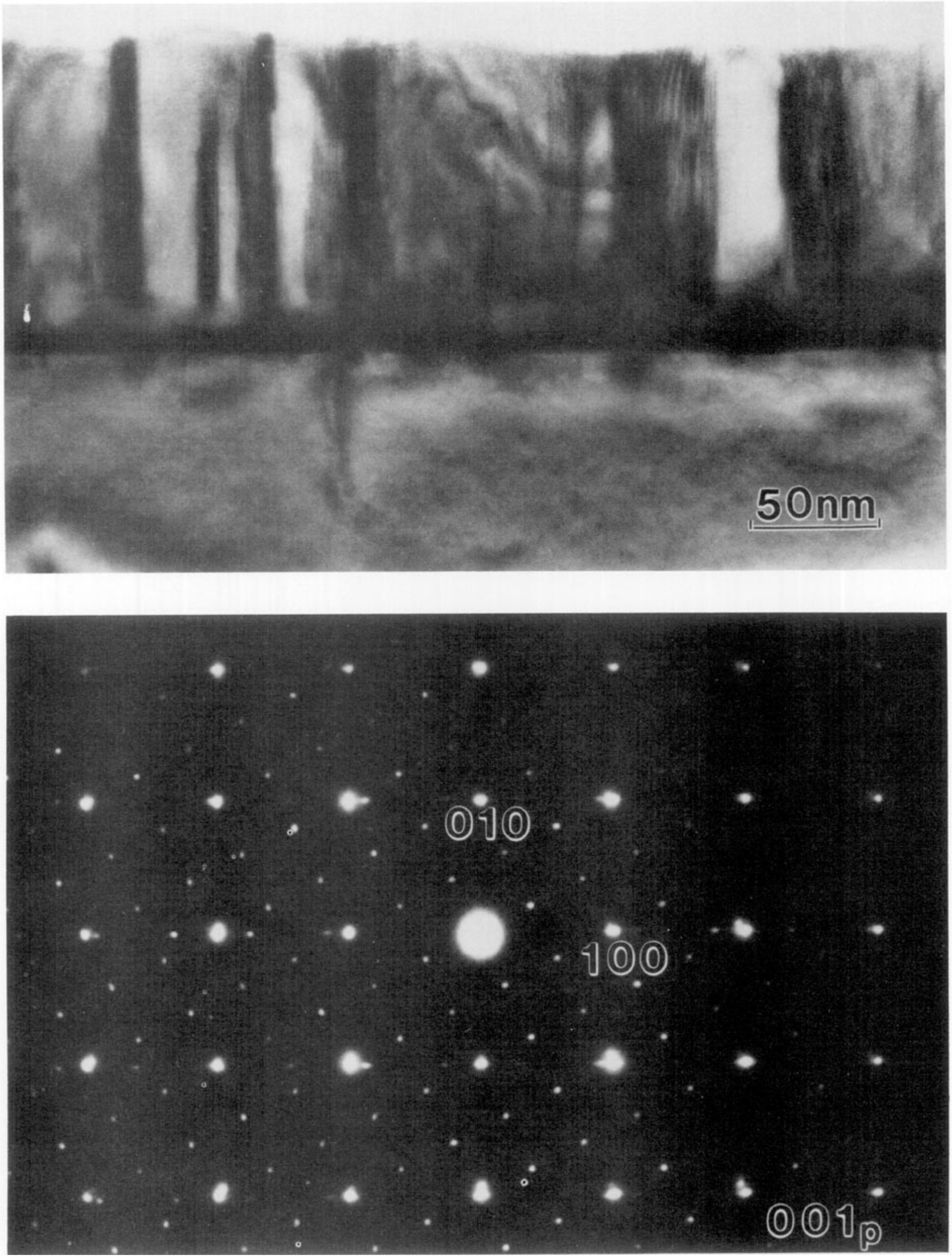

FIG. 3. Cross-section TEM micrograph and electron diffraction pattern of a 1500 Å thick LCO film prepared by cooling in 760 Torr O_2.

perovskite subcell of the monoclinic structure aligned with the cube axes of the underlying $SrTiO_3$ substrate. Several different variants of the monoclinic structure form in the cube oriented regions of the film, with the *c*-axis either in the plane of the substrate, or perpendicular to it. This is consistent with the x-ray results discussed earlier. Some regions of the film, however, also contain columnar grains with a second basic orientation relationship with the substrate. These appear as the dark grains in Fig. 3, and give rise to the horizontal streaked diffraction spots in the diffraction pattern. The spots in the diffraction pattern are best indexed as arising from grains that have an orientation in which the ⟨111⟩ direction in the monoclinic structure is aligned with the cube axes of the substrate and the ⟨112⟩ direction is normal to the substrate. It is possible that grains of the other perovskite structures identified in this system are present in the films, but the similarity of their perovskite cell dimensions makes it difficult to distinguish them unambiguously from the monoclinic structure. It should, however, be pointed out that aside from LCO, there was no evidence of any of the other La–Cu–O phases, including the more complex monoclinic $La_2Cu_2O_5$ phase recently reported by Cava *et al.* (8) as the $n = 2$ member of a new homologous series $La_{4+4n}Cu_{8+2n}O_{14+8n}$.

