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We have studied structural and transport properties of epitaxial Na_xCoO_2 thin films on (0001) sapphire substrate prepared by topotaxially converting an epitaxial Co_3O_4 film to Na_xCoO_2 with annealing in Na vapor. The films are *c*-axis oriented and in-plane aligned with $[10\bar{1}0]Na_xCoO_2$ rotated by 30° from $[10\bar{1}0]$ sapphire. Different Na vapor pressures during the annealing resulted in films with different Na concentrations, which showed distinct transport properties. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2117619]

Layered cobaltate Na_xCoO_2 has attracted much attention recently due to its exceptional properties.[1] It has an unusually high thermoelectric power with low mobility, low resistivity, and high carrier density.[1] The Fermi surface[2] and electrical properties[3] of Na_xCoO_2 depend on the Na concentration: $Na_xCoO_2 \cdot 1.3H_2O$ is a superconductor for x around 0.3;[4,5] at $x=0.5$, it is a charge-ordered insulator;[6] and at higher Na concentrations it becomes a metal following the Curie–Weiss law.[3,7] The triangular structure of the CoO_2 planes and the strong electron correlation effect have been recognized as sources of rich properties of Na_xCoO_2.[8] For example, the large thermopower in Na_xCoO_2 has been attributed to the spin entropy due to the strong electron correlation effects.[9] Na_xCoO_2 has been prepared in polycrystalline and single-crystalline forms, but there are very few reports on Na_xCoO_2 thin films.[10–12] Recently, Ohta *et al.*[10] reported epitaxial Na_xCoO_2 films by reactive solid phase epitaxy; however, the Na concentration in the films was not well controlled. In this letter, we describe the structural and transport properties of epitaxial Na_xCoO_2 thin films fabricated by a process which is similar to that used by Ohta *et al.*,[11] but allows some degree of control of the Na concentration in the film. Films with different Na concentrations showed very different transport properties.

The epitaxial Na_xCoO_2 films were fabricated using a two-step process. First, an epitaxial Co_3O_4 film was grown by pulsed laser deposition (PLD) on a (0001) sapphire substrate. A KrF excimer laser was used with an energy density of 3.7 J/cm^2 on a CoO target. The substrate was kept at 650–700 °C during the deposition in 200 mTorr flowing oxygen. At a repetition rate of 8 Hz, the deposition rate is 0.11 Å/s. The Co_3O_4 film was then sealed in an alumina crucible with sodium bicarbonate ($NaHCO_3$) or sodium acetate ($NaOOCCH_3$) powder and heated to 800 °C for 2.5 h to form the Na_xCoO_2 film. A topotaxial conversion occurred, during which the crystallographic alignment of Co_3O_4 was inherited by Na_xCoO_2. The thickness of the Co_3O_4 film was around 1600 Å, which became ~3000 Å following the topotaxial conversion to Na_xCoO_2.

X-ray diffraction scans of an epitaxial Co_3O_4 film on a (0001) sapphire substrate are shown in Fig. 1. Co_3O_4 has a spinel structure with a space group Fd3m. The θ-2θ scan in Fig. 1(a) shows only peaks arising from diffraction off (111) Co_3O_4 planes apart from the substrate peak, indicating a phase-pure Co_3O_4 film with [111] direction normal to the substrate surface. The rocking curve of the Co_3O_4 111 peak had a full width at half maximum (FWHM) of 0.24° in ω, equal to our instrumental resolution. A lattice parameter $a=8.087\pm0.001$ Å was obtained. A ϕ scan of the 220 Co_3O_4 peak is shown in Fig. 1(b), where $\phi=0°$ is aligned parallel to the $[10\bar{1}0]$ in-plane direction of the sapphire substrate. The presence of six 220 peaks (where a single crystal would show only three) indicates an epitaxial Co_3O_4 film with two twinned variants related by a 60° rotation. The FWHM in ϕ is 0.55°. The in-plane epitaxial relationship is that [110] Co_3O_4 is rotated by ±30° from $[10\bar{1}0]Al_2O_3$.

