Reactive Solid-Phase Epitaxy: A Powerful Method for Epitaxial Film Growth of Complex Layered Oxides

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反応性固相エピタキシャル成長法： 層状複合酸化物の高品質エピタキシャル薄膜を作製するための強力な手法

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High-quality epitaxial film growth for several complex oxides having layered structure by “Reactive Solid-Phase-Epitaxy (R-SPE¹⁾)” is reviewed. Materials focused are $\text{InGaO}_3(\text{ZnO})_m$ ($m = \text{integer}$), LaCuOS and Na_xCoO_2 ($x \sim 0.8$). For the epitaxial film growths of the complex systems with a complicated layered crystal structure, it is necessary to form an epitaxial template layer before the film deposition, followed by the thermal annealing of the bilayer films. The layers subsequently deposited on the template layer may be amorphous, polycrystalline or powder, which allows control of the epitaxially grown films in the R-SPE method.

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1. Introduction

COMPLEX oxides with a multi-layered structure may exhibit exceptional properties originating from the spatial confinement of conductive electrons or holes in the two-dimensional layer, which is similar to that in a multi-quantum-well (MQW) in semiconductors. Thus, such a structure may be regarded, in a sense, as a “natural MQW.” Natural MQW is of great importance for the realization of next generation electronics; “oxide electronics.” In order to fully utilize intrinsic potential of natural MQW, single-crystalline or high-quality epitaxial film of complex layered oxides is absolutely essential.

Generally, epitaxial films of semiconductors are fabricated by conventional vapor phase epitaxy (VPE) method such as RF-sputtering,²⁾ vacuum evaporation, chemical vapor deposition (CVD), molecular beam epitaxy (MBE)³⁾ and pulsed-laser deposition (PLD).⁴⁾ However, such VPE methods cannot be directly applied to the growth of complex oxides due to the fact described below: It is generally recognized in the vapor phase growth process that the two-dimensional Frank Van der Merwe growth mode,⁵⁾ which is necessary for the single-crystalline film growth, becomes dominant at temperatures higher than $\sim 60\%$ of melting points of the compounds in question. Therefore, very high growth temperature ($> 1000^\circ\text{C}$) is required to grow single-crystalline films of oxides because of their high melting point ($\sim 2000^\circ\text{C}$). Such high-temperature deposition process in turn invokes an intrinsic problem for the growth of complex oxides, e.g., a difficulty in controlling chemical composition because an element with higher vapor pressure evaporates much faster than the other elements during the deposition (Fig. 1 (upper)). In an extreme case that an element has an evaporation rate faster than

the sticking rate of the deposition precursor, it is impossible to grow the complex oxides.

To overcome the difficulty in a conventional VPE, we have developed “Reactive Solid-Phase-Epitaxy (R-SPE)” as illustrated in Fig. 1 (lower),¹⁾ where a bilayer laminate composed of a thin epitaxial layer of simple oxide or metal grown on a substrate and a polycrystalline layer or powder source is thermally annealed at high-temperatures ($> 1000^\circ\text{C}$). The solid-state chemical reaction at high-temperatures leads to the formation of the thin single-crystalline layer on the substrate, which may act as “an epitaxial template” for successive homoepitaxial growth of the film. High-quality epitaxial films of $\text{InGaO}_3(\text{ZnO})_m$ (where $m = \text{integer}$)¹⁾ $\text{In}_2\text{O}_3(\text{ZnO})_m$,⁶⁾ LaCuOCh (where $\text{Ch} = \text{S or Se}$),⁷⁾ ZnRh_2O_4 ⁸⁾ and Na_xCoO_2 (where $x \sim 0.8$)⁹⁾ with a layered structure were successfully fabricated using this technique, which would have been impossible by conventional VPE. Here I review high-quality epitaxial film growth of $\text{InGaO}_3(\text{ZnO})_5$, LaCuOS and $\text{Na}_{0.8}\text{CoO}_2$ by R-SPE.

