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Stress dependence of growth mode change of epitaxial layered cobaltite γ-$Na_{0.7}CoO_2$

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Abstract

We report stress dependence of growth characteristics of epitaxial γ-$Na_{0.7}CoO_2$ films on various substrates deposited by pulsed laser deposition method. On the sapphire substrate, the γ-$Na_{0.7}CoO_2$ thin film exhibits spiral surface growth with multi-terraces and highly crystallized texture. For the γ-$Na_{0.7}CoO_2$ thin film grown on the (1 1 1) $SrTiO_3$ substrate, the nano-islands of ~30 nm diameter on the hexagonal grains are observed. These islands indicate that the growth mode changes from step-flow growth mode to Stranski–Krastanow (SK) growth mode. On the (1 1 1) MgO substrate, the large grains formed by excess adatoms covering an aperture between hexagonal grains are observed. These experimental demonstrations and controllability could provide opportunities of strain effects of Na_xCoO_2, physical properties of thin films, and growth dynamics of heterogeneous epitaxial thin films.

Keywords: Thermoelectric material; Growth mode; Epitaxial thin film; Na_xCoO2

1. Introduction

Recently, families of sodium cobalt oxide Na_xCoO_2 have been widely researched for thermoelectric application due to their large thermoelectric power and low resistivity [1–3]. Since Na_xCoO_2 has the triangular lattice of Co ion and the low-spin state of Co ion which exist in a $Co^{3+}(S = 0)$ or $Co^{4+}(S = 1/2)$ state depending on an amount Na^+ ion, it is interesting in Na_xCoO_2 system that the CoO_2 layer of Na_xCoO_2 can exhibit an interesting physical phenomena of frustration and spin liquid state [4]. In addition, rich phase diagram of Na_xCoO_2 with respect to x also shows various physical properties of paramagnetic metal, charge-ordered insulator, Curie–Weiss metal, spin density wave metal, superconductor of $Na_{0.35}CoO_2\cdot 1.3H_2O$ with T_C about 5 K [5–7].

Single crystal and powder samples of Na_xCoO_2 have been widely studied and have given the significant physical property and information of Na_xCoO_2 system [8–10]. For the case of thin film sample, strain effect can vary physical property and can be controlled by growth parameters such as substrate, deposition rate, substrate temperature, oxygen partial pressure, etc. Understanding the growth of heterogeneous thin films has also been an important subject since many technically important applications have these structures. We have controlled the epitaxial β- and γ-Na_xCoO_2 thin films on (0 0 1) sapphire substrates by the control of the deposition rate and have observed the change of the growth mode [11]. The β-phase has a monoclinic unit cell with a space group symmetry of $C2/m$ and lattice constants of $a = 0.490$, $b = 0.283$, $c = 0.572$ nm and $\beta = 105.96^\circ$. The γ-phase has a hexagonal structure with a space group symmetry of $P6_3/mmc$ and lattice constants of $a = 0.284$ and $c = 1.081$ nm [12–14]. In this study, we report the stress dependence of growth mode change of epitaxial layered cobaltite γ-$Na_{0.7}CoO_2$ by pulsed laser deposition (PLD) on (0 0 1) sapphire, (1 1 1) $SrTiO_3$ and (1 1 1) MgO substrates. By changing (0 0 1) sapphire substrate to (1 1 1) $SrTiO_3$ and (1 1 1) MgO substrates, the growth dynamics and morphology of the thin films completely changed, which emphasizes the importance of strain field on the growth of the layered compound of Na_xCoO_2. Therefore, Na_xCoO_2 thin films can be an interesting example to study

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growth dynamics of heterogeneous epitaxial thin film with low bulk modulus along the CoO_2 layer.

2. Experiment

Na_xCoO_2 thin films have been grown by PLD method. The (0 0 1) sapphire, (1 1 1) $SrTiO_3$ and (1 1 1) MgO substrates were 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/cm^2) Nd:YAG laser was used for the deposition and the distance between target and substrate was ~4 cm. The deposition rate of 0.002 nm/pulse was obtained by 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 to ensure the same growth condition on various substrates. The thickness of γ-Na_xCoO_2 thin films was ~100 nm determined by the cross-sectional images of scanning electron microscope (SEM). The tentative composition of γ-$Na_{0.7}CoO_2$ was obtained by energy dispersive X-ray spectrometer (EDS). The surface morphologies and topographies of γ-$Na_{0.7}CoO_2$ thin films were observed by SEM and atomic force microscope (AFM).