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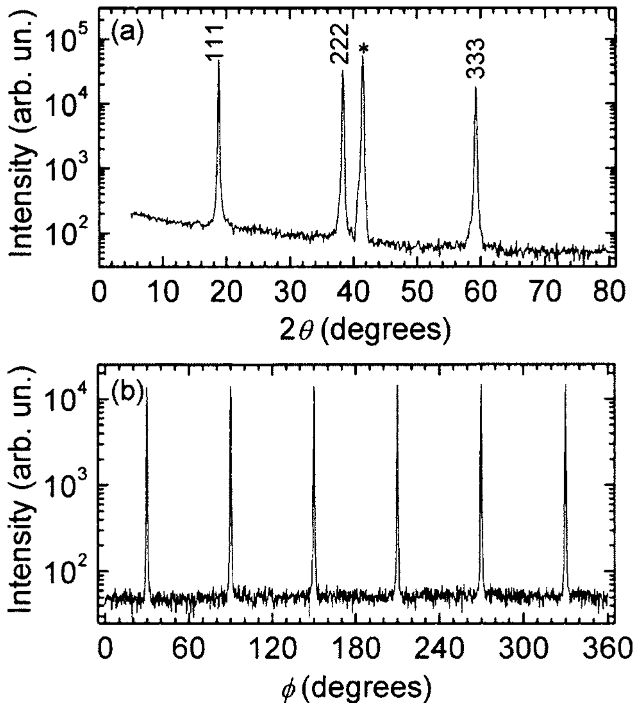

FIG. 1. (a) θ-2θ x-ray diffraction scan of a Co_3O_4 film grown on a (0001) sapphire substrate. The 0006 sapphire substrate peak is marked by an asterisk (*). (b) ϕ-scan of the 220 Co_3O_4 peak at $\chi=54.7°$, indicating that the film is epitaxial. $\phi=0$ is parallel to the $[10\bar{1}0]$ in-plane direction of the substrate.

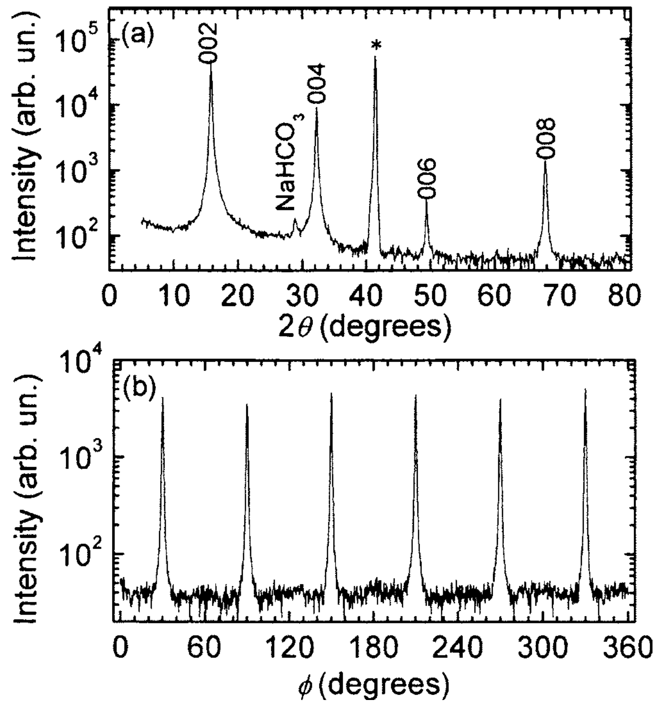

FIG. 2. (a) θ-2θ x-ray diffraction scan of a Na_xCoO_2 film on a (0001) sapphire substrate. The 0006 sapphire substrate peak is marked by an asterisk (*). (b) ϕ-scan of the $10\bar{1}2$ Na_xCoO_2 peak at $\chi=23.6°$, indicating that the film is epitaxial. $\phi=0$ is parallel to the $[10\bar{1}0]$ in-plane direction of the substrate.