2. Homologous series of $\text{InGaO}_3(\text{ZnO})_m$ ($m = \text{integer}$)¹⁾

Homologous series of $\text{LnMO}_3(\text{ZnO})_m$ ($\text{Ln} = \text{In, Sc or Lu}$, $\text{M} = \text{Al, Ga, In, or Fe}$, $m = \text{integer}$)^{10)–17)} may exhibit the quantum effect due to its natural MQW structure. The crystal structure of $\text{LnMO}_3(\text{ZnO})_m$ ($\text{Ln} = \text{In}$, $\text{M} = \text{Ga}$, $m = 5$, Fig. 2) consists of an alternative stack of LnO_2^- layers (Ln^{3+} ion locates at an octahedral site formed by oxygen) and MO^+ ($\text{ZnO})_m$ blocks (M^{3+} and Zn^{2+} ions take at trigonal-bipyramidal and tetrahedral coordination, respectively), making up the superlattice structure along the $[0001]$.^{15)–17)} A unique feature of this material is that thickness of the $\text{MO}^+(\text{ZnO})_m$ block is varied by simply changing the chemical composition, while

Fig. 1. (upper) Difficulty of conventional pulsed-laser deposition for layered complex oxide, $A_kB_mC_nO_x$ (A , B and C : metallic atom, k , m , n and x : arbitrary integer). Amorphous or polycrystalline film of $A_kB_mC_nO_x$ is obtained by low-temperature deposition. An element with higher vapor pressure ($A-O$) evaporates much faster than the other elements ($B-O$ and $C-O$) during high-temperature deposition. (lower) Basic concept of R-SPE method. A bilayer laminate composed of a thin epitaxial layer of simple oxide ($A-O$ or $B-O$ or $C-O$) or metal grown on a substrate and a polycrystalline layer or powder source of target $A_kB_mC_nO_x$ is thermally annealed at high-temperatures ($\sim 1000^\circ\text{C}$). The solid-state reaction at high-temperatures leads to the formation of the thin single-crystalline layer on the substrate, which may act as "an epitaxial template" for successive homoepitaxial SPE growth of the film.

that of the LnO_2^- layer is unchanged. This may give the control for electrical and optical properties related to the carrier confinement effects because thickness of the $MO^+(\text{ZnO})_m$ block corresponds to the quantum well width.

Although many studies have studied the electronic conductive^{18)–20)} and thermoelectric energy conversion characteristics²¹⁾ of $LnMO_3(\text{ZnO})_m$ ($Ln = \text{In}$, $M = \text{In}$ or Ga), no noticeable features inherent to the layered structure have been identified yet due to absence of high-quality single-crystalline epitaxial film. We have engaged in intensive efforts to fabricate epitaxial $\text{InGaO}_3(\text{ZnO})_m$ films at high temperatures by conventional PLD method on (111)-face of yttria-stabilized-zirconia (YSZ) substrate. When substrate temperatures were increased up to 800°C , the resulting polycrystalline films were composed of a mixture of In_2O_3 and ZnGa_2O_4 , irrespective of varying several deposition parameters. Thus, we concluded that epitaxial film of $\text{InGaO}_3(\text{ZnO})_m$ is impossible to fabricate by simple PLD method.

Although single-crystalline film growth of $LnMO_3(\text{ZnO})_m$ is very difficult, bulk single crystals of $\text{LuFeO}_3(\text{ZnO})_m$ have been grown by means of the solid-state reaction of the mixture between Lu_2O_3 , Fe_2O_3 and ZnO powders and successive grain growth in a platinum tube at 1550°C .¹⁷⁾ This suggests that a small single-crystalline grain grows efficiently as a result of homoepitaxial growth from the solid-phase at high tempera-

ture. This consideration leads to the expectation that single-crystalline $LnMO_3(\text{ZnO})_m$ films can be grown from the solid-phase if a thin single-crystalline layer is once formed just on the substrate.

