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Topotactic Reductive Synthesis of *A*-site Cation-Ordered Perovskite $YBaCo_2O_x$ (x = 4.5−5.5) Epitaxial Thin Films

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Abstract

***A*-site cation-ordered perovskite $YBaCo_2O_x$ epitaxial films were synthesized via a combination of pulsed-laser deposition and topotactic reduction method. The oxygen contents (x) of the films could be varied in a range of x = 4.5−5.5 by changing the reduction reaction temperatures. The *c*-axis length and resistivity of the $YBaCo_2O_x$ films decreased with decreasing x at x > 5.0, while those drastically increased at x ~ 4.5. We also found that the metal insulator transition was substantially suppressed in the film with x ~ 5.5 due to the epitaxial strain effect.**

1. Introduction

A-site cation-ordered perovskite cobaltites, $RBaCo_2O_x$ (R = rare earth element), have attracted great attention because of their intriguing features, such as colossal magnetoresistance, spin-crossover, and anisotropic character [1]. Such physical properties of the cobaltites are widely controllable through variations of the rare earth element, cell parameter, and particularly oxygen content (x), although the allowable oxygen content range in a conventional high-temperature synthesis is limited [2]. Recently, low-temperature topotactic synthesis was developed to expand the oxygen range. For example, $YBaCo_2O_{4.5}$ can be obtained by reacting $YBaCo_2O_5$ with a reducing agent of NaH at 210°C, while the conventional synthesis methods produce $YBaCo_2O_x$ with $5.0 \leq x \leq 5.54$ [2,3]. The expansion of x range would result in wider variation of conductivity. However, the transport properties of $YBaCo_2O_x$ have not been systematically studied owing to the difficulty in measuring intrinsic resistivity values of powder specimens. In this study, we fabricated $YBaCo_2O_x$ (x = 4.5−5.5) epitaxial thin films using pulsed-laser deposition (PLD) and topotactic reduction methods, and investigated their lattice parameters and transport properties as a function of oxygen content x.

2. Experimental

A-site cation-ordered perovskite $YBaCo_2O_x$ precursor films were grown on $SrTiO_3$(001) (STO) substrates by PLD technique, using a KrF eximer laser. The substrate temperature and oxygen partial pressure were kept at 900−950°C and 200 mTorr, respectively, during each deposition run. The obtained precursor films were further subjected to topotactic reduction by using CaH_2 at reaction temperature (T_r) of 100−400°C for 24 h in an evacuated Pyrex tube. Crystal structures were characterized by X-ray diffraction (XRD) measurement using Cu-$K\alpha$ radiation. The chemical composition of the films was evaluated by using energy dispersive X-ray spectrometry (EDS). In-plane resistivity (ρ) of the films was measured by using a four- and two-probe methods with Au electrodes.

3. Results and Discussion

Figure 1 shows the 2θ–θ XRD pattern of the precursor $YBaCo_2O_x$ film, indicating that the film has *c*-axis-oriented *A*-site cation-ordered perovskite structure. From EDS measurement, the oxygen content (x) is roughly estimated to be x ~ 5.5. Thus, the precursor film on STO substrate can be regarded as layer stacking of $[YO_{0.5}]$ – $[CoO_2]$ – [BaO] – $[CoO_2]$, as illustrated in the inset of Fig. 1. Reciprocal space mapping measurement confirmed that the precursor film was grown coherently on STO substrate, and had pseudo tetragonal lattice with $a/2 = b$ = 3.905 Å and c = 7.485 Å, while bulk $YBaCo_2O_{5.5}$ is reported to have orthorhombic lattice with $a/2$ = 3.923 Å, b = 3.819 Å and c = 7.516 Å [2]. Notably, the film has smaller out-of-plane (*c*-axis) length and larger in-plane area ($S = a/2 \times b$ = 15.25 Å^2) than bulk $YBaCo_2O_{5.5}$ (S = 14.98 Å^2). These results indicate that the film is affected by tensile-like strain from the substrate.

After the reaction with CaH_2 at T_r = 200°C, the XRD peaks shifted toward lower diffraction angle, as shown in Fig. 1. This suggests that the oxygen vacancies are introduced into the film without changing the cation framework during the reaction. Figure 2 shows the x values and lattice parameters of the precursor and CaH_2-treated $YBaCo_2O_x$ films, evaluated by EDX and XRD measurements, respectively. The x value decreased with T_r, indicating that CaH_2 worked well as a reducing reagent. Below T_r = 125°C, x was in the range of 5.0 to 5.5, and the *c*-axis length decreased with decreasing x, similar to the case of bulk $YBaCo_2O_x$ ($5.0 \leq x \leq 5.5$) [2]. At T_r = 200−350°C, x was suppressed to ~4.5, and the *c*-axis length significantly increased to 7.608 Å, which is close to the $c \cdot \sin\beta$ (= 7.599 Å) value for bulk $YBaCo_2O_{4.5}$ [3]. The film became amorphous after higher temperature treatment (T_r = 400°C).

