Kinetically-controlled thin-film growth of layered $\beta$- and $\gamma$-$Na_xCoO_2$ cobaltate

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Abstract

We report growth characteristics of epitaxial $\beta$-$Na_{0.6}CoO_2$ and $\gamma$-$Na_{0.7}CoO_2$ thin films on (001) sapphire substrates grown by pulsed-laser deposition. Reduction of deposition rate could change structure of $Na_xCoO_2$ thin film from $\beta$-phase with island growth mode to $\gamma$-phase with layer-by-layer growth mode. The $\gamma$-$Na_{0.7}CoO_2$ thin film exhibits spiral surface growth with multiterraced islands and highly crystallized texture compared to that of the $\beta$-$Na_{0.6}CoO_2$ thin film. This heterogeneous epitaxial film growth can give opportunity of strain effect of physical properties and growth dynamics of $Na_xCoO_2$ as well as subtle nature of structural change.
Families of sodium cobalt oxide $\text{Na}_x\text{CoO}_2$ are attractive materials due to their large thermoelectric power and low resistivity, which can be applied for thermoelectric applications.\(^1,2\) The large thermoelectric power is attributed to the spin entropy from the low-spin state of Co ion.\(^3\) Occurrence of superconductivity of $\text{Na}_{0.35}\text{CoO}_2\cdot1.3\text{H}_2$ with $T_C$ about 5 K and rich phase diagrams of $\text{Na}_x\text{CoO}_2$ with respect to $x$ also inspire many theoretical and experimental interests of novel ground states due to its two-dimensional transition-metal oxide triangular lattice.\(^4\)

Until now, physical properties of single crystal and powder of $\text{Na}_x\text{CoO}_2$ have been widely studied\(^5, 6, 7, 8, 9\) but there have been no rigorous reports about thin film studies of $\text{Na}_x\text{CoO}_2$. Since the thin film is interesting in its own due to strain effect as well as the fact that most application can be done in thin film structure, the thin film growth of $\text{Na}_x\text{CoO}_2$ can give an opportunity of manipulation of physical properties by changing strain field using different substrates and growth parameters (substrate temperature, oxygen partial pressure, etc). In this study, we report the thin film growth of differently structured epitaxial $\text{Na}_x\text{CoO}_2$ by Pulsed Laser Deposition (PLD) on (001) sapphire.

The crystal structure of $\text{Na}_x\text{CoO}_2$ consists of two-dimensional triangular $\text{CoO}_2$ layers of edge-sharing $\text{CoO}_6$ octahedra separated by an insulating layer of $\text{Na}^+$ ions. There are four known phases of $\text{Na}_x\text{CoO}_2$ with slightly different structures such as $\alpha$-, $\alpha'-$, $\beta$-, and $\gamma$- phases of $\text{Na}_x\text{CoO}_2$ distinguished by stacking order of $\text{CoO}_2$ layers and $\text{Na}-\text{O}$ environments. Figure 1 shows schematic structures of $\beta$-$\text{Na}_x\text{CoO}_2$ and $\gamma$-$\text{Na}_x\text{CoO}_2$ in a-c plane. The $\beta$-phase has a monoclinic unit cell with a space group symmetry of $C2/m$ and lattice constants of $a = 4.902$, $b = 2.828$, $c = 5.720$ Å and $\beta = 105.96^\circ$. The $\gamma$-phase has a hexagonal structure with a space group symmetry of $P6_3/mmc$ and lattice constants of $a = 2.840$ and $c = 10.811$ Å.\(^10, 11, 12\) In $\gamma$-$\text{Na}_x\text{CoO}_2$, in-plane direction of $\text{CoO}_6$ octahedron in $\text{CoO}_2$ layer is alternating with the nearest $\text{CoO}_2$ layers, whereas, in $\beta$-$\text{Na}_x\text{CoO}_2$, the direction is parallel with the nearest $\text{CoO}_2$ layers. These structural varieties of $\text{Na}_x\text{CoO}_2$ imply that the bulk modulus along the plane is small and the stress is an important parameter for the growth of the epitaxial thin films because of various possible stacking structures of $\text{CoO}_2$ layer and possibility of stacking fault as seen in bulk $\text{Na}_x\text{CoO}_2$.

$\text{Na}_x\text{CoO}_2$ thin films have been grown by PLD method. The $\text{Na}_{0.8}\text{CoO}_2$ target, which was used in PLD, was prepared by a conventional solid-state reaction method. $\text{Na}_2\text{CO}_3$ (99.995 %) and $\text{Co}_3\text{O}_4$ (99.998 %) were mixed in molar ratio of $\text{Na} : \text{Co} = 0.8 : 1.0$ and the mixed
powder was pressed into pellet and calcined at 750°C for 12 h. The calcined pellet was reground, pressed into pellet, and sintered at 850°C for 24 h. (001) sapphire substrate was used for the thin film growth and the substrate temperature of optimal thin film growth was 480°C. A frequency tripled (355 nm, ~ 2 J/cm²) Nd:YAG laser was used for the deposition and the distance between target and substrate was ~ 4 cm. The deposition rates in the range of 0.02 ~ 0.2 Å/pulse were controlled by repetition of laser pulse and an eclipse method, in which a shadow mask was placed between the target and the substrate. The energy of an adatom was reduced by the eclipse method because direct high-energy particles would be rejected by the shadow mask. Optimal oxygen pressure of 400 mTorr was maintained during the deposition.

The γ-Na₀.₇CoO₂ thin film was grown with layer-by-layer growth mode by the low deposition rate of 0.02 Å/pulse using the eclipse method on (001) sapphire substrates. When the deposition rate was increased, the mixed phase of β- and γ-NaₓCoO₂ was observed. By the condition of the high deposition rate of 0.2 Å/pulse, only the β-Na₀.₆CoO₂ thin film was grown with island growth mode. For the structural determinations of β- and γ-NaₓCoO₂ thin films, x-ray diffraction data were obtained by conventional laboratory x-ray as well as synchrotron x-ray sources at 5C2 in Pohang Light Source. The thicknesses of β- and γ-NaₓCoO₂ thin films were ~1000 and ~2000 Å, respectively, determined from the cross-sectional images of scanning electron microscope (SEM). The tentative compositions of β-Na₀.₆CoO₂ and γ-Na₀.₇CoO₂ were obtained by energy dispersive x-ray spectrometer (EDS). The surface morphologies and topographies of β-Na₀.₆CoO₂ and γ-Na₀.₇CoO₂ thin films were observed by SEM and atomic force microscope (AFM).

Figure 2 (a) shows the x-ray diffraction pattern of the epitaxially grown (00l) β-Na₀.₆CoO₂ thin film on (001) sapphire substrate. The full width at half maximum (FWHM) of the (001) rocking curve is about 1.4°. The out-of-plane lattice constant of 5.459 Å was obtained from the (00l) peaks and this value is slightly smaller than that of bulk β-NaₓCoO₂. To check the in-plane orientation, we performed x-ray scattering with Φ-scan geometry. Figure 2 (b) shows Φ-scan of (112) peak of β-Na₀.₆CoO₂ thin film and (104) peak of the sapphire substrate. The (112) peaks of β-Na₀.₆CoO₂ thin film are located 30° off from the (104) plane of sapphire substrate. The sixfold symmetry of (112) peaks from the twinned grains is observed, representing that the a-lattice of β-Na₀.₆CoO₂ thin film is oriented along the hexagonal symmetry of a-axis lattice of (001) sapphire substrate. The FWHM of in-plane
(\overline{1}12) peak is equal to 1.3°. From the 2θ values of the (111) and the (\overline{1}12) peaks, we obtain a monoclinic a-axis lattice constant of 4.886 Å and b-axis lattice constant of 2.818 Å that are close to the bulk lattice constant (a = 4.902, b = 2.828 Å) of β-Na0.6CoO2. To check a strain of the film, h, k, and l scans near the (\overline{1}12) plane were performed. The data indicated that the strain along the in-plane direction was low estimated from the small FWHM of h, k scans and the strain along the out-of-plane direction was high resulting from the large FWHM of l scan. To investigate the growth rate effects, we have grown NaxCoO2 thin film on (001) sapphire substrates using the same target with the low deposition rate of 0.02 Å/pulse by the eclipse method.

Figure 3 (a) shows the x-ray diffraction pattern of the epitaxially grown (00l) γ-Na0.7CoO2 thin film on (001) sapphire substrate. The FWHM of the (002) rocking curve is about 0.8° and this FWHM of γ-Na0.7CoO2 thin film is smaller than that of β-Na0.6CoO2 thin film, indicating that the (00l) γ-Na0.7CoO2 thin film shows better crystallized texture along the out-of-plane direction. The c-lattice constant of 10.848 Å was obtained from the (002) peak. Figure 3 (b) shows Φ-scan of (104) peak of the epitaxial γ-Na0.7CoO2 thin films and (104) peak of the (001) sapphire substrate. The sixfold symmetry represents the hexagonal structure of γ-Na0.7CoO2 thin film with twins. The FWHM of in-plane (104) peak is equal to 0.6° and this indicates that the γ-Na0.7CoO2 thin film also shows better crystallized texture along the in-plane direction than that of the β-Na0.6CoO2 thin film. From the 2θ value of (104) peak, we obtain a hexagonal a-axis lattice constant of 2.812 Å that is similar to the bulk γ-Na0.7CoO2. Thus, γ-Na0.7CoO2 film grown by the low deposition condition shows better-crystallized texture both in-plane and out-of-plane direction.

Figure 4 (a) and (b) show the AFM images of epitaxial β-Na0.6CoO2 and γ-Na0.7CoO2 thin films, respectively. The large grains with typical tetrahedral islands are observed in β-Na0.6CoO2 thin film. The shape indicates that the diffusion length along the surface is short during deposition and the kinetics of the step is limited locally resulting from the high deposition rate. The root mean square (rms) surface roughness has the large value of 220 Å (Figure 4 (c) and (d)). However, the spiral patterns with multi-terraces are observed in γ-Na0.7CoO2 thin film, and this indicates that epitaxial γ-Na0.7CoO2 thin film was grown with atomically flat surface by monolayer steps. The surface roughness of γ-Na0.7CoO2 thin film is extremely smooth with the rms roughness of 8 Å. Figure 4 (e) and (f) show the sectional contour graphs of the #1-line and the #2-line in γ-Na0.7CoO2 thin film. The large
terraces with a width of 1000 ∼ 2000 Å are observed and the terrace heights are nearly half or same of one lattice unit along the c-axis. This large width of the terraces represents that the surface diffusion of adatoms along the surface is long enough and the kinetics of the step is widespread due to the low deposition rate inhibiting from frequent nucleation of adatoms [13]. Therefore, γ-Na0.7CoO2 thin film shows layer-by-layer growth following the ideal step flow growth mode, closely.

In conclusion, we have grown the epitaxial β-Na0.6CoO2 and γ-Na0.7CoO2 thin films on the (001) sapphire substrate deposited by PLD method. On the low deposition rate of 0.02 Å/pulse, the γ-Na0.7CoO2 thin film was grown with layer-by-layer growth. When a deposition rate was increased, a mixed phase of β- and γ-Na2CoO2 was observed. By the condition of the high deposition rate of 0.2 Å/pulse, the β-Na0.6CoO2 thin film was grown with tetrahedral islands. The γ-Na0.7CoO2 thin film exhibits spiral surface growth with multi-terraces and highly crystallized texture. These experimental demonstrations and controllability could provide opportunities of strain effects of Na2CoO2 and physical properties of thin films and growth dynamics of heterogeneous epitaxial thin films.

This work was supported by Korea Research Foundation Grant. (KRF-2004-005-C00045).
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FIG. 1: Schematic structures of $\beta$-$\text{Na}_x\text{CoO}_2$ and $\gamma$-$\text{Na}_x\text{CoO}_2$. Rhombus and filled circle symbolizes a CoO$_6$ octahedron and Na ions, respectively. $\beta$-$\text{Na}_x\text{CoO}_2$ has a monoclinic structure with $\beta = 105.96^\circ$. In $\gamma$-$\text{Na}_x\text{CoO}_2$, in-plane direction of CoO$_6$ octahedron in CoO$_2$ layer has the opposite direction of in-plane direction of CoO$_6$ octahedron in the nearest CoO$_2$ layers.

FIG. 2: (a) X-ray diffraction pattern of the epitaxial $\beta$-$\text{Na}_{0.6}\text{CoO}_2$ thin films. (b) $\Phi$-scan of (112) peaks of the epitaxial $\beta$-$\text{Na}_{0.6}\text{CoO}_2$ thin films and (104) peaks of (001) sapphire substrate.
FIG. 3: (a) X-ray diffraction pattern of the epitaxial $\gamma$-Na$_{0.7}$CoO$_2$ thin films. (b) $\Phi$-scan of (104) peaks of the epitaxial $\gamma$-Na$_{0.7}$CoO$_2$ thin films and (104) peaks of (001) sapphire substrate.
FIG. 4: AFM images of (a) $\beta$-Na$_{0.6}$CoO$_2$ thin film and (b) $\gamma$-Na$_{0.7}$CoO$_2$ thin film. Sectional contour graph of (c) the #1-line in $\beta$-Na$_{0.6}$CoO$_2$ thin film, (d) the #2-line in $\beta$-Na$_{0.6}$CoO$_2$ thin film, (e) the #1-line in $\gamma$-Na$_{0.7}$CoO$_2$ thin film, (f) the #2-line in $\gamma$-Na$_{0.7}$CoO$_2$ thin film. The $\gamma$-Na$_{0.7}$CoO$_2$ thin film shows spiral surface growth with multi-terraces. The terrace heights in (e) and (f) are nearly half or same of one lattice unit.