The crystallinity and phase purity of the film after the topotaxial conversion depend sensitively on the annealing conditions. Under the optimized condition (800 °C for 2.5 h), the film is completely converted into Na_xCoO_2 without decomposition. X-ray diffraction scans of a Na_xCoO_2 film, which was converted from a Co_3O_4 film by annealing with $NaHCO_3$ powder, are shown in Fig. 2. Na_xCoO_2 has a hexagonal $P6_322$ structure. In the θ-2θ scan in Fig. 2(a), 00ℓ peaks of Na_xCoO_2 are observed beside a substrate peak, indicating a *c*-axis-oriented film. A weak peak of $NaHCO_3$ is also present due to the $NaHCO_3$ dust on the film surface resulting from the annealing process, which is also confirmed by a Raman scattering measurement. The ϕ-scan of the $10\bar{1}2$ Na_xCoO_2 peak is shown in Fig. 2(b), where $\phi=0$ is parallel to the $[10\bar{1}0]$ direction of the sapphire substrate. The six-fold symmetry indicates a topotaxial conversion from the epitaxial Co_3O_4 film with the angle between $[10\bar{1}0]$ Na_xCoO_2 and $[10\bar{1}0]$ sapphire being 30°. Lattice constants $c=11.02\pm0.003$ Å and $a=2.456\pm0.003$ Å were obtained. The rocking curves showed a broad FWHM of 2° in ω and 1.02° in ϕ. These values indicate that the crystalline quality of the topotaxially converted Na_xCoO_2 film is not as high as that of the starting Co_3O_4 film.

Figure 3(a) is a bright-field cross-sectional transmission electron microscopy (TEM) image of a Na_xCoO_2 film. It shows the film with a smooth surface. An x-ray energy dispersive spectroscopy (EDS) analysis shows a generally uniform distribution of Na concentration in the film. Occasionally, thin layers of amorphous material, such as the white line shown in Fig. 3(a), occur in the film, which have higher Na concentration than that in the crystalline Na_xCoO_2 film. A much thicker amorphous layer, nonuniform and discontinuous, was observed at the film/substrate interface, whose chemical composition is similar to the substrate (Al_2O_3). Figures 3(b) and 3(c) are selected area electron diffraction (SAED) patterns corresponding to the film and the substrate, respectively. They show an epitaxial relationship between the Na_xCoO_2 film and the substrate of $Na_xCoO_2(0001)\times[10\bar{1}0]\|$ sapphire $(0001)[2\bar{1}\bar{1}0]$, which is consistent with the x-ray diffraction analysis. The smeared intensity distribution of reflections in Fig. 3(b) indicates distortions of crystal

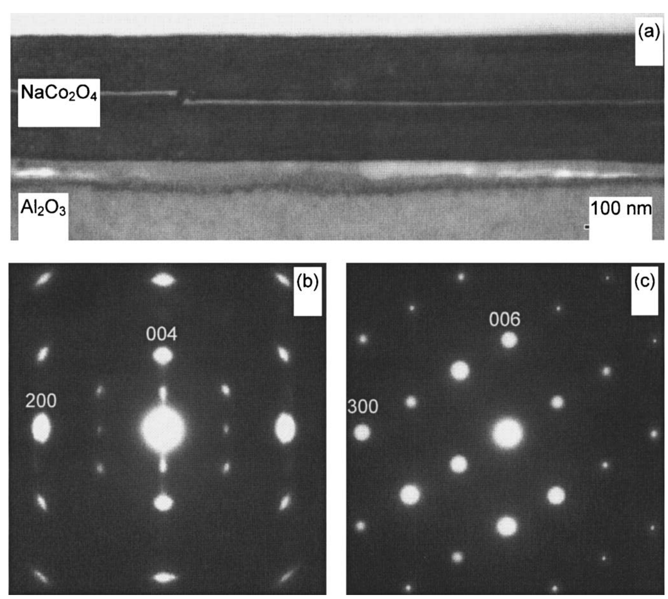

FIG. 3. (a) Bright-field TEM image of a Na_xCoO_2 film on a sapphire substrate. The white line in the middle of the film corresponds to a thin layer of Na-rich amorphous material. (b) SAED pattern from the film. (c) SAED pattern corresponding to the substrate.

