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Epitaxial Film Growth and Superconducting Behavior of Sodium–Cobalt Oxyhydrate, $Na_xCoO_2\cdot yH_2O$ ($x \sim 0.3$, $y \sim 1.3$)

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We have developed a unique multistep film growth technique, combining reactive solid-phase epitaxy (R-SPE) with an intercalation process, to fabricate epitaxial films of superconducting sodium–cobalt oxyhydrate, $Na_{0.3}CoO_2\cdot 1.3H_2O$. An epitaxial film of $Na_{0.8}CoO_2$ grown on an α-Al_2O_3(0001) substrate by R-SPE was subjected to oxidation and hydration treatment, leading to the formation of a $Na_{0.3}CoO_2\cdot 1.3H_2O$ epitaxial film. The film exhibited metallic electrical resistivity with a superconducting transition at 4 K, similar to that of bulk single crystals. The present technique is suitable and probably the only method for the epitaxial growth of superconducting $Na_{0.3}CoO_2\cdot 1.3H_2O$.

Since the discovery of superconducting sodium−cobalt oxyhydrate, $Na_{0.3}CoO_2\cdot 1.3H_2O$ (superconducting transition temperature, $T_c \sim 4$ K)[1] in 2003, a number of researchers have worked hard to clarify the mechanism for the emergence of the superconductivity.[2−14] A high-quality epitaxial film of $Na_{0.3}CoO_2\cdot 1.3H_2O$ may play a complementary role to the bulk single crystal in understanding the chemical and physical properties of this material; moreover, the film is more favorable for particular applications. However, the growth of an epitaxial film of $Na_{0.3}CoO_2\cdot 1.3H_2O$ has not been successful so far most likely because of the complicated crystal structure and difficulty in controlling the film composition.

A $Na_{0.3}CoO_2\cdot 1.3H_2O$ crystal (space group $P6_3/mmc$, $a = 0.2823$ nm, $c = 1.9621$ nm)[1] has an extremely complicated layered crystal structure, composed of CoO_2^-, Na^+, and H_2O layers stacked along the [0001] direction.[15] Moreover, it contains volatile chemical species of Na and H_2O, which make the use of conventional high-temperature vapor-phase-epitaxy methods such as sputtering, molecular beam epitaxy, and pulsed-laser deposition (PLD) almost impossible for the fabrication of epitaxial films because of extremely large differences in vapor pressure among Na and/or H_2O and Co.

To overcome these difficulties, we have separated the entire growth process into three elementary steps: (1) the reactive solid-phase epitaxy (R-SPE) process, which is particularly suited for the growth of layered compounds,[16−20]

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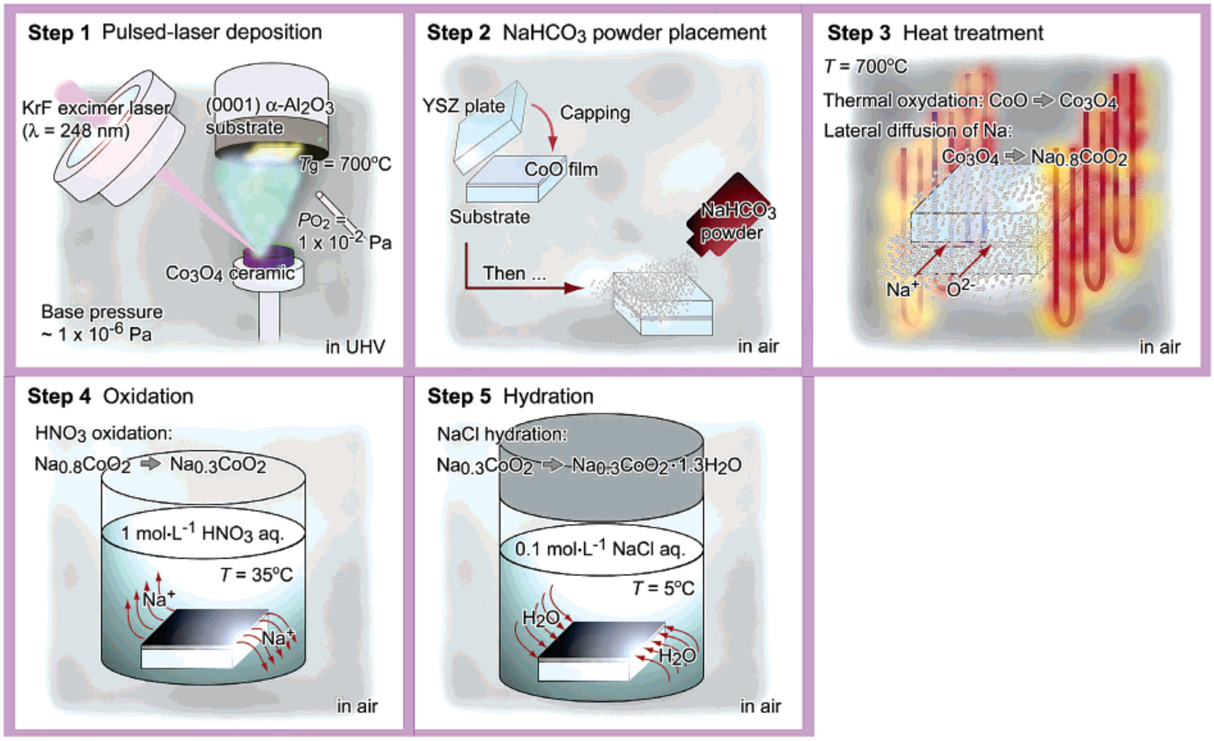

