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Stabilization of Sr-rich ultrathin epitaxial films of $La_{2-x}Sr_xCuO_4$

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ABSTRACT

Varying the level of Sr in $La_{2-x}Sr_xCuO_4$ produces a wide array of electrical properties, spanning metallic, semiconducting, insulating, and superconducting. While the system has been extensively studied, ultrathin films with high Sr content have not been reported. Using oxide molecular beam epitaxy, ultrathin $La_{2-x}Sr_xCuO_4$ films ($0 < x < 1$) were grown to explore the ability to stabilize high Sr content in such films. The resulting crystallinity, surface roughness, and electrical properties of the samples are studied. The films are single crystalline with low surface roughness. Increasing the Sr content from $x = 0$ to $x = 1.0$ causes an initial increase and subsequent decrease in the c-axis lattice parameter and the surface roughness as a function of doping. The films exhibit analogous electrical properties to their bulk and thicker film counterparts. The ability to create ultrathin $La_{2-x}Sr_xCuO_4$ films at high Sr levels shows promise for inducing unexpected electric properties through dopant modulation effects, such as cation ordering, digital superlattices, and atomically precise interfaces.

1. Introduction

The relationship in cuprate oxides of how the structure and properties change as a function of doping is of great interest in many fields. In particular, bulk studies of the classic cuprate, $La_{2-x}Sr_xCuO_4$ (LSCO), have shown that the system spans a wide range of electrical and ionic properties of interest for both basic physics studies and electrochemical applications, including superconductivity, solid oxide fuel cells, and catalysis [1–7]. For many of these studies and applications, it is desirable to stabilize these materials in thin film form.

Stabilizing oxides in thin or ultrathin film form can uncover properties not found in the analogous bulk oxides. For instance, nanoscale control in layered perovskite oxides (such as atomically precise interfaces [8], superlattices [9], and dopant cation ordering [10–12]) has revealed unexpected electrical phenomena, including enhanced superconducting transition temperatures, room temperature magnetoelectric multiferroics, and massive band gap changes. In these digital architectures, high doping levels allow for the ability to significantly modulate dopant cation placement or local concentration, providing the greatest potential to reveal new emergent properties. Thus, in order to explore many of these advanced film architectures in the LSCO system, one must first be able to stabilize smooth ultrathin LSCO films with high Sr doping levels.

There have been a number of previous studies on LSCO films grown by electron beam co-evaporation [13], reactive co-evaporation [14], molecular beam epitaxy [15–18], pulsed laser deposition, magnetron sputtering, metal organic chemical vapor deposition, and metal organic deposition [19–21]. However, the vast majority of studies have focused on the superconducting nature of this system, and thus have focused on films of low Sr content ($x < 0.35$).

Nevertheless, high Sr content LSCO films show promising properties, as well. At higher Sr values ($0.35 < x < 1.0$), LSCO exhibits metallic and semiconducting behavior, making these films of interest for a variety of energy applications, including solid oxide fuel cell cathodes, thermoelectrics, and catalysis. Moreover, for applications involving oxygen-mobility, high Sr doping of LSCO gives a different oxygen diffusion mechanism compared to conventional $La_2CuO_{4+\delta}$ (vacancy vs. interstitial, respectively) [5]. This allows for the possibility of not only tuning conventional electrical transport, but also tuning oxygen transport through heterostructuring. For all of these reasons, a more detailed exploration of the structure and properties of ultrathin (< 15 nm) cuprate oxide films at high Sr levels ($0.3 < x < 1.0$) is necessary.

In this report, we demonstrate the synthesis of high quality epitaxial ultrathin (< 15 nm) films of the LSCO system ($x = 0.0$–1.0). The films were grown using oxide molecular beam epitaxy (O-MBE) with 100% pure ozone and shuttered sources. The films exhibit excellent crystallinity and low surface roughness (< 2 nm). Upon increasing x, the c-axis lattice parameter first increases and then decreases, consistent with bulk samples. The films also exhibit electrical transport consistent with bulk samples and thicker films, including a $T_{C(onset)}$ at $x = 0.25$ of 18 K. The stabilization of highly-doped LSCO in ultrathin form opens the door

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to their exploration in dopant modulated heterostructures relevant to a variety of energy applications.

2. Experimental details

Thin films of LSCO were grown via oxide molecular beam epitaxy (O-MBE) in the Physics and Astronomy Department at the University of Minnesota (UMN). The films were heated, grown, and cooled in 100% pure ozone (background pressure $\sim 1 \times 10^{-3}$ Pa) to ensure full oxidization of the films. The $x = 0$ sample was cooled without ozone in order to minimize the effects of excess oxygen in the $x = 0$ composition. Pure sources of lanthanum (La), strontium (Sr), and copper (Cu) were used for the deposition, with source shutters controlled by a custom LabView program. A quartz crystal monitor was used to monitor the deposition rate of each source material both before and after the deposition. The former rate was used to determine the open shutter time for desired deposition, while the latter rate was used to evaluate any drift over the course of the deposition.

Samples were deposited layer by layer in the following sequence: $AO/BO_2/AO/AO/BO_2/AO$, where A corresponds to La or Sr, and B corresponds to Cu. Pauses of 15 s were introduced after the deposition of each Cu layer and before the deposition of the subsequent A layer. For samples with both La and Sr in the AO layers (i.e. $x > 0$), the La and Sr shutters were opened simultaneously for the calibrated amount of time to complete one monolayer of the desired composition. The approximate growth rate per unit cell was 2–3 min, depending on source rates. All films were grown to a thickness of 10 unit cells (20 formula units) on (001)-oriented $LaSrAlO_4$ substrates (a = b = 3.756 Å, c = 12.635 Å) [22]. Substrates were ultrasonically cleaned with acetone and isopropanol before loading into chamber. For each growth, the substrate heater set point was adjusted to obtain a reading of 575 °C on the thermocouple located behind the substrate. It is expected that the temperature of the substrate surface during growth was much higher than 575 °C.