Based on this idea, we have developed the R-SPE method. The R-SPE procedure (Fig. 3) for the growth of single-crystalline $\text{InGaO}_3(\text{ZnO})_5$ films is as follows. **Step 1:** a ZnO epitaxial layer was grown on a (111)-YSZ substrate by PLD at 600°C .²²⁾ Thickness of the ZnO epitaxial layer was ~ 2 nm, evaluated by grazing incidence X-ray reflectivity (GIXR) measurements. **Step 2:** a 150-nm-thick polycrystalline $\text{InGaO}_3(\text{ZnO})_5$ film was deposited on the ZnO epitaxial layer at room temperature (25°C). X-ray photoelectron spectroscopy (XPS) revealed that the chemical composition of the deposited $\text{InGaO}_3(\text{ZnO})_5$ film differs insignificantly from that of the target.²³⁾ **Step 3:** The resultant bilayer film was fully covered by placing a YSZ plate ($10\text{ mm} \times 10\text{ mm} \times 0.5\text{ mm}^1$) on the film surface to suppress vaporization of ZnO and In_2O_3 during the annealing in step 4. **Step 4:** The bilayer film was annealed at 1400°C for 0.5 h in air. **Step 5:** The film was cooled down to room temperature in the furnace. Finally, a YSZ cap plate was removed and the surface of the annealed film looks very clean without chemical reaction with the YSZ plate.

Figure 4(b) shows a cross-sectional high-resolution transmission electron microscopy (HRTEM, JEM-4010, acceleration voltage: 400 kV, JEOL Co.) image of the $\text{InGaO}_3(\text{ZnO})_5$ film grown by the R-SPE method. A periodic stripe pattern with an interval of 1.9 nm, which corresponds to d_{0003} in $\text{InGaO}_3(\text{ZnO})_5$, is seen in an atomic-scale resolution (Fig. 4(a)), which directly shows the superlattice structure of the $\text{InGaO}_3(\text{ZnO})_5$ film epitaxially grown on the (111)-YSZ surface. Atomically flat terraces and steps are observed in topographic atomic force microscope (AFM, SPI-3800N, S.I.I.) image of the $\text{InGaO}_3(\text{ZnO})_5$ film (Fig. 4(c)). The step height is 1.9 nm, corresponding to the space between the adjacent InO_2^- layers. These results clearly demonstrate that single-crystalline films of homologous series $\text{InGaO}_3(\text{ZnO})_m$ are successfully grown on YSZ substrates by the R-SPE method.

To clarify the growth mechanism in the R-SPE method, we have investigated the change in the crystallographic orientation of the bilayer films grown on the (111)-YSZ substrate during thermal annealing using HRTEM.²⁴⁾ Figure 5 shows the HRTEM images of the bilayer film after annealing at various temperatures. Amorphous $\text{InGaO}_3(\text{ZnO})_5$ film slightly containing crystallized small grain are observed on the ZnO layer (2-nm-thick) in the as-prepared film (Fig. 5(a)). The distribution of the tilt angle of 0002 ZnO was ~ 0.03 degrees evaluated by high-resolution X-ray diffraction (HR-XRD, ATX-G, Rigaku Co.). After annealing at 800°C (Fig. 5(b)), randomly oriented polycrystalline grains of $\text{InGaO}_3(\text{ZnO})_5$, whose sizes become much larger compared to those in the as-deposited film, are observed on the ZnO epitaxial layer. The distribution of the tilt angle of 0002 ZnO is unchanged (~ 0.03 degrees) by the annealing at 800°C . These observations suggest that the crystallization and the grain growth of $\text{InGaO}_3(\text{ZnO})_5$ starts to occur below 800°C , without reacting the polycrystalline $\text{InGaO}_3(\text{ZnO})_5$ with the ZnO epitaxial layer. When the film is annealed at 1000°C the ZnO epitaxial is no longer detected and a ~ 50 -nm-thick single-crystalline $\text{InGaO}_3(\text{ZnO})_5$ layer is formed just on the substrate (Fig. 5(c)). It implies that the solid-state reaction between the polycrystalline $\text{InGaO}_3(\text{ZnO})_5$ and the ZnO epitaxial layer occurs at temperatures higher than 1000°C , leading to the formation of the epitaxial layer. At this temperature, the tilt angle of 0001 $\text{InGaO}_3(\text{ZnO})_5$ exhibits a rather large distribution of ~ 0.5