Figure 1. Schematic of the fabrication process for a $Na_{0.3}CoO_2 \cdot 1.3H_2O$ epitaxial film. Step 1: Pulsed-laser deposition of a highly (111)-oriented epitaxial film of CoO on the (0001) face of an α-Al_2O_3 substrate. Step 2: Surface capping by a YSZ, single-crystal plate and placement of a $NaHCO_3$ powder on the YSZ plate. Step 3: Heat treatment of the film at 700 °C in air. Step 4: Oxidation treatment of the film in a 1 mol·L^{-1} HNO_3 aqueous solution (35 °C) for 5 min. Step 5: Hydration treatment of the film in a 0.1 mol·L^{-1} NaCl aqueous solution (5 °C) for 5 h.

to prepare $Na_{0.8}CoO_2$,[21] (2) the oxidation process to convert $Na_{0.8}CoO_2$ to $Na_{0.3}CoO_2$, and (3) the hydration process to introduce H_2O into $Na_{0.3}CoO_2$. Using this multistep film growth technique, we have successfully grown $Na_{0.3}CoO_2 \cdot 1.3H_2O$ films on the (0001) face of α-Al_2O_3 substrates. The films were confirmed to have grown epitaxially on the substrate by X-ray diffraction (XRD), and electrical conductivity measurements revealed that the films become superconducting with a T_c value of ~4 K, which reasonably agrees with the value reported for the single crystal.

The method of fabricating $Na_{0.3}CoO_2 \cdot 1.3H_2O$ epitaxial films is schematically illustrated in Figure 1. **Step 1**: An epitaxial film of (111)-oriented CoO was grown on the (0001) face of an α-Al_2O_3 substrate (10 mm × 10 mm × 0.5 mm^t) at 700 °C by the PLD method using a Co_3O_4 sintered disk as a target. **Step 2**: The surface of the PLD-deposited CoO film was fully capped by a Y_2O_3-stabilized ZrO_2 (YSZ), single-crystal plate (10 mm × 10 mm × 0.5 mm^t) to keep the surface of the film clean. Then, $NaHCO_3$ powder was put on the YSZ plate. **Step 3**: The capped film was annealed at 700 °C for 1 h in air, after which epitaxial films of $Na_{0.8}CoO_2$ [21] were obtained. **Step 4**: The $Na_{0.8}CoO_2$ epitaxial film was immersed in a 1 mol·L^{-1} HNO_3 aqueous solution[22] at 35 °C for 5 min to convert the film into a $Na_{0.3}CoO_2$ film. **Step 5**: Finally, the $Na_{0.3}CoO_2$ film was immersed in a 0.1 mol·L^{-1} NaCl aqueous solution for 5 h at 5 °C to introduce H_2O molecules to the film.

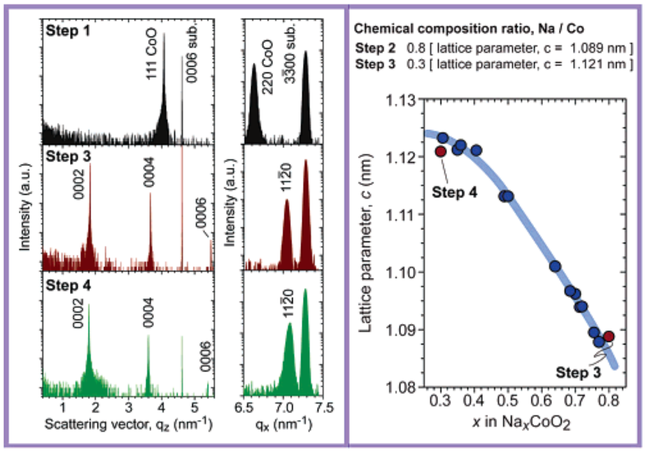

Figure 2. (Left panel) Out-of-plane and in-plane Bragg XRD patterns for the films obtained at steps 1, 3, and 4, respectively. Epitaxial films of CoO, $Na_{0.8}CoO_2$, and $Na_{0.3}CoO_2$ were obtained at steps 1, 3, and 4, respectively. (Right panel) Change in the lattice parameter of the Na_xCoO_2 films obtained at steps 3 and 4 as a function of the Na content, *x*. Values of powder and crystal from refs 1, 2, 6, and 7 are also plotted for comparison.