In order to introduce additional oxygen in the structure to form the tetragonal phase ($\delta \leq 0.2$), the as-deposited films were annealed at 600–650°C for 30 min in an oxygen atmosphere of 300–450 bar. No changes in the X-ray diffraction patterns were observed for the films annealed at temperatures below 550°C, whereas film peeling and/or surface damage was observed at higher temperatures and pressures. For the above annealing conditions, films containing the orthorhombic or mixed orthorhombic–monoclinic phases were converted completely to the monoclinic phase, as evidenced by the shifts in the positions of the first-order and second-order diffraction peaks to lower angles. A shift in the diffraction peaks to somewhat lower angles was also observed after anneal for the films originally containing only the monoclinic phase, as shown in Fig. 2. Additional low-intensity peaks at $2\theta = 22.2$ and 45.3° (not shown in the figure) were also observed in these films. These peaks can be indexed as the (001) and (002) reflections, respectively, of the tetragonal phase. Further annealing of the films for up to 180 min did not help in increasing the fraction of the tetragonal phase.

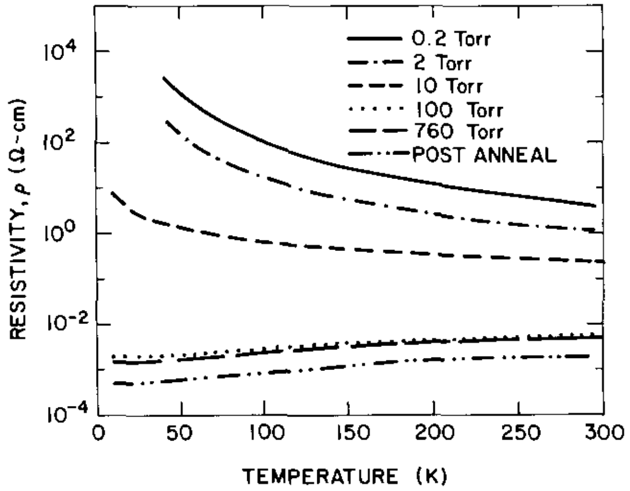

FIG. 4. Resistivity vs temperature of LCO films deposited at 700°C and cooled under different O_2 pressures. The corresponding X-ray diffraction patterns of the films are shown in Fig. 2.

Resistivity versus temperature results for films deposited in 200 mTorr O_2 at 700°C, and then cooled down slowly under different oxygen pressures, are displayed in Fig. 4. With increasing O_2 concentration during the cooldown cycle after deposition, there is a progressive drop in the room-temperature resistivity values. Moreover, there is a transition from insulating behavior for films cooled under low O_2 pressures, to a metallic behavior for films cooled under higher pressures. No evidence of superconductivity was observed in any of the films down to 5 K. The insulator–metal transition occurs at the orthorhombic–monoclinic phase boundary as seen from the corresponding X-ray data of the films in Fig. 2. This is consistent with the bulk measurements of Bringley *et al.* where an insulator–metal transition was also observed in going from the oxygen-deficient orthorhombic phase, with a homogeneity range between $0.43 \leq \delta \leq 0.5$, to the monoclinic and tetragonal phases with higher oxygen content (4). The insulator–metal transition which occurs with oxygenation was also observed in the postannealed films. The resistivity decreased with increasing oxygen content, with the film containing the mixed tetragonal and monoclinic phases exhibiting the lowest resistivity as shown in Fig. 4.

Thermodynamic calculations by Dwivedi *et al.* (9) suggest that the formation of the La_2CuO_4 phase is energetically much more favorable than that of $LaCuO_3$. The latter is in fact thermodynamically unstable under normal conditions due to the difficulty in oxidizing the Cu^{2+} ions to Cu^{3+}. Remarkably, the reduction in free energy achieved from the growth of the film with preferential orientation on the substrate is sufficient to permit stabilization of the metastable LCO phase with respect to a 1 : 1 mixture of La_2CuO_4 and CuO. Under our growth conditions, the oxygen activity is sufficiently low that $LaCuO_3$ is not formed. Instead, the orthorhombic, oxygen-deficient $La_2Cu_2O_5$ phase ($\delta = 0.5$), where copper is in the +2 valence state, is stabilized at the growth temperature. This is in contrast to the synthesis in the bulk, where the tetragonal $LaCuO_3$ is stabilized at high oxygen pressures and the orthorhombic $La_2Cu_2O_5$ phase can be obtained only by deoxygenation of the tetragonal form. The orthorhombic LCO thin films grown by the PLD can be readily converted to the intermediate monoclinic phase with additional uptake of oxygen during the cool-down cycle. However, further oxygenation to form the tetragonal phase is not easily accomplished, even when the films are postannealed under relatively high oxygen pressure. This suggests that there is a substantial activation barrier for the introduction of additional oxygen in the structure beyond the monoclinic phase, perhaps because of the preferential growth orientation of the original oxygen-deficient phase which serves to restrict the movement of the cations necessary for the phase transformation.

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