For the γ-$Na_{0.7}CoO_2$ thin films with thicknesses of 0.1, 2, 20 and 100 nm, in the early stage of the thickness of 0.1 nm, circular nanocrystals were observed for the nucleation of $Na_{0.7}CoO_2$. At the thickness of 2 nm, triangular islands indicating hexagonal crystal nature of γ-$Na_{0.7}CoO_2$ thin film were observed. At the thickness of 20 nm, the size of this triangular island increased with film thickness and the spaces between the triangular islands decreased with film thickness. At the thickness of 100 nm, the spiral patterns with multi-terraces were observed and there are no spaces between the grains. In this thickness range, γ-$Na_{0.7}CoO_2$ thin film showed step-flow growth mode with atomically flat surface.

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of the epitaxially grown (0 0 1) γ-$Na_{0.7}CoO_2$ thin film on (0 0 1) sapphire, (1 1 1) $SrTiO_3$ and (1 1 1) MgO substrates. There are sharp narrow peaks indicating a large grain size at the $\theta - 2\theta$ scans. The six-fold symmetry is observed at the Φ-scans and this represents the hexagonal structure of γ-$Na_{0.7}CoO_2$ thin film with

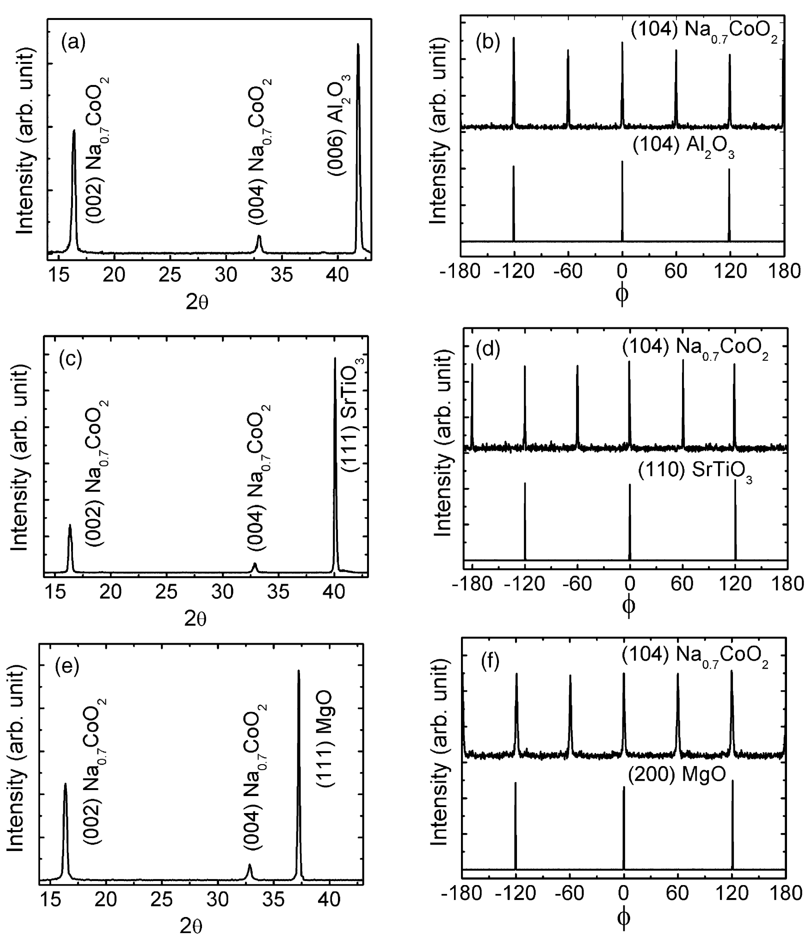

Fig. 1. (a) X-ray diffraction pattern of the epitaxial γ-$Na_{0.7}CoO_2$ thin film grown on the Sapphire substrate. (b) Φ-scan of (1 0 4) peaks of the epitaxial γ-$Na_{0.7}CoO_2$ and (1 0 4) peaks of (0 0 1) sapphire substrate. (c) X-ray diffraction pattern of the epitaxial γ-$Na_{0.7}CoO_2$ thin film grown on the (1 1 1) $SrTiO_3$ substrate. (d) Φ-scan of (1 0 4) peaks of the epitaxial γ-$Na_{0.7}CoO_2$ and (1 1 0) peaks of (1 1 1) $SrTiO_3$ substrate. (e) X-ray diffraction pattern of the epitaxial γ-$Na_{0.7}CoO_2$ thin film grown on the (1 1 1) MgO substrate. (f) Φ-scan of (1 0 4) peaks of the epitaxial γ-$Na_{0.7}CoO_2$ and (2 0 0) peaks of (1 1 1) MgO substrate.