Fabrication and low temperature thermoelectric properties of Na$_x$CoO$_2$ ($x=0.68$ and 0.75) epitaxial films by the reactive solid-phase epitaxy

Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan

J.-Y. Lin and J. J. Lin
Institute of Physics, National Chiao Tung University, Hsinchu 30010, Taiwan

C.-H. Hsu
National Synchrotron Radiation Research Center (NSRRC), Hsinchu 30076, Taiwan

Y. K. Kuo
Department of Physics, National Dong Hua University, Hualien 97401, Taiwan

H. L. Liu, M. H. Hsu, Y. S. Gou, and J. Y. Juang
Department of Physics, National Taiwan Normal University, Taipei 10610, Taiwan

(Received 15 December 2006; accepted 4 January 2007; published online 8 February 2007)

The authors have fabricated Na$_x$CoO$_2$ thin films via lateral diffusion of sodium into Co$_3$O$_4$ (111) epitaxial films (reactive solid-phase epitaxy [Ohta et al., Cryst. Growth Des. 5, 25 (2005)]). The environment of thermal diffusion is key to the control of the sodium content in thin films. From the results of x-ray diffraction and in-plane $P_{\text{eff}}$, the epitaxial growth and the sodium contents of these films were identified. The thermoelectric measurements show a large thermoelectric power similar to that observed in single crystals. The quasiparticle scattering rate is found to approach zero at low temperatures, consistent with the small residual resistivity, indicating high quality of the Na$_x$CoO$_2$ thin films. © 2007 American Institute of Physics. [DOI: 10.1063/1.2437131]

The research on sodium cobaltate Na$_x$CoO$_2$ (NCO) has led to observations of many unusual physical properties exhibited in related compounds, such as the thermoelectric power, chargeordered insulator at $x=0.5$, and antiferromagnetic metal at $x=0.75$. Furthermore, the discovery of superconductivity in Na$_{x}$CoO$_2$·yH$_2$O was indeed a surprise. Many theoretical and experimental works have focused on the fascinating and yet puzzling ground states of NCO due to its two-dimensional triangular lattice and the mixed valence character. For the purpose of research and applications, scientists have been trying to fabricate NCO in its thin film form with modulated sodium concentrations $x$. Owing to the high vapor pressure of Na, however, it is difficult to directly grow high-quality epitaxial NCO thin films by pulsed-laser deposition, not to mention controlling well-controlled sodium contents.

In order to overcome the high vapor pressure of sodium and its associated detrimental consequences in the firsthand growth of NCO thin films, we divided the procedures of growing epitaxial NCO (0001) films into two parts. First, a layer of ~125 nm thick Co$_3$O$_4$ (111) thin film was deposited on sapphire (0001) substrates by pulsed-laser deposition (KrF excimer laser, $\lambda=248$ nm) with $T_{\text{substrate}}=680$ °C and $P_{\text{oxygen}}=0.2$ Torr. Subsequently, thermal-diffused sodium was deployed to the obtained Co$_3$O$_4$ (111) to intercalate sodium into the Co$_2$O$_3$ layers. In our scheme, in order to keep the film surface clean and smooth during the sodium diffusion process, the Co$_2$O$_3$ (111) film was capped with a sapphire sheet as a sandwich arrangement. This fabrication process has been developed by Ohta et al. The process is named the reactive solid-phase epitaxy (R-SPE). For more details, see Ref. 5. In order to fabricate Na$_{0.68}$CoO$_2$ (NCO68) film, we used sodium carbonate powder to muffle the “sandwiched” Co$_2$O$_3$ (111) film and pressed the whole assembly into a pellet, depicted as specimen A in Fig. 1. The lateral diffusion process was carried out at 700 °C for 10 h and cooled in air with the rate <10 °C/h. For preparing the Na$_{0.75}$CoO$_2$ (NCO075) film, the sandwiched Co$_2$O$_3$ (111) film was first muffled by NCO075 powder obtained by rapid heat-up sintering and then encapsulated in Na$_2$CO$_3$, as depicted schematically in Fig. 1 (specimen B). The pellet was then kept at 750–800 °C with oxygen flow for 5 h. After the

![Color online] Schematics of the encapsulation schemes for preparing NCO thin films with $x=0.68$ (specimen A) and 0.75 (specimen B). The diameter of the pellets is 20 mm, and the size of the substrates is about 5×5 mm$^2$. 