Figure 2 (left panel) shows out-of-plane and in-plane Bragg XRD (Cu Kα_1, ATX-G, Rigaku Co.) patterns[23] for the films after steps 1, 3, and 4, respectively, demonstrating that the PLD-grown (111)-oriented CoO epitaxial film (step 1) was converted into a (0001)-oriented Na_xCoO_2 epitaxial film by

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(22) When the R-SPE-grown $Na_{0.8}CoO_2$ epitaxial film was treated with a Br_2 solution, almost all Na^+ ions in the $Na_{0.8}CoO_2$ lattice were deintercalated during the Br_2 treatment. After that, we immersed the film into distilled water to introduce H_2O and/or H_3O^+ into the lattice. As a result, the crystal structure was decomposed into $Co(OH)_2$. Therefore, we judged that a Br_2−water treatment is not appropriate for our epitaxial film.

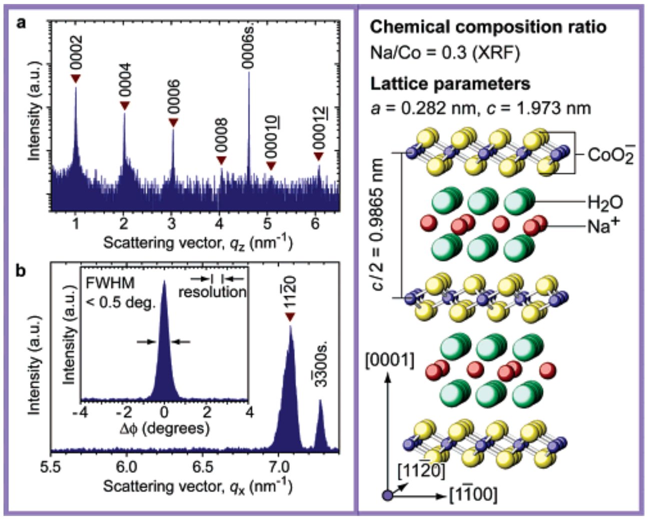

Figure 3. (Left panel) Out-of-plane (a) and in-plane (b) Bragg XRD patterns of the film obtained at step 5. Intense Bragg peaks of 000*l* $Na_{0.3}CoO_2{\cdot}1.3H_2O$ are seen together with 006 α-Al_2O_3 in part a. Only the intense Bragg peak of $11\bar{2}0$ $Na_{0.3}Co_2{\cdot}1.3H_2O$ is seen with $3\bar{3}00$ α-Al_2O_3 in part b. An in-plane X-ray rocking curve of $11\bar{2}0$ $Na_{0.3}CoO_2{\cdot}1.3H_2O$ (inset) indicates that the $Na_{0.3}CoO_2{\cdot}1.3H_2O$ film is heteroepitaxially grown on the α-Al_2O_3 substrate. (Right panel) Schematic drawing of the crystal structure of $Na_{0.3}CoO_2{\cdot}1.3H_2O$ obtained at step 5.

the heat treatment (step 3). The q_z value of 000*l* Na_xCoO_2 becomes small by the oxidation treatment (step 4), indicating that the lattice constant *c* of Na_xCoO_2 films expands from 1.089 nm (step 3) to 1.121 nm (step 4) as a result of the oxidation treatment. The chemical composition ratios of Na/Co, *x*, in the Na_xCoO_2 films were evaluated to be 0.8 (step 3) and 0.3 (step 4) from the reported relationship[1,2,6,7] between *c* and *x* in Na_xCoO_2 (Figure 2, right panel). The *x* values were also evaluated by X-ray fluorescence analysis (XRF; ZSX 100e, Rigaku Co.) and found to agree reasonably with each other. From these results, we concluded that epitaxial films of CoO, $Na_{0.8}CoO_2$, and $Na_{0.3}CoO_2$ were obtained at steps 1, 3, and 4, respectively.