Fig. 2

Fig. 3

Fig. 2. Schematic crystal structure of $\text{InGaO}_3(\text{ZnO})_m$ ($m=5$). Crystal symmetry: hexagonal ($m=\text{even}$) or rhombohedral ($m=\text{odd}$), space group: $P6_3/mmc$ ($m=\text{even}$) or $R\bar{3}m$ ($m=\text{odd}$).

Fig. 3. Fabrication procedure for single-crystalline films of $\text{LnMO}_3(\text{ZnO})_m$ ($\text{Ln}=\text{Lu}$ or In , $M=\text{Al}$, Ga , In or Fe , $m=\text{integer}$) by the R-SPE method. Step 1: Extremely thin ($\sim 2\text{-nm}$ -thick) ZnO epitaxial layer is grown on a YSZ substrate by PLD at 600°C . Step 2: a 150-nm-thick amorphous $\text{LnMO}_3(\text{ZnO})_m$ film is deposited on the ZnO epitaxial layer at room temperature (25°C). Step 3: The resultant bilayer film is fully covered by placing a YSZ plate ($10\text{ mm} \times 10\text{ mm} \times 0.5\text{ mm}^3$) on the film surface. Step 4: The bilayer film is annealed at 1400°C for 0.5 h in air.

Fig. 4. (a) (b) Cross-sectional HRTEM lattice image of the R-SPE grown $\text{InGaO}_3(\text{ZnO})_5$ single-crystalline film. Schematic crystal structure is also shown for comparison. (c) Topographic AFM image of the $\text{InGaO}_3(\text{ZnO})_5$ film. Atomically flat terraces and steps are observed. The step height is 1.9 nm, corresponding to the space between the adjacent InO_2^- layers.

degrees, because randomly oriented $\text{InGaO}_3(\text{ZnO})_5$ grains still remain in the area above the growth front of the epitaxial $\text{InGaO}_3(\text{ZnO})_5$ layer. Finally, an almost perfect superlattice structure of $\text{InGaO}_3(\text{ZnO})_5$ is formed over the entire area of the film after the annealing at 1400°C (Fig. 5(d)). The distribution of 0001 $\text{InGaO}_3(\text{ZnO})_5$ tilt angle was significantly reduced to less than 0.1 degrees, which is consistent with the result of the HRTEM observation. From these observations, the R-SPE process is summarized as follows: First, a thin single-crystalline layer of $\text{InGaO}_3(\text{ZnO})_m$ is formed epitaxially on the substrate by the solid-state chemical reaction at $\sim 1000^\circ\text{C}$. Then, homoepitaxial growth of $\text{InGaO}_3(\text{ZnO})_m$ film takes place at 1400°C on the first layer via the solid-phase to form the single-crystalline film.

Recently we have clarified the intrinsic carrier transport for $\text{InGaO}_3(\text{ZnO})_5$ using single-crystalline film grown by R-SPE²⁵⁾ and successfully fabricated high-performance transparent field-effect transistors.²⁶⁾ The device exhibited excellent performance such as an on-to-off current ratio of $\sim 10^6$ and a field-effect mobility of $\sim 80\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ and normally-off characteristics with operation insensitive to visible light irradiation. The result provides a step toward the realization of transparent electronics for next-generation optoelectronics.²⁷⁾

3. Layered oxychalcogenide, LaCuOCh ($\text{Ch}=\text{S}$ and Se)⁷⁾

We recently found LaCuOCh ($\text{Ch}=\text{S}$ or Se) is a novel transparent p -type semiconductor, which has been explored by an extension of our chemical design concept for p -type semiconducting oxides^{28)–32)} to the oxychalcogenide system.³³⁾ LