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Fabrication and X-ray absorption spectroscopy in layered cobaltate Na_xCoO_2 thin films

W.J. Chang[a,*], J.-Y. Lin[b], T.Y. Chung[a], J.M. Chen[c], C.-H. Hsu[a], S.Y. Hsu[c], T.M. Uen[a], K.H. Wu[a], Y.S. Gou[a,d], J.Y. Juang[a,d]

[a]*Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan*
[b]*Institute of Physics, National Chiao Tung University, Hsinchu 30010, Taiwan*
[c]*National Synchrotron Radiation Research Center (NSRRC), Hsinchu 30076, Taiwan*
[d]*Department of Physics, National Taiwan Normal University, Taipei 11677, Taiwan*

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Abstract

Na_xCoO_2 ($x \sim 0.68$) thin films were fabricated on sapphire (0 0 0 1) substrates via the lateral diffusion of sodium into Co_3O_4 (1 1 1) films, which were grown by pulsed-laser deposition. From the results of X-ray diffraction and in-plane resistivity ρ_{ab}, the single phase and the metallic behaviors of these Na_xCoO_2 films can be identified. For the same sodium content x, ρ_{ab} is consistent with that of single crystals. In addition, the O 1*s* X-ray absorption near edge spectra of thin films are measured and compared with those of single crystals.

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Keywords: Na_xCoO_2 thin film; Layered cobaltates; Lateral diffusion; X-ray diffraction; X-ray absorption spectroscopy

Recently, the layered cobaltate Na_xCoO_2 has generated much interest of researchers due to its superconductivity in hydrated compounds at $x = 0.35$ [1], a large thermoelectric power [2], a charge ordered insulator at $x = 0.5$, and the antiferromagnetic metal at $x = 0.75$ [3]. Many theoretical and experimental works are focused on the fantastic ground states of Na_xCoO_2 due to its two-dimensional triangular lattice. Because of the high vapor pressure of Na in these materials, it is difficult to grow single phase and high-quality epitaxial Na_xCoO_2 thin films by pulsed-laser deposition (PLD). For this reason, reactive solid-phase growth via lateral diffusion of sodium was applied on the growth of the epitaxial Na_xCoO_2 thin films [4].

First, Co_3O_4 (1 1 1) thin films were grown on Al_2O_3 (0 0 0 1) substrates by PLD, KrF excimer laser (248 nm), with $T_{substrate} = 680\,^{\circ}C$, $P_{oxygen} = 0.2$ Torr, and $d = 125$ nm. To keep the surface clean in the process of thermal diffusion, Co_3O_4(1 1 1) thin films were capped by Al_2O_3 substrates when placing specimens in a ceramic boat with Na_2CO_3 powder. They were then put on the ceramic boat into the quartz tube oven for thermal diffusion. The diffusion process was operated at 700 °C for 10 h in air with the heating (and cooling) rate <10 °C/h. After the lateral diffusion of sodium, Co_3O_4(1 1 1) thin films became Na_xCoO_2 (0 0 1) epitaxial thin films with the thickness ~250 nm.

To check the crystal structure of Co_3O_4 and Na_xCoO_2 thin films, we have performed the X-ray diffraction (XRD) measurements, as shown in Fig. 1. From the results of XRD, Co_3O_4 (1 1 1) are epitaxial growth on sapphire (0 0 0 1) substrates, which are similar to the results of Ohta *et al.* [4] and Venimadhav *et al.* [5]. The lateral-diffused Na_xCoO_2 thin films also show single phase and are epitaxial to the substrates with (0 0 1) orientation. Because of the affiliated mutuality between the crystal structures and Na content of Na_xCoO_2 materials, we judge the Na content by comparing the XRD results with the structure phase diagram [6]. From the *c*-axis lattice constant of Na_xCoO_2 thin films, 10.9328(8) Å, we infer $x \sim 0.68$ in our specimens.

As shown in the inset (a) of Fig. 2, the roughness of layered cobaltate thin films was measured by the atomic force microscopy (AFM) after thermal-diffusion process.

*Corresponding author. Tel.: +886 3 5731653; fax: +886 3 5720728.
E-mail address: waithen.ep86@nctu.edu.tw (W.J. Chang).

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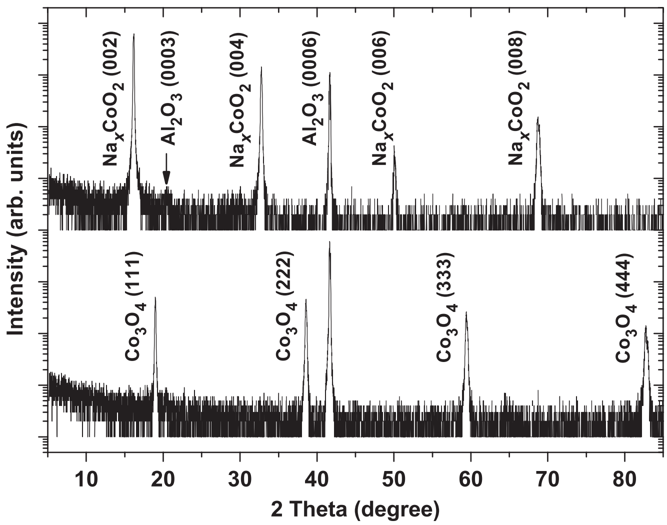

Fig. 1. X-ray diffraction of Na_xCoO_2 (0 0 1) after sodium lateral diffusion (upper panel) and Co_3O_4 (1 1 1) thin films on sapphire (0 0 0 1) substrates (lower panel). The results indicate that the both of thin films are in single phase.

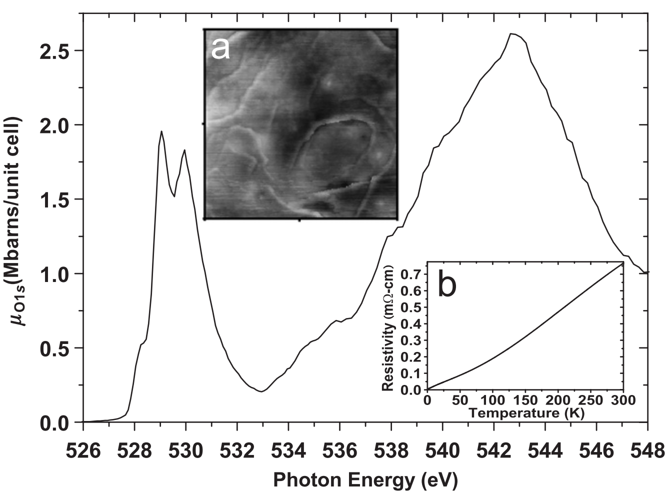

Fig. 2. Main panel: Isotropic O K-edge X-ray absorption spectrum, $(I_{E//c}+I_{E\perp c})/2$, of the Na_xCoO_2 thin film at room temperature. Inset (a): AFM image ($5\,\mu m \times 5\,\mu m$) of the Na_xCoO_2 thin film shows the layered structure of this cobaltate. Inset (b): The ρ_{ab}–T curve illustrates the high quality of this thin film.

The RMS roughness is about 1.67 nm. The ρ_{ab}–T measurements have been done by PPMS of Quantum Design®. In Fig. 2 (b), the ρ_{ab}–T curve of thin films is identical to that of single crystals [3] around $x = 0.68$, and with a much smaller residual resistivity, $\rho(300\,K)/\rho(0.4\,K) = 145$, indicating that there are very few impurities or defects in the thin films.

Beside the electric transport measurements, X-ray absorption near edge spectroscopy (XANES) has been a powerful tool to investigate the electronic state of these compounds, as in the case of perovskite manganites [7]. The main panel of Fig. 2 illustrates the O K-edge fluorescent spectrum, which characterize the hybridization of Co $3d$ and O $2p$ of the Na_xCoO_2 (0 0 1) thin film at room temperature. At the pre-edge, the O K-edge XANES shows three absorption peaks of Co^{3+} and Co^{4+} $3d$ bands, in which the t_{2g} orbitals split into a_{1g} and e_g' orbitals under trigonal crystal field [8,9]. All the three pre-edge peaks resembles those of the $x = 0.67$ single crystal with respect to the peak energy and the relative intensity [8]. These results suggest that the Na_xCoO_2 (0 0 1) thin film has an electronic structure similar to that of the single crystal with the same Na content. Currently, the anisotropy of Na_xCoO_2 from the orbital symmetry of a_{1g} and e_g' orbitals remains controversial. Further investigation of polarized-dependant XANES is certainly desirable.

In summary, we have successfully fabricated Na_xCoO_2 thin films with $x = 0.68$ via the lateral diffusion of sodium. Judged from the results of XRD and ρ_{ab}–T curve, the thin films quality is as decent as that of single crystals. XANES of Na_xCoO_2 thin film shows an electronic structure similar to that of the single crystal, too.

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