

# Combinatorial molecular beam epitaxy of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$

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## ABSTRACT

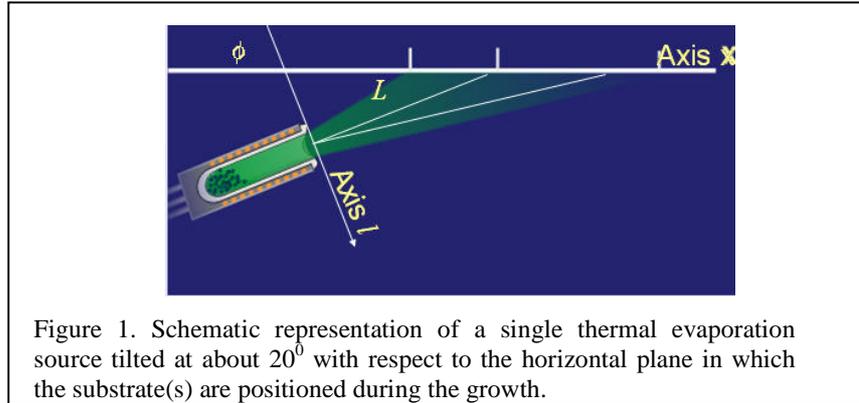
Using combinatorial molecular beam epitaxy (COMBE), we have deposited a one-dimensional (1D) combinatorial library of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (LSCO) single-crystal thin films with different Sr content above the optimum doping level. A study of this LSCO library allows a detailed evaluation of the COMBE method. We have also developed and tested a custom-made multiple-probe transport measurement set-up that allowed us to measure the  $R(T)$  curves from more than 2,000 different samples (pixels in the 1D combinatorial library of LSCO) within one week. We also studied in detail the dependence of the crystal structure (specifically, the  $c$ -axis lattice constant) on the Sr content and on the type of epitaxial strain (compressive or tensile). For the films grown on LSAO substrates, we found that the  $c$ -axis lattice constant of LSCO films *decreased* as the Sr content was increased. This we attribute to the reduction in epitaxial strain that occurs because of Sr-doping-induced decrease of in-plane lattice constant of LSCO. Next, we have detected a small deviation of the beam profile from the linear dependence, noticeable for the deposition area larger than  $1''$ . If an array of substrates is used whereby some substrates are separated by more than  $1''$  and if the stoichiometry is optimized at or close to the center of the array, in the films positioned at the outer edges of the array this effect causes slight off-stoichiometry and generation of secondary-phase defects.