Using a Panalytical X'Pert Diffractometer with Cu K_α radiation at the Characterization Facility at UMN, the crystallinity and lattice parameters of the films were characterized via X-ray diffraction (XRD) and the surface roughness and thickness of the films were characterized via X-ray reflectivity (XRR). Each film was examined from 2theta = 0.4–65°. The c-axis lattice parameter of each film was obtained by multiplying the calculated d-spacing of the 006 film peak by six. Atomic force microscopy (AFM) was performed using a Scanning Probe Microscope Bruker Nanoscope V Multimode 8 to assess surface roughness and morphology of the films. A root mean square (RMS) roughness value was obtained for each sample to determine the roughness of each film using Gwyddion software.

Transport properties of the films were characterized using the 4-pt probe technique in a modified Physical Property Measurement System (PPMS) at the Center for Nanoscale Materials at Argonne National Laboratory. Four electrical contacts of sputtered gold were applied to each sample and then wired to an electrical puck using a wire-bonder. Custom LabView programs were used to control the PPMS, which stepped the temperature down in 5 K steps from 300 K to 50 K, and then in 2 K steps from 50 K to 2 K, measuring the resistivity of the film at each step.

3. Results and discussion

Fig. 1 shows the X-ray diffraction data of the samples. The presence of the characteristic K_2NiO_4 structural peaks of (0 0 2n) indicates epitaxial growth of the films on the LSAO substrates. The presence of thickness fringes around the film peaks indicates the highly smooth nature of the ultrathin film surfaces. This is corroborated by simulation fits to the X-ray reflectivity data (Table 1), which also show low surface roughness values that are near or less than one unit cell in height. The simulated XRR thickness values verify the ultrathin nature of the films.

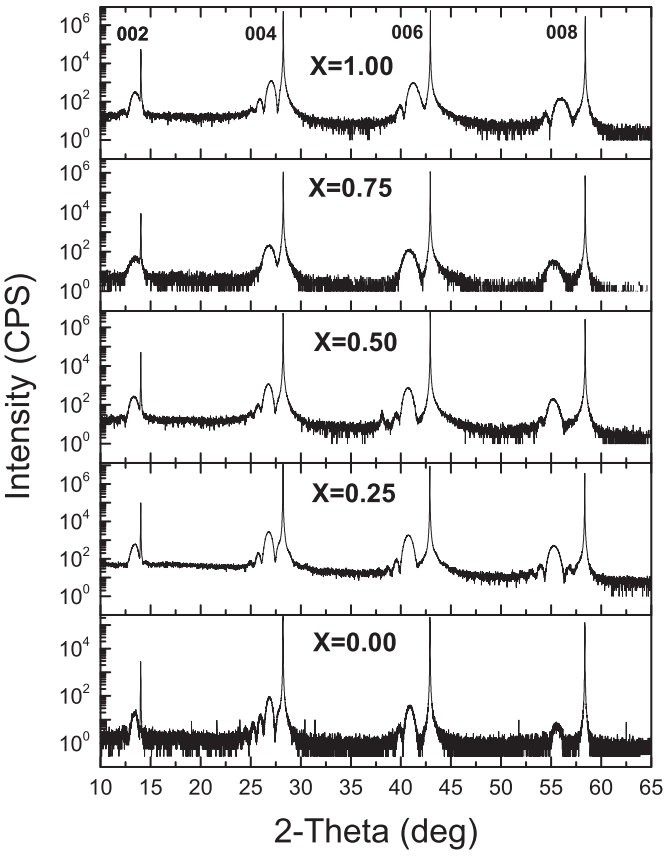

Fig. 1. X-ray diffraction of the LSCO thin films with varying Sr content (x). Peak indices are shown at top and correspond to both that film and LSAO substrate peak.

Table 1
Estimates of film roughness and thickness as a function of Sr content (x) obtained from fitting X-ray reflectivity data.

x	Surface roughness (nm)	Film thickness (nm)
0	0.8	13.2
0.25	0.7	11.9
0.50	1.4	12.6
0.75	1.3	11.5
1.0	1.1	13.3

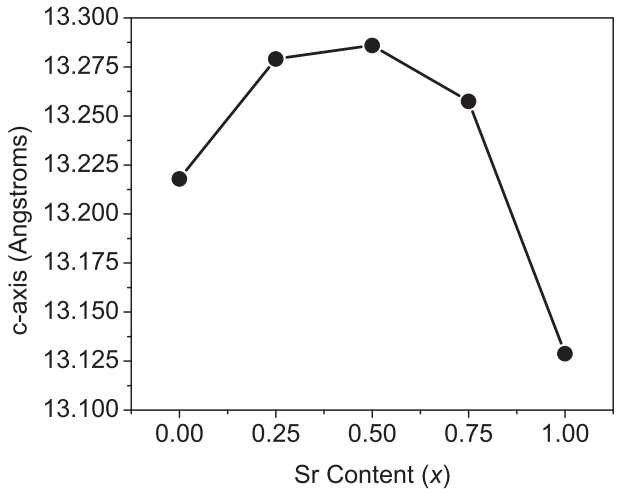

Fig. 2. Out-of-plane c-axis lattice parameter of films as a function of Sr content (x).