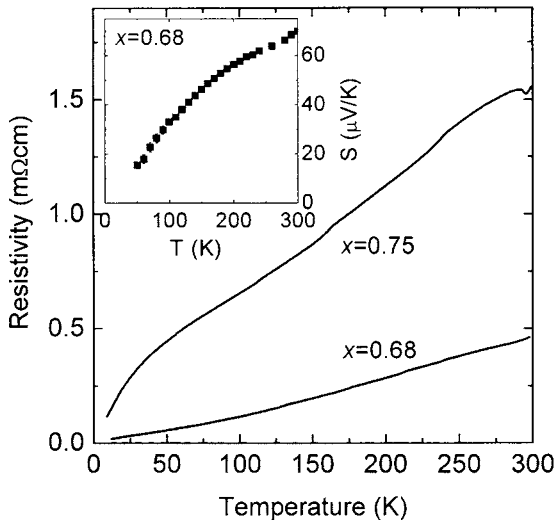

FIG. 4. Resistivity vs temperature curves for two Na_xCoO_2 films with different Na concentrations. Inset: Thermopower vs temperature for a Na_xCoO_2 film with $x=0.68$.

planes in the thin film, consistent with high-resolution TEM observations of waviness in the Na_xCoO_2 lattice planes. Details of the microstructure investigation of the Na_xCoO_2 films will be published elsewhere.

The Na concentration of the Na_xCoO_2 films depends on the powder used for the annealing. At 800 °C, the equilibrium vapor pressure is 0.155 Torr for $NaHCO_3$ and 444 Torr for $NaOOCCH_3$. EDS measurements show that the Na concentration is always $x=0.68\pm0.03$ for films annealed in $NaHCO_3$. The x value in films annealed in $NaOOCCH_3$ depends on the annealing conditions, and for the optimized condition given above (800 °C for 2.5 h) $x=0.75\pm0.02$. Figure 4 shows the resistivity versus temperature curves of two Na_xCoO_2 films with different Na concentrations. The temperature dependence for the film annealed in $NaOOCCH_3$, marked by "$x=0.75$," is characteristic of bulk and single-crystal Na_xCoO_2 samples with $x=0.75$.[3,12] The downturn at low temperatures has been attributed to a phase transition to an antiferromagnetic spin-density wave.[13] The resistivity behavior of the film annealed in $NaHCO_3$, marked by "$x=0.68$," is consistent with single crystals with lower Na concentrations.[3] The inset to Fig. 4 shows the thermopower, S, versus temperature for a film with $x=0.68$. A temperature gradient was generated by a resistive heater attached on one end of the film while the other end was mounted on a cold finger. A pair of type-E (chrome-constantan) thermocouples and a pair of 25 μm gold wires were used to measure the temperature gradient and the difference of electric potential, respectively, to obtain the thermoelectric power. The magnitude of S at 300 K, as well as the overall temperature dependence shown in the figure, is consistent with the result from the in-plane measurement of single crystals with $x=0.7$.[9] These results further confirm the Na concentration measurements by EDS.

In conclusion, epitaxial thin films of Na_xCoO_2 were prepared by annealing PLD-grown epitaxial Co_3O_4 films in Na vapor. The Na compounds used during annealing, $NaHCO_3$ and $NaOOCCH_3$, have different Na vapor pressures, resulting in Na_xCoO_2 films of two different Na concentrations. The topotaxial conversion led to a poorer crystallinity in the Na_xCoO_2 films than in Co_3O_4 films. Nevertheless, the films are c-axis oriented with in-plane alignment with the substrate. The temperature dependent transport properties are distinctly different for films of different Na concentrations, and they are consistent with the bulk results. Our results demonstrate that some degree of control of the Na concentration in the Na_xCoO_2 films can be achieved by using Na compounds of different vapor pressures during annealing.

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