**Keywords:** Molecular beam epitaxy, high temperature superconductors, combinatorial library

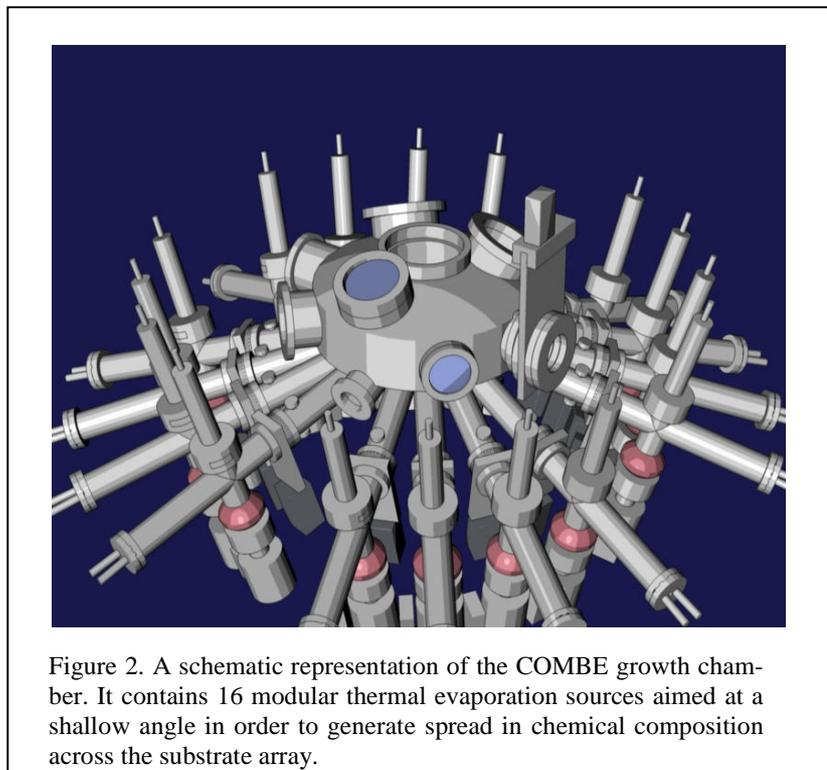
## 1. INTRODUCTION

Atomic layer-by-layer molecular-beam epitaxy (ALL-MBE) can provide atomically smooth single-crystal film of complex oxides with excellent reproducibility. [1,2] The uniformity in film composition and thickness depends on the uniformity of molecular beams across the substrate (or an array of substrates). Recently a new technique, combinatorial molecular-beam epitaxy (COMBE), has been designed specifically for synthesis of 1D and 2D combinatorial libraries of thin films of complex oxides including high temperature superconductors (HTS). [3,4] The first COMBE apparatus was constructed at Oxxel Laboratory in Bremen, Germany and has been recently transferred to the Brookhaven National Laboratory. This system allows several important parameters, including the film stoichiometry, to be varied systematically in a combinatorial way. In this paper we present experimental data on combinatorial synthesis of 1D libraries of the HTS compound  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$  (LSCO).

The design of our COMBE system has been reported elsewhere [3,4]. The metal atom sources are aimed at the substrate at a steep angle, close to  $20^\circ$  (see Figure 1) and this renders a large composition spread (gradient) across the substrate array. The gradient in thickness expected from beam simulations is about 4 % per cm along the  $x$  axis (which lies in the vertical mirror symmetry plane).



Our COMBE growth chamber contains 16 thermal evaporation sources; a schematic representation of the chamber is shown in Figure 2. For greater flexibility, we use pairs of identical sources placed in opposition, i.e., with the atomic beam impinging at the same angle with respect to the substrate, but from the opposite sides. Since the sources are placed on a circle centered on the axis normal to the substrate (see Fig. 2), this means that the pairs of complementary sources are placed at  $180^\circ$  from one another. This arrangement enables us to control the gradient of the corresponding atomic flux across the substrate, over a wide range.



The maximum gradient is obtained when one source is closed and its counterpart is open. The minimal value (close to zero) of the gradient is obtained when both sources are open and emit equal atomic fluxes. Any intermediate value can be obtained by adjusting the deposition rates from the opposite sources of the same element. This can be accomplished e.g., by adjusting the temperature of each of these two sources, or (much faster to accomplish) by shuttering the two sources appropriately.

To measure the deposition rate and its gradient across the substrate arrays accurately before each growth, a Quartz-Crystal rate Microbalance (QCM) monitor is mounted on a dedicated three-degrees-of freedom (x, y, z) manipulator, motorized and computer-controlled. The linear profile of the deposition rate as measured in the COMBE system is shown in Fig. 3 for one element (Sr).