---

a)Electronic mail: wei.ep90g@nctu.edu.tw
b)Also at the Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan; Electronic mail: jyjuang@cc.nctu.edu.tw
temperature may have reached specimen A, the equilibrium sodium concentration at high surface conditions. It is suggestive from the apparent concentration of NaOH·H2O can be indexed from the database, but y is still undetermined.

lateral diffusion of sodium, the Co3O4 (111) films evidently converted into NCO (0001) films with the thickness expanding to ~250 nm.

Alternatively, Venimadhav et al.7 have used NaCOOCCH3 powder to cover Co3O4 (111) films in the annealing process to obtain NCO075 films. However, there were some unsettled issues concerning the uniformity and surface quality of the films obtained by that scheme. We also had tried other process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unsettled issues concerning the uniformity and defects in the samples that presumably resulted from quenching process schemes to obtain specimens with surface quality of the films obtained by that scheme. We also were some unset
FIG. 4. (Color online) (a) In-plane resistivity $\rho_{ab}$ vs $T$ curves (solid lines) of NCO thin films with $x=0.68$ and 0.75. The gray dash line illustrates the $\rho_{ab}-T$ of hydrolyzed NCO0075 in Fig. 2(d). Upper inset: $S(T)$ measurement for NCO0068. Lower inset: atomic force microscopic image ($5 \times 5 \text{ \mu m}^2$ and rms=1.67 nm) of NCO0068 thin films was measured after thermal-diffusion process. (b) Temperature dependence of the far-infrared conductivity of the NCO0068 thin film. The inset shows the temperature dependence of the Drude scattering rate $1/\tau_D$.

structural and transport property comparisons. Our films notably show an even smaller residual resistivity with the residual resistivity ratios $\text{RRR}=\rho(300 \text{ K})/\rho(0.4 \text{ K})=145$ and 37, which are comparable or better than the RRR of the single crystals in Ref. 2, for $x=0.68$ and 0.75, respectively. In addition, the $\rho_{ab}-T$ of hydrolyzed NCO0075 is illustrated by the gray dash line, which shows the characteristic of lower sodium concentration ($x<0.75$) and larger residual resistivity. The in-plane Seebeck coefficient $S(T)$ represents yet another prominent property of this class of materials. We used a calibrated chip resistor glued to one end of the thin film as a pulsed-heat source. The temperature gradient was measured by using a differential thermocouple, and the corresponding Seebeck voltage was measured between the two signal leads connected by a pair of copper wires. The upper left inset of Fig. 4(a) shows that $S(300 \text{ K})$ is nearly 80 $\mu \text{V/K}$ and is strongly temperature dependent for the NCO068, consistent with the results of single crystals in the previous literature. Unfortunately, due to the rapid deteriorating effects mentioned above, $S(T)$ for NCO0075 thin films is not available yet. In any case, the results presented above indicate that the preparation schemes in this letter can indeed produce films with very high quality.

Finally, we discuss briefly the implications of low residual resistivity at low temperatures. For this purpose, infrared spectroscopy has been proven to be the effective tool for the analysis of the transport properties of a broad range of conducting systems. Figure 4(b) shows the temperature dependent behavior of the far-infrared conductivity spectra for the NCO0068 film. At 300 K, the low-frequency conductivity for $\omega<100 \text{ cm}^{-1}$ can be described by a Drude peak, which grows in intensity and sharpens as the temperature is lowered. By fitting the Drude conductivity and the measured infrared reflectance self-consistently, a nearly temperature independent Drude plasma frequency $\omega_{pd} \sim 2400 \text{ cm}^{-1}$ is obtained, whereas the scattering rate $1/\tau_D$ monotonically decreases with decreasing temperature [see the inset of Fig. 4(b)]. Such behavior is typical of conventional metals. Notably, the $1/\tau_D(20 \text{ K})$ is about 6 $\text{cm}^{-1}$ compared with $1/\tau_D(300 \text{ K})=68\text{cm}^{-1}$, consistent with the small residual resistivity (or large RRR). Since the residual resistivity and $1/\tau_D(20 \text{ K})$ are proportional to the concentration of impurities or defects in the film, the transport and optical results indicate the high quality of the NCO0068 thin film.

In summary, NCO thin films with $x=0.68$ and 0.75 were fabricated via R-SPE. The thin film quality is at least as decent as that of single crystals, judging from the results of XRD, $\rho_{ab}(T)$, and $S(T)$ curves. The environmental control of different equilibrium Na vapor pressures are achieved reproducibly by the present encapsulation schemes, which presumably have been very effective in providing sodium needed for forming NCO and at the same time preventing moisture from getting in to the films.

This work was supported by MOE ATU program and the National Science Council of Taiwan, under Grant Nos. NSC 95-2112-M-009-038-MY3, 95-2112-M-009-036-MY3, and 95-2112-M-009-035-MY3.