Preparation of Superconducting Thin Films of Infinite-Layer Nickelate Nd_{0.8}Sr_{0.2}NiO_{2}

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The recent observation of superconductivity in thin films of infinite-layer nickelate Nd_{0.8}Sr_{0.2}NiO_{2} has received considerable attention. Despite the many efforts to understand the superconductivity in infinite-layer nickelates, a consensus on the underlying mechanism for the superconductivity has yet to be reached, partly owing to the challenges with the material synthesis. Here, we report the successful growth of superconducting infinite-layer Nd_{0.8}Sr_{0.2}NiO_{2} films by pulsed laser deposition and soft chemical reduction. The details on the growth process are discussed.

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Despite decades of research on cuprate superconductors, an understanding of what exact features of a material essentially support superconductivity has remained elusive. On an empirical basis, it seems natural to expect that superconductivity can be achieved through the synthesis of cuprate analogs that share common features including spin one-half, two-dimensionality, and strong antiferromagnetic correlations.\(^1\) Along this direction, Chaloupka et al. proposed that LaNiO_{3}/LaMO_{3} (M stands for a trivalent cation Al, Ga, etc.) superlattices would create superconductivity, which however has not been realized to date although the nickel-oxide superlattices have been successfully synthesized.\(^2\) The recent report of superconductivity in an infinite-layer nickelate Nd_{0.8}Sr_{0.2}NiO_{2} has opened an alternative route to achieve superconductivity in transition metal oxide materials in addition to cuprates.\(^3\) Compared with cuprates, the superconducting nickelates comprise a similar two-dimensional (2D) square lattice, iso-electronic 3d\(^9\) valence state, and a superconducting dome in the phase diagram.\(^4\) However, in sharp contrast to cuprates, the parent compound NdNiO_{2} of superconducting nickelates does not exhibit any magnetic order down to 1.7 K,\(^10\) indicating that the underlying superconducting mechanism differs from that of cuprate superconductors for which magnetisms are generally believed to be crucial for mediating Cooper pairs. Although various theoretical models have been proposed to explain the superconductivity in the superconducting nickelates,\(^11\)–\(^50\) a consensus model has not yet reached partly owing to the challenges with the synthesis, and only very few reports exist on achieving superconducting films of infinite-layer nickelates.\(^3,5,11\)–\(^56\) At present, superconductivity has not been observed in bulk Nd_{1−δ}Sr_{δ}NiO_{2}.\(^57\)–\(^60\)

In this Letter, we report the successful growth of superconducting infinite-layer Nd_{0.8}Sr_{0.2}NiO_{2} films. The pervoskite precursor phase nickelate films were prepared using pulsed laser deposition (PLD). The infinite-layer phase was acquired by a soft-chemistry reduction method. The thickness and out-plane x-ray diffraction (XRD) pattern of the prepared films were examined using a SmartLab x-ray diffractometer. The superconductivity was confirmed by transport measurements using a Quantum Design physical property measurement system (PPMS) with a standard four-probe configuration. The wire connection was made by melting indium.

The laser target contained a stoichiometric mixture of SrCO_{3} (Alfa Aesar, 99.99%), Nd_{2}O_{3} (Alfa Aesar, 99.99%), and NiO (Sigma Aldrich-Chemie GmbH, 99.995%) prepared by a solid-state reaction in air at 1100 °C for 24 hours. The products of this reaction were ground and re-heated, and this process was repeated five times. The resulting polycrystalline materials was pressed into a pellet and sintered for 24 hours at 1200 °C in air. The heating and cooling rate of the sintering were kept at 3 °C/min.

The nickelate films were grown by PLD using a 248-nm KrF excimer laser (COMPex 201, Coherent). The SrTiO_{3} (001) substrates (5×5 mm, without chem-
ical etching to achieve a TiO$_2$ terminated surface) were pre-annealed at 900°C with an oxygen partial pressure of $1 \times 10^{-5}$ Torr. During growth, the substrate temperature was kept at 600°C under an oxygen partial pressure of 150 mTorr. After deposition, the films were cooled to room temperature at a rate of 5°C per minute in the same oxygen partial pressure. The laser beam size was about 0.8 $\times$ 3.2 mm$^2$ realized by using an aperture. The pulse energy of the laser was set from 640 mJ/cm$^2$ to 960 mJ/cm$^2$ for the growth of NdNiO$_3$ and Nd$_6$Sr$_{10}$NiO$_{14}$. The laser frequency was set to 4 Hz.

The infinite-layer nickelate phase was acquired by the soft-chemistry reduction method. As shown in Fig. 1(b), the as-grown nickelate films were wrapped in clean aluminum foil and then sealed with 0.1 g CaH$_2$ powder (Alfa Aesar, 98%) in quartz tubes which were pumped to a vacuum better than 1 Torr. The laser beam size was about 0.8 $\times$ 3.2 mm$^2$. The laser was set from 640 mJ/cm$^2$ to 960 mJ/cm$^2$ for the growth of NdNiO$_3$ and Nd$_6$Sr$_{10}$NiO$_{14}$. The laser frequency was set to 4 Hz.