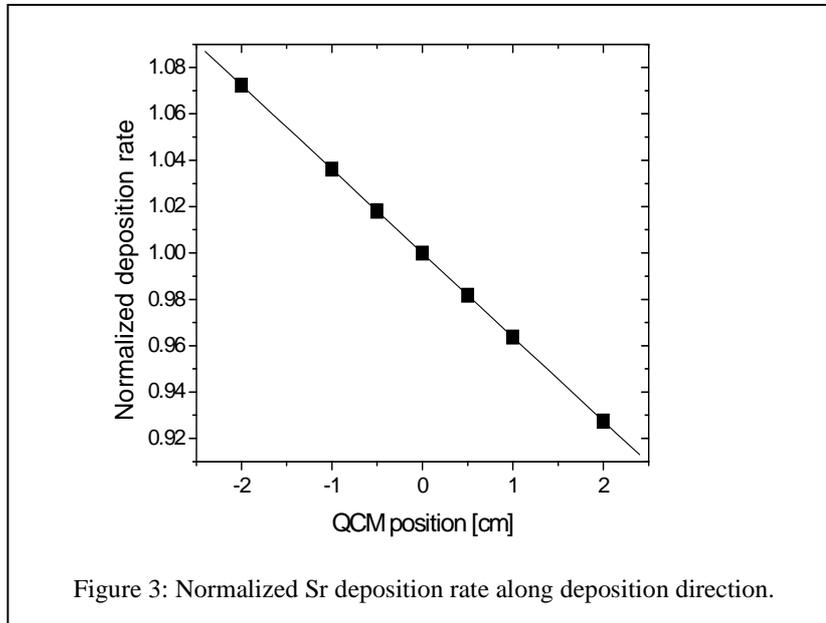
During the growth the atomic fluxes were monitored using a state-of-art, 16-channel Atomic Absorption Spectroscopy system. The film quality was controlled by in-situ reflection high-energy electron diffraction (RHEED) system with a capability to switch fast from one to another substrate position and display simultaneously up to 20 RHEED patterns, so each of the grown films was monitored in real time. Selected films were also characterized by Rutherford backscattering (RBS) at Charles Evans Associates in Mountain View, CA, and in Forschungszentrum Rossendorf, Dresden, Germany, for absolute calibration of deposition rates. The deposition rates measured by QCM were in good agreement (within a couple percent) with RBS analysis.

For combinatorial synthesis the important role is played by sample characterization. Here, essentially every film was characterized in detail by RHEED, atomic force microscopy (AFM), and X-ray diffraction (XRD). We have constructed a custom-designed multiple-probe set-up to measure the spread of resistance within each film from room temperature down to 4.2 K. This set-up allowed us to measure the resistance-versus-temperature curves for up to 62 samples simultaneously. Before this COMBE experiment we deposited a large number of single-phase, homogeneous LSCO films on both  $\text{LaSrAlO}_4$  (LSAO) and  $\text{SrTiO}_3$  (STO) substrates. In STO substrates, the lattice constant is  $a = 3.905 \text{ \AA}$ . This is 3 % larger than the in-plane lattice constant of bulk LSCO,  $a = 3.777 \text{ \AA}$  for optimal doping ( $x = 0.15$ ). Hence, LSCO films are under tensile strain on STO. In contrast, LSAO has a 0.5 % shorter lattice constant,  $a = 3.755 \text{ \AA}$  and LSCO film are under compressive strain. It has been reported by several groups that compressive strain enhances the critical temperature as compared to films under tensile strain [5-8].

