

Growth of the infinite layer phase of $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ by laser ablation

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Pulsed laser deposition (PLD) has been used to prepare tetragonal $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ thin films that have the parent structure of the high T_c copper oxide superconductors. Low-temperature deposition using a single source target has been shown to kinetically trap c -axis oriented, infinite layer $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ materials on $\langle 100 \rangle \text{SrTiO}_3$ substrates. In addition, electrical measurements indicate that neodymium substitution drives the system from an insulating to a weakly metallic state.

The tetragonal, infinite layer phase of SrCuO_2 , which consists of alternating Sr^{2+} and CuO_2^- layers, represents the parent structure of the high T_c copper oxide superconductors.^{1,2} This system is in principle ideally suited for investigating high T_c superconductivity since it contains only the essential CuO_2 planes and ionic layers. However, it has not been possible to prepare and systematically dope this important phase using conventional solid state methods,² although two alternative approaches have been successful.³⁻⁸ Ultrahigh pressure (20–65 kbar) and high-temperature (1000 °C) reaction have been used to prepare tetragonal SrCuO_2 and metal-substituted SrCuO_2 .³⁻⁵ These high-pressure studies have shown that doping SrCuO_2 with Nd^{3+} or La^{3+} yields a superconducting phase. Unfortunately, the ceramic products obtained from the high-pressure syntheses are not optimal for detailed physical studies that are needed to understand superconductivity in these materials.

A very different approach to the preparation of SrCuO_2 and related materials involves pulsed laser ablation and deposition (PLD).⁶⁻⁸ PLD is a well-established technique for the growth of high-quality, epitaxial films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and other high T_c superconductors.⁹ The low growth temperatures accessible with PLD also suggest that this technique should be uniquely suited to the preparation of metastable copper-oxide phases such as tetragonal SrCuO_2 . Indeed, our group and others have recently reported that the infinite layer phase of SrCuO_2 can be prepared using PLD.⁶⁻⁸ Herein, we describe the growth of the first series of Nd^{3+} -substituted SrCuO_2 ($\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$) thin films by PLD. Our studies show that low-temperature growth (accessible by PLD) kinetically traps c -axis oriented, tetragonal $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ on $\langle 100 \rangle$ oriented SrTiO_3 substrates. These low-temperature/low-pressure PLD studies of $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ contrast the high-pressure/high-temperature methods used previously to prepare this material, and thus suggest the opportunity for better controlled investigations of superconductivity in this system.

A KrF excimer laser (pulse energy = 1–2 J/cm²; repetition rate = 5 Hz) was used to deposit thin films of $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ onto $\langle 100 \rangle$ oriented SrTiO_3 substrates at temperatures between 500 and 700 °C. The films were deposited using single source $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ targets in an

oxygen atmosphere (10–200 mTorr). The $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ targets were prepared by the reaction of stoichiometric mixtures of SrCO_3 , Nd_2O_3 , and CuO at 950 °C in air.⁶ The target materials consist predominantly of an orthorhombic phase; this phase does not contain CuO_2 layers.^{6,10}

Ablation of orthorhombic $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ targets onto $\langle 100 \rangle$ oriented SrTiO_3 substrates yields thin films that are structurally distinct from the target phase. X-ray diffraction scans (θ - 2θ) of the new $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ films (Fig. 1) can be indexed as the tetragonal, infinite layer phase with the c -axis oriented perpendicular to the $\langle 100 \rangle$ SrTiO_3 substrate surface. The observation of the (100) and (200) SrTiO_3 substrate and the (001) and (002) $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ film peaks, as well as the (400) and (004) peaks (not shown), confirms the c -axis orientation of these films. The