We then performed the hydration treatment of the $Na_{0.3}CoO_2$ epitaxial film (step 5). Figure 3a shows an out-of-plane XRD pattern of the resultant film, which was taken at 5 °C. Intense Bragg XRD peaks are resolved at scattering vectors $q_z \sim 1$, 2, 3, 4, 5, and 6 nm^{-1} together with 0006 α-Al_2O_3. The lattice parameter, *c*, was calculated to be 1.973 nm, which corresponds to that of $Na_xCoO_2{\cdot}1.3H_2O$ ($x = 0.29-0.30$; $c = 1.977-1.969$ nm) reported by Schaak et al.[8] The XRF analysis revealed that the *x* value in the $Na_xCoO_2{\cdot}1.3H_2O$ film is 0.3. An intense Bragg XRD peak of $11\bar{2}0$ $Na_{0.3}CoO_2{\cdot}1.3H_2O$ is seen in Figure 3b together with $3\bar{3}00$ α-Al_2O_3. Six-fold symmetry was observed in the in-plane rocking curve of $11\bar{2}0$ $Na_{0.3}CoO_2{\cdot}1.3H_2O$ (inset of Figure 3b; one peak in the 6-fold symmetry is shown here). These observations indicate that the $Na_{0.3}CoO_2{\cdot}1.3H_2O$ film keeps an epitaxial relation of (0001) $[11\bar{2}0]$ $Na_xCoO_2{\cdot}1.3H_2O$||(0001) $[1\bar{1}00]$ α-Al_2O_3. Thus, we conclude that a $Na_{0.3}CoO_2{\cdot}1.3H_2O$ epitaxial film was successfully fabricated by the intercalation of H_2O into the $Na_{0.3}CoO_2$ film.

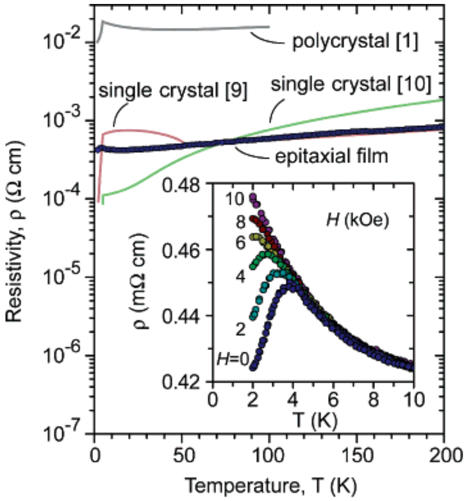

Figure 4. Temperature dependence of the electrical resistivity of the 275-nm-thick $Na_{0.3}CoO_2{\cdot}1.3H_2O$ epitaxial film grown on the (0001) face of an α-Al_2O_3 substrate. The inset shows the magnetic field dependence of the resistivity below 10 K. Temperature dependences of the electrical resistivity for the polycrystalline compact[1] and single crystals[9,10] of $Na_{0.3}CoO_2{\cdot}1.3H_2O$ are also shown for comparison. Superconducting transition behavior is seen at around 4 K.

Electrical resistivity of the grown films was measured by the ac four-probe method with silver paint contacts (PPMS, Quantum Design). Figure 4 shows the temperature dependence of the electrical resistivity of a 275-nm-thick $Na_{0.3}CoO_2{\cdot}1.3H_2O$ epitaxial film grown on the (0001) face of the α-Al_2O_3 substrate. The electrical resistivity is 5.9×10^{-4} Ω cm at 100 K, which is $\sim{}^1/_{40}$ that of the polycrystalline compact[1] (2×10^{-2} Ω cm), and comparable to that of single crystals.[9,10] It decreased with a decrease in the temperature and then gradually increased with a further decrease in the temperature below ~30 K. As shown in the inset of Figure 4, it suddenly decreased at ~4 K, exhibiting a sharp peak, which became broad and shifted to the lower temperature side with the application of an external magnetic field. These observations, which are similar to those reported in $Na_{0.3}CoO_2{\cdot}1.3H_2O$, clearly indicate that the $Na_{0.3}CoO_2{\cdot}1.3H_2O$ epitaxial film becomes a superconductor with $T_c \sim 4$ K, which is comparable to that of polycrystalline compacts[1] or bulk single crystals.[9,10] A small upturn in the resistivity was also seen at around 10 K, and although its origin is unknown, a similar behavior was also observed in polycrystalline material.[1]

In summary, we have demonstrated that superconducting oxyhydrate $Na_{0.3}CoO_2{\cdot}1.3H_2O$ epitaxial films were successfully grown on the (0001) face of an α-Al_2O_3 substrate by a novel multistep film growth technique in which R-SPE and the intercalation process are combined. The obtained epitaxial film exhibited a temperature dependence of electrical resistivity similar to that of the single crystal, exhibiting a superconductive transition at ~4 K. The present growth method may be applicable to the growth of intercalated compounds with a layered structure.

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(23) We used Cu Kα_1 ($\lambda = 0.154\,05$ nm) radiation, which was monochromated using Ge(220) crystals, in all of the XRD analyses. We converted 2*θ* values, which were obtained by XRD measurements, into scattering vector *q* using Bragg's equation because lattice spacing, the *d* value, can be more easily obtained using a *q* value rather than a 2*θ* value in the case of an epitaxial film.