Figure 2 shows the structural characterization of the nickelate films. The NdNiO$_3$ film peaks at 23.76° and 48.56° correspond to the (001) and (002) reflections, respectively [see Fig. 2(a)]. After chemical reduction, as shown in Fig. 2(b) the film peaks at 26.77° and 55.85° identify the infinite-layer NdNiO$_2$ and correspond to (001) and (002) reflections, respectively. For a typical film of Nd$_6$Sr$_{10}$NiO$_{14}$ shown in Fig. 2(c), the peaks at 23.75° and 48.45° correspond to (001) and (002) reflections, respectively, and both peaks are slightly broader than those of the undoped phase in Fig. 2(a). After chemical reduction, the peaks at 26.45° and 54.77° correspond to (001) and (002) reflections, respectively, as expected for a film of an infinite-layer Nd$_6$Sr$_{10}$NiO$_{14}$ [Fig. 2(d)]. The intensity is comparable to the precursor. It was reported that the Nd$_6$Sr$_{10}$NiO$_{14}$ films were difficult to grow due to the formation of a secondary phase which shows only a single peak with 2θ less than 48°. [52]

In Fig. 3 we show the measured Nd$_6$Sr$_{10}$NiO$_{14}$ film resistance as a function of temperature revealing that a superconducting transition occurs below 9 K and the zero resistivity is achieved at about 3.5 K. The superconducting transition temperature of our film is slightly lower than that reported in the literature, which probably stems from the variation of the hole concentration in the films prepared under different growth and reduction conditions. To study the stability of the superconducting Nd$_6$Sr$_{10}$NiO$_{14}$ films, we measured the resistivity of a typical film which had been kept in the glovebox for 30 days after chemical reduction and had been exposed to air longer than 10 hours during XRD and other measurements. The fact that the superconducting transition is almost identical with the same critical temperature $T_c$, as shown in Fig. 3(c), implies that the 9-nm-thick superconducting film without a capping layer is fairly stable.

The growth window is extremely narrow probably because the formation energy of the desired 113 phase differs only slightly from that of the secondary phase. Nevertheless, we find that the XRD pattern...
of the precursor 113 phase is a good criterion to obtain superconducting films. The (002) peak of the secondary phase locates at about 47.8°, while for the 113 phase the (002) peak is at the 2θ larger than 48° and thickness-dependent. During the optimization, we adjusted the laser spot size and laser pulse energy with the growth temperature at 600 °C and an oxygen partial pressure of 150 mTorr unchanged, and keep the thickness at 8 nm to 10 nm. The out-plane XRD pattern of a typical film grown with a larger laser spot size of 1.5×5.0 mm² is shown in Fig. 4(a). The fact that the location of the (002) peak at 47.8° and a weak hump of the (001) reflection indicates that the film contains both the 113 phase and the secondary phase. After reduction [Fig. 4(b), black curve], infinite-layer phase was partly achieved as the XRD pattern is weaker and smaller than the film of Fig. 2(d). The transport measurement shows an insulating behavior at low temperature. In Fig. 4(c) we show the XRD patterns around the (002) reflection for the films grown still with the large spot size but by using different pulse energy from 600 mJ/cm² to 1200 mJ/cm², and the 2θ of the (002) peaks is always less than 48°. Figures 4(a), 4(b), and 4(d) plot the XRD patterns for the films grown using a smaller laser spot size of 0.8×3.2 mm² with an optical aperture and different pulse energy, for which the variation of the 2θ of the (002) reflection from 48.0° to 48.4° and the appearance of the (001) peak reflect a competition between the secondary phase and the desired 113 phase. As shown in Figs. 4(a) and 4(b), the precursor film with a higher concentration of the 113 phase than the secondary phase tends to be reduced to the infinite-layer phase with a larger 2θ for the (002) peak, and it is more likely a superconducting one at low temperature [see Fig. 4(e)]. With the criterion of the (002) peak position, we found that the best laser pulse energy window is from 800 to 960 mJ/cm², and we manage to produce at least one superconducting sample out of the ten films under such conditions [Fig. 4(d)]. From our results, the laser spot size and pulse energy are two key factors to reduce the secondary phase and to improve the reproducibility of superconducting films.

The reduction process is relatively straightforward if the pure 113 phase is achieved. In Fig. 5(a) we show the out-plane XRD pattern of a typical NdNiO₃ film, which consists of both the 113 phase and the secondary phase. After the reduction, the peak from the secondary phase moves to the smaller 2θ angle, while the (002) peak of the 113 phase moves to the larger 2θ angle, representing the transformation from the 113 perovskite phase to the infinite-layer phase. For a pure sample, we varied the annealing temperature with the annealing time fixed to 5 hours. In our case, we found that the temperature of 290 °C is a good reduction condition to achieve the infinite-layer phase [Figs. 5(d)–5(f)].
In summary, we have successfully synthesized superconducting infinite-layer Nd$_{0.8}$Sr$_{0.2}$NiO$_2$ thin films using pulsed laser deposition and the soft-chemistry reduction method. The details on the film growth and the subsequent topotactic reduction process are discussed. Our results provide important information for the preparation of superconducting nickelate films, which is a crucial step in this field.

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