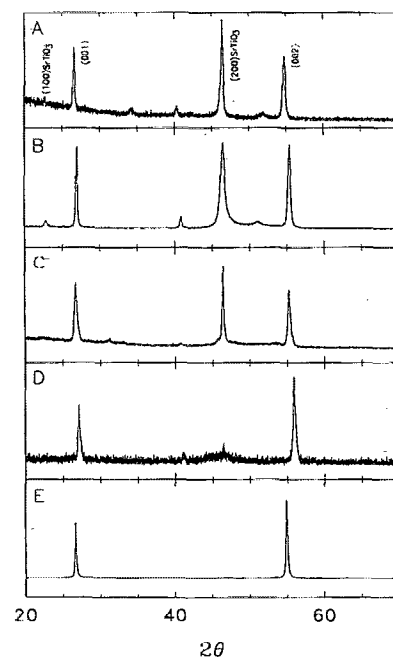


FIG. 1. X-ray diffraction scans (θ - 2θ) of ≈ 5000 Å thick films of (a) SrCuO_2 , (b) $\text{Sr}_{0.92}\text{Nd}_{0.08}\text{CuO}_2$, (c) $\text{Sr}_{0.84}\text{Nd}_{0.16}\text{CuO}_2$, and (d) $\text{Sr}_{0.76}\text{Nd}_{0.24}\text{CuO}_2$ deposited on $\langle 100 \rangle \text{SrTiO}_3$. The intensity (y) axis is arbitrary. The films can be indexed as the c -axis oriented tetragonal SrCuO_2 phase; (e) is a simulation of this phase. These films were grown with a substrate temperature of 500 °C and an oxygen pressure of 10 mTorr, the substrate-target separation was 4 cm.

value of the c -axis calculated from these experimental data are 3.35, 3.34, 3.31, and 3.27 Å for the $x=0, 0.08, 0.16$, and 0.24 materials, respectively.¹¹ The decrease in the c -axis lattice constant with increasing x is consistent with the substitution of the smaller Nd^{3+} cation ($r=1.11$ Å) for Sr^{2+} ($r=1.26$ Å), and previous high-pressure studies.³ We have also quantified the incorporation of Nd^{3+} in the films using Rutherford backscattering (RBS). The RBS measurements show that the neodymium concentration within the films is the same ($\pm 5\%$) as the targets. These results confirm that metal-ion evaporation from the targets is stoichiometric, and suggest that x provides a measure of the average dopant concentration. The tetragonal, infinite layer structural assignment has been further confirmed through electron diffraction (ED) studies. A typical ED pattern along the (001) zone axis and a simulation for the infinite layer material are shown in Fig. 2.¹² The a -axis calculated from the experimental data, 3.93 Å is consistent with the proposed tetragonal structure of $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ ³ and not with the structure of the orthorhombic target. Hence, we conclude that it is possible to deposit highly oriented films of tetragonal $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ using PLD.

Since it has not been possible to prepare tetragonal

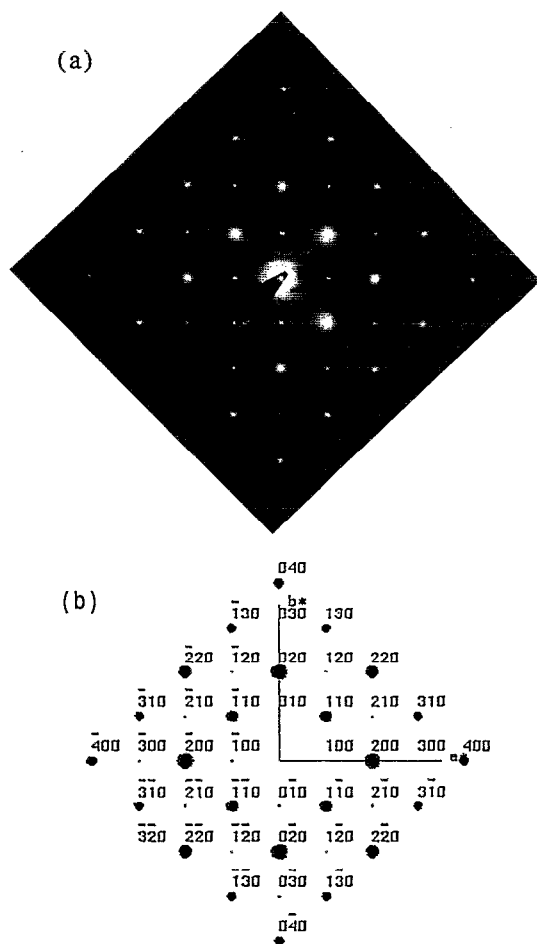


FIG. 2. (a) Electron diffraction pattern record along the (001) zone axis of a $\text{Sr}_{0.92}\text{Nd}_{0.08}\text{CuO}_2$ film. (b) The simulated electron diffraction pattern for the tetragonal $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ phase.

$\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ using conventional solid state methods we have also examined the factors that control the growth of this important phase by PLD. We find that at higher growth temperatures (> 500 °C) the amount of orthorhombic impurity increases, and that at 700 °C the films consist exclusively of this phase. These data suggest that low-temperature growth (accessible by PLD) kinetically traps the metastable infinite layer phase of the $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ series of materials. In addition, films grown at 500 °C on (100) oriented MgO substrates ($\approx 7\%$ lattice mismatch) exhibit a small increase in impurity concentration versus films grown on (100) SrTiO_3 ($\approx 1\%$ mismatch). These data indicate that lattice matching also helps to stabilize the infinite layer phase.

In addition, we have characterized the electrical properties of the $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ materials as a function of x . We find that SrCuO_2 ($x=0$) is an insulator in agreement with previous reports.^{3,6} Preliminary studies of the $x=0.08, 0.16$, and 0.24 materials show that the resistivity changes systematically with increasing x (Fig. 3). Transport is activated between 300 and 5 K for $x=0.08$. In contrast, the $x=0.16$ materials exhibit metallic behavior above 175 K, activated transport between 25 and 50 K, and a transition to a zero-resistance state at ≈ 20 K. As the doping level is increased further (i.e., $x=0.24$) we observe metallic conductivity over a wider temperature range (300–45 K) and a resistive drop at 45 K. Previously, a superconducting onset has been reported at 40 K in ceramic $\text{Sr}_{0.86}\text{Nd}_{0.14}\text{CuO}_2$ prepared by high-pressure synthesis. However, the samples prepared by the high-pressure technique exhibit activated transport from (300–40 K in contrast to our $x=0.16, 0.24$ thin films. Although the resistivity transitions in our samples are indicative of superconductivity, dc magnetization measurements show that the $x=0.16, 0.24$ films are not bulk superconductors. Nevertheless, the systematic changes in electrical properties

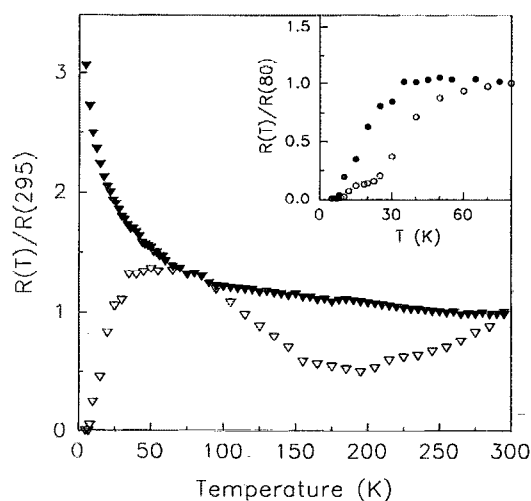


FIG. 3. Normalized resistance vs temperature curves recorded on $\text{Sr}_{0.92}\text{Nd}_{0.08}\text{CuO}_2$ (\blacktriangledown) and $\text{Sr}_{0.84}\text{Nd}_{0.16}\text{CuO}_2$ (\triangledown) films. Conduction is activated up to 300 K in the $x=0.08$ film, but is metallic above 175 K in the $x=0.16$ material. The inset shows the transition to a zero resistance state in $\text{Sr}_{0.84}\text{Nd}_{0.16}\text{CuO}_2$ (\bullet) and $\text{Sr}_{0.76}\text{Nd}_{0.24}\text{CuO}_2$ (\circ).

with increasing Nd^{3+} concentration are consistent with electron doping of the infinite layer material. It is expected that control of the oxygen stoichiometry will yield bulk superconducting materials.

In summary, we have used PLD to prepare a series of highly oriented $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ thin films that have the parent structure of the copper oxide high T_c superconductors. Mechanistic studies have shown that the low-temperature growth accessible with PLD is critical to the formation of this important phase, and suggests that this technique may be generally useful for the preparation of new materials. In addition, electrical measurements have shown that neodymium substitution systematically drives the system from an insulating to weakly metallic state.

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¹¹Small impurity peaks, which may be indexed as the orthorhombic phase, are occasionally detected in the diffraction scans. Since these impurity peaks represent < 10% of the product we conclude that the major phase obtained by PLD is the desired tetragonal one.

¹²The elemental composition determined by x-ray fluorescence analysis at the same time as the ED pattern shows only Sr, Nd, and Cu. The diffraction patterns thus correspond to the $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ films and not the substrate.