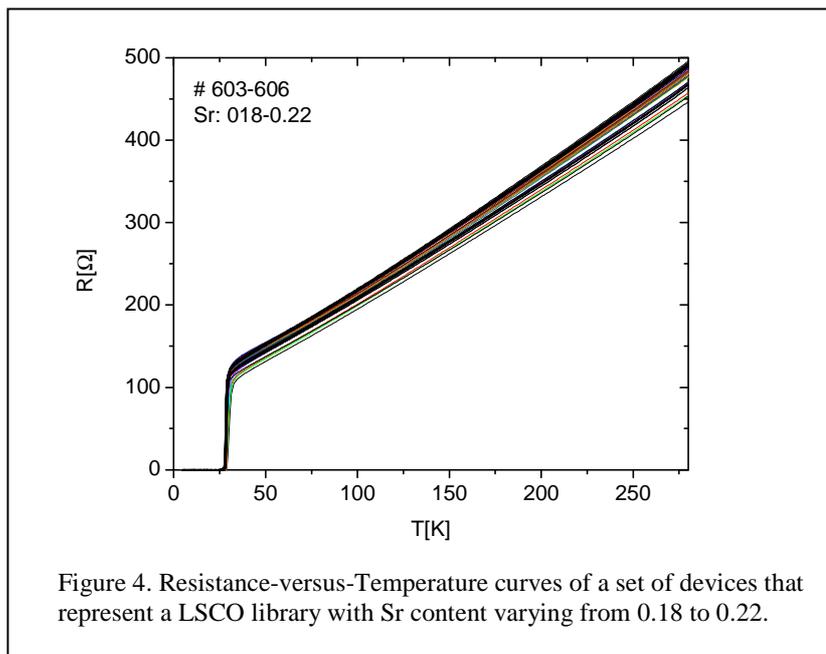
## 2. EXPERIMENTAL

We have carried out nine synthesis experiments of 1D combinatorial libraries of LSCO with Sr content ranging from optimal doping ( $x = 0.15$ ) to strongly overdoped ( $x = 0.37$ ). In each growth experiment, we used the following technique. We used only one Sr source to provide maximal gradient of the Sr content. The Sr source was placed next to the La source so that their deposition directions were close to one another (less than  $20^\circ$  off). The deposition rates of Sr, La and Cu sources were adjusted so that the ratio of (La + Sr) : Cu was equal to 2:1 at each point within the deposition area. Four substrates (size: 10 mm x 10 mm x 1mm) were placed in the growth chamber in the 1D array

that was aligned with the mean of the Sr and La deposition directions. The variation of the normalized deposition rate of Sr along the deposition direction is shown in Figure 3. The Sr rate varies by 4 % over 1 cm.

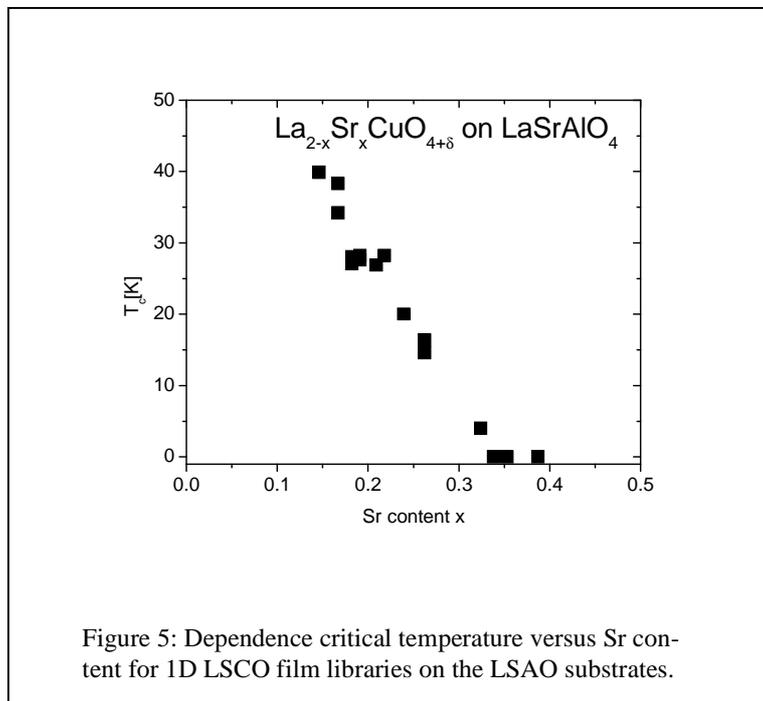


Hence, the typical variation of Sr content within one 1D library, end-to-end was 18 %. All LSCO films had 120 unit-cells-thick layers; this corresponds to the film thickness of 780 Å. The films were deposited on LSAO or STO substrates.



To measure accurately the spread in resistance and in  $T_c$ , each film was patterned into a narrow (50  $\mu\text{m}$  wide) strip line at the center-line of the substrate and oriented along the Sr gradient. The strip had 64 leads and contacts attached to it laterally and this allowed us to simultaneously measure resistance of 61 pixels along the Sr gradient. The voltage contacts were separated from one another by 150  $\mu\text{m}$ .

A typical set of resistance versus temperature curves from one such film is shown in Figure 4; this particular set is from a slightly overdoped LSCO film with Sr content ranging from 0.18 to 0.22. The normal-state resistance and  $T_c$  both decrease as the Sr content increases. This is qualitatively in agreement with the known LSCO electronic phase diagram. The dependence of  $T_c$  on the Sr content  $x$  in some of our LSCO samples is shown in Figure 5.

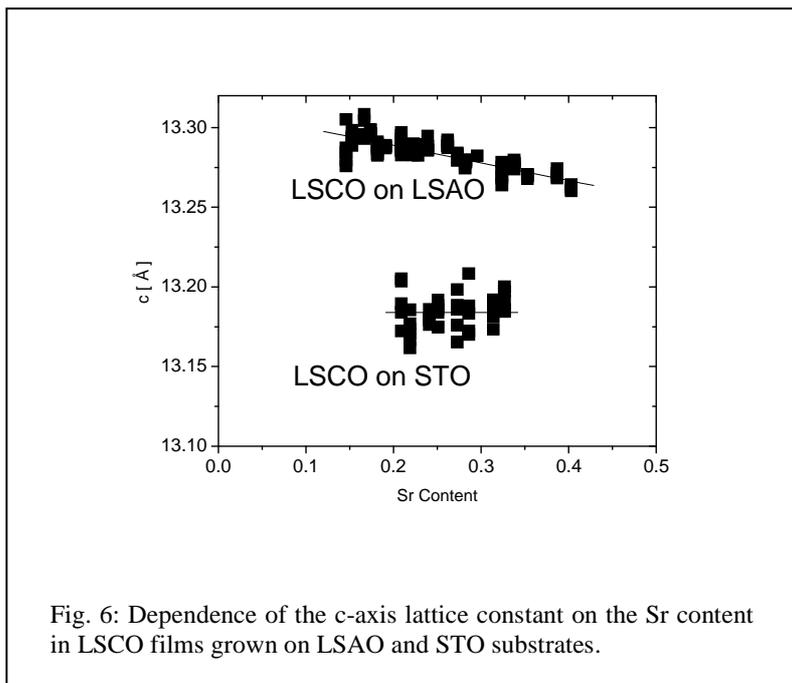


Once the Sr content reached and surpassed  $x = 0.33$ , the films were not superconducting any more. This is also in good agreement with the data obtained on single-phase growth experiments. [6]

We measured XRD ( $\vartheta$ -2 $\vartheta$  scans) at four different positions of each film along the Sr gradient line and determined the  $c$ -axis lattice constant. The results are shown in Figure 6, where we plot the  $c$ -axis lattice parameter as a function of the Sr content  $x$  for the entire data set including LSCO films on LSAO as well as on STO substrates.

In LSCO films on LSAO substrates, increase in the Sr content causes a clear and systematic decrease of the  $c$ -axis lattice constant. In contrast, in all LSCO films deposited on STO substrates the  $c$ -axis lattice period is essentially