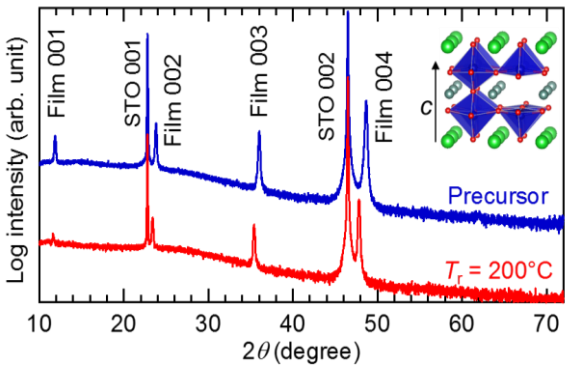

Fig. 1 2θ–θ X-ray diffraction patterns of the precursor and CaH_2-treated $YBaCo_2O_x$ films. The inset shows crystal structure of $YBaCo_2O_{5.5}$, where Y and Ba atoms are drawn as gray and green spheres, respectively.

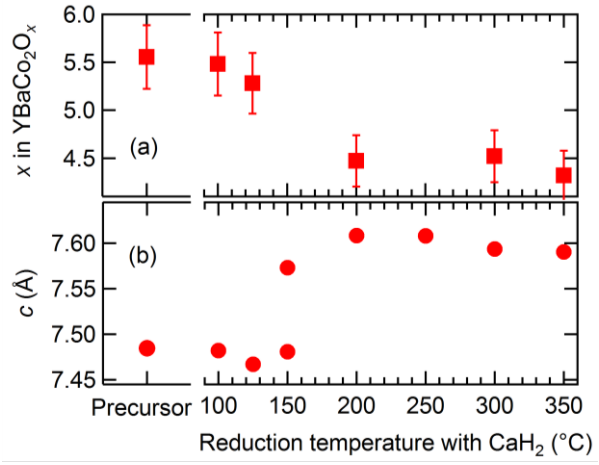

Fig. 2 (a) oxygen contents and (b) c-axis lengths for the precursor and CaH_2-treated $YBaCo_2O_x$ films.

Figure 3 shows the resistivity versus temperature (ρ–T) curves for the precursor (x ~ 5.5), CaH_2-treated films at T_r = 125°C (x ~ 5.3) and T_r = 250°C (x ~ 4.5), and bulk $YBaCo_2O_{5.5}$. The precursor $YBaCo_2O_{5.5}$ film shows semiconducting behavior ($d\rho/dT < 0$) below 380 K, in contrast to bulk $YBaCo_2O_{5.5}$ which undergoes metal-insulator transition (MIT) at 297 K [2]. In case of bulk $YBaCo_2O_{5.5}$, large change in lattice parameters is considered to be an important factor driving the MIT [2]. Therefore, this difference in conductivity between bulk and film is probably due to the epitaxial lattice strain effect in the film. After the CaH_2–treatment at T_r = 125°C, the ρ value decreased from 5.1×10^{-3} to 9.8×10^{-4} Ωcm at 300 K, possibly because generated oxygen vacancies supply conduction electrons, as reported in bulk $GdBaCo_2O_x$ with $5.0 \le x \le 5.5$ [1]. On the other hand, the $YBaCo_2O_{4.5}$ film prepared at T_r = 200°C shows insulating behavior with the higher ρ value, reflecting the change in Co oxidation state from 2+/3+ to 2+.

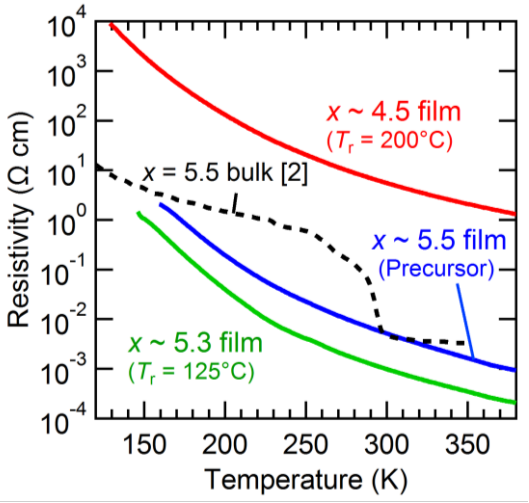

Fig. 3 ρ-T curves of the $YBaCo_2O_x$ (x ~ 4.5, 5.3 and 5.5) films and bulk $YBaCo_2O_{5.5}$. Data of the bulk is cited from ref. 2.

4. Conclusions

We successfully fabricated $YBaCo_2O_x$ (x = 4.5−5.5) epitaxial thin films with *A*-site cation-ordered perovskite structure by using PLD and topotactic reduction methods. The $YBaCo_2O_{5.5}$ precursor film shows semiconducting behavior, in contrast to bulk which exhibits MIT, owing to the epitaxial strain effect. The resistivity and the *c*-axis length of the $YBaCo_2O_x$ films decreased with decreasing x at x > 5.0, while those increased at x ~ 4.5.

Acknowledgements

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