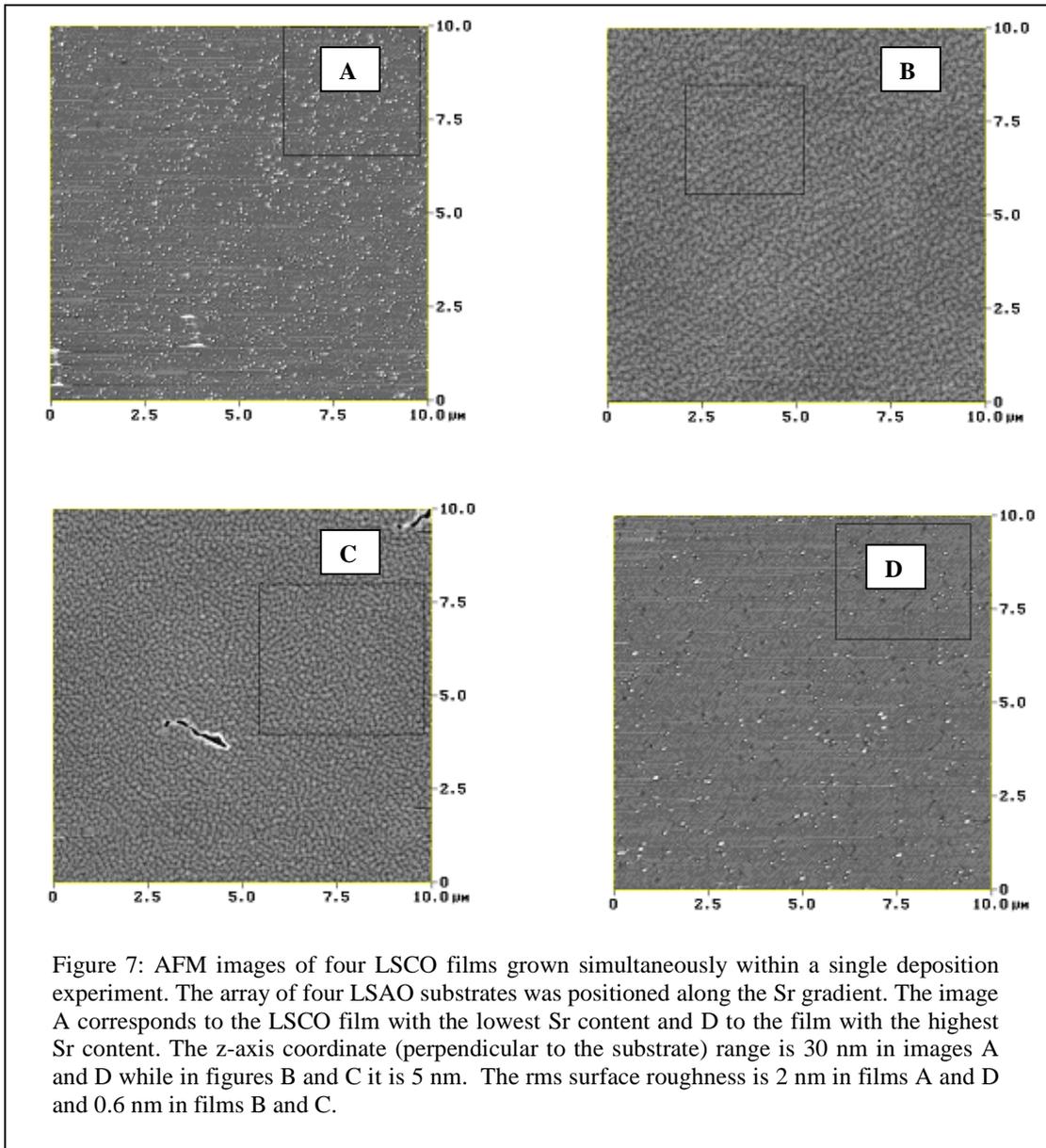
constant within the experimental error. The spread in the  $c$ -axis lattice parameter is larger in this case; we attribute this to the difference in the crystal quality of the LSAO and STO substrates. The crystal quality of the commercially available STO substrates, grown by the flame-fusion method, is typically significantly lower than the quality of the LSAO substrates, grown by the Chochralski method, and this could account for the large scattering in the  $c$ -axis lattice parameter for LSCO films on STO substrates shown in Figure 6.



Our explanation for the systematic decrease of the  $c$ -axis lattice parameter with increase in Sr content for LSCO films grown on the LSAO substrates is as follows. In this case, the films is under compressive strain, and its in-plane lattice constant  $a_0$  is reduced compared to that in the bulk LSCO samples. Assuming that the unit cell volume is (approximately) conserved, we expect the out-of-plane lattice constant  $c_0$  to expand and be larger than in the bulk. Since it is well-documented that increase of the Sr content leads to a decrease of the in-plane lattice parameter, we suppose that compressive strain should be reduced as  $x$  is increased. As a consequence,  $c_0$  should get shorter as the doping level  $x$  is increased – exactly as we have observed. To further test this explanation, one should measure the  $a_0$  and  $b_0$  lattice parameters as well, and we hope to do this at the National Synchrotron Light Source at BNL.

Finally, we have studied our films in great detail using AFM. Roughness analysis of the AFM data showed that two films positioned at the outer ends of the array contain precipitates which appear identical and which we believe to be caused by excess in La content. From an extensive study of growth of hundreds of such films, we know that this type of precipitates (with the typical diameter of say 50 nm and the height of ca. 3 nm) are usually a sign of Cu defi-

cit – they are observed when during deposition the ratio of (La + Sr) : Cu is higher than 2:1, by several percent or more. The nucleation of these precipitates we attribute to small deviation of the La beam profile from the linear dependence, which actually is noticeable when the deposition area is larger than 1". We have verified this also by numerical simulations. Indeed if an array of substrates is used with some films separated more than 1" and if the stoichiometry is optimized at or close to the center of the array, this effect causes slight off-stoichiometry in the films positioned at the outer edges of the array, and this causes nucleation of secondary-phase defects.



**Table 1**

Growth Experiment	Film No.	Chemical composition	Substrate	$T_c$ [K]	Lattice constant $c_0$ [Å]	AFM: Density of defects [ $1 / \mu\text{m}^2$ ] / Height [nm] / Width [nm]
1	573	$\text{La}_{1.73}\text{Sr}_{0.27}\text{CuO}_{4+\delta}$	STO	<4.2	13.1827±0.005	29 / .3±3 / 0±16
	574	$\text{La}_{1.71}\text{Sr}_{0.29}\text{CuO}_{4+\delta}$	STO	<4.2	13.1843±0.005	No defects
	575	$\text{La}_{1.69}\text{Sr}_{0.31}\text{CuO}_{4+\delta}$	STO	<4.2	13.1846±0.005	2.4 / .5±5 / 54±17
	576	$\text{La}_{1.67}\text{Sr}_{0.33}\text{CuO}_{4+\delta}$	STO	<4.2	13.1925±0.005	2.65 / 3.2±2.4 / 35±14
2	579	$\text{La}_{1.85}\text{Sr}_{0.21}\text{CuO}_{4+\delta}$	STO	-	13.1908±0.005	58 / 3.6±2.8 / 36±15
	580	$\text{La}_{1.80}\text{Sr}_{0.22}\text{CuO}_{4+\delta}$	STO	5-6	13.1724±0.005	12 / 9.7±5.1 / 82±24
	581	$\text{La}_{1.75}\text{Sr}_{0.24}\text{CuO}_{4+\delta}$	STO	-	13.1801±0.005	1.4 / 1.2±1.4 / 36±20
	582	$\text{La}_{1.74}\text{Sr}_{0.25}\text{CuO}_{4+\delta}$	STO	-	13.1831±0.005	34 / 7.3±4.4 / 73±35
3	583	$\text{La}_{1.87}\text{Sr}_{0.15}\text{CuO}_{4+\delta}$	LSAO	40-41	13.2863±0.005	32.4 / 9±7 / 80±58
	584	$\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4+\delta}$	LSAO	-	13.2935±0.005	1.3 / 5.5±4.3 / 91±38
	585	$\text{La}_{1.83}\text{Sr}_{0.17}\text{CuO}_{4+\delta}$	LSAO	37-38	13.2989±0.005	0.02 / 22±2.3 / 1580±86
	586	$\text{La}_{1.81}\text{Sr}_{0.18}\text{CuO}_{4+\delta}$	LSAO	-	13.2961±0.005	0.16 / 6.4±4.8 / 442±300
4	587	$\text{La}_{1.82}\text{Sr}_{0.18}\text{CuO}_{4+\delta}$	LSAO	-	13.2876±0.005	Dense defects
	588	$\text{La}_{1.81}\text{Sr}_{0.19}\text{CuO}_{4+\delta}$	LSAO	-	-	Dense defects
	589	$\text{La}_{1.79}\text{Sr}_{0.21}\text{CuO}_{4+\delta}$	LSAO	-	13.2936±0.005	1.03 / 5.3±8.4 / 267±161
	590	$\text{La}_{1.78}\text{Sr}_{0.22}\text{CuO}_{4+\delta}$	LSAO	-	13.2865±0.005	8.2 / 8±7 / 150±70
5	591	$\text{La}_{1.76}\text{Sr}_{0.23}\text{CuO}_{4+\delta}$	LSAO	-	13.2863±0.005	16.1 / 9.5±6.3 / 102±41
	592	$\text{La}_{1.75}\text{Sr}_{0.24}\text{CuO}_{4+\delta}$	LSAO	18-20	13.2881±0.005	1.37 / 8.0±5.1 / 157±47
	593	$\text{La}_{1.73}\text{Sr}_{0.26}\text{CuO}_{4+\delta}$	LSAO	14-16.5	13.2895±0.005	0.036 / 6.3±4.3 / 260±63
	594	$\text{La}_{1.72}\text{Sr}_{0.27}\text{CuO}_{4+\delta}$	LSAO		13.2823±0.005	0.94 / 3.4±3.0 / 61±37
6	595	$\text{La}_{1.71}\text{Sr}_{0.28}\text{CuO}_{4+\delta}$	LSAO	<4.2	13.2770±0.005	4.2 / 7.2±5.2 / 230±190
	596	$\text{La}_{1.69}\text{Sr}_{0.30}\text{CuO}_{4+\delta}$	LSAO	<4.2	13.2823±0.005	0.35 / 8.5±5.4 / 325±90
	597	$\text{La}_{1.67}\text{Sr}_{0.32}\text{CuO}_{4+\delta}$	LSAO	<4.2	13.2710±0.005	0.020 / 50±14 / 507±30
	598	$\text{La}_{1.65}\text{Sr}_{0.34}\text{CuO}_{4+\delta}$	LSAO	<4.2	13.2769±0.005	4.9 / 5.5±3 / 100±26
7	599	$\text{La}_{1.63}\text{Sr}_{0.34}\text{CuO}_{4+\delta}$	MgO	<4.2	-	-
	600	$\text{La}_{1.62}\text{Sr}_{0.35}\text{CuO}_{4+\delta}$	LSAO	<4.2	13.2696±0.005	1.30 / 3.9±1.7 / 142±62
	601	$\text{La}_{1.58}\text{Sr}_{0.39}\text{CuO}_{4+\delta}$	LSAO	<4.2	13.2705±0.005	0.04 / 4±2.2 / 170±90
	602	$\text{La}_{1.57}\text{Sr}_{0.40}\text{CuO}_{4+\delta}$	LSAO	<4.2	13.2618±0.005	7.2 / 1.7±1.6 / 64±36
8	603	$\text{La}_{1.80}\text{Sr}_{0.18}\text{CuO}_{4+\delta}$	LSAO	27-28	13.2856±0.005	17.4 / 3.8±2.7 / 62±20
	604	$\text{La}_{1.79}\text{Sr}_{0.19}\text{CuO}_{4+\delta}$	LSAO	27-28	13.2881±0.005	0.30 / 26±20 / 773±93
	605	$\text{La}_{1.77}\text{Sr}_{0.21}\text{CuO}_{4+\delta}$	LSAO	26-27	13.2855±0.005	0.06 / 23±5 / 740±46
	606	$\text{La}_{1.76}\text{Sr}_{0.22}\text{CuO}_{4+\delta}$	LSAO	27-28	13.2868±0.005	12.8 / 4.9±3.3 / 76±26
9	607	$\text{La}_{1.76}\text{Sr}_{0.23}\text{CuO}_{4+\delta}$	STO	-	13.1823±0.005	14 / 3.2±2.7 / 53±25
	608	$\text{La}_{1.75}\text{Sr}_{0.24}\text{CuO}_{4+\delta}$	STO	-	13.1973±0.005	No defects
	609	$\text{La}_{1.73}\text{Sr}_{0.26}\text{CuO}_{4+\delta}$	STO	-	13.2037±0.005	0.06 / 9±4.2 / 130±76
	610	$\text{La}_{1.72}\text{Sr}_{0.27}\text{CuO}_{4+\delta}$	STO	-	13.1844±0.005	4.9 / 3.0±2.7 / 53±23

### 3. CONCLUSIONS

Using combinatorial molecular beam epitaxy (COMBE), we have deposited 1D combinatorial library of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  single-crystal thin films with different Sr content above the optimum doped level. A comprehensive study of this LSCO library allowed us to characterize the COMBE method in detail, and the results are presented here for the first time.

We have also developed and tested a custom-made multiple-probe transport measurement set-up that allowed us to measure within one week more than 2000  $R(T)$  curves from different pixels in the 1D combinatorial library of LSCO. We have also studied in detail the dependence of the crystal structure (specifically, the  $c$ -axis lattice constant) as a function of Sr content and the type of epitaxial strain (compressive or tensile).

For the LSCO films grown on the LSAO substrate, we found the  $c$ -axis lattice constant of films to *decrease* as the Sr content was increased. This we attribute to the reduced epitaxial strain due to decrease of in-plane lattice constant with Sr doping. Next, we have detected a small deviation of the beam profile from the linear dependence, noticeable for the deposition area larger than 1". If an array of substrates is used with some films separated by more than 1" and if the stoichiometry is optimized at or close to the center of the array, this effect causes slight off-stoichiometry and in the films positioned at the outer edges of the array and gives rise to nucleation of secondary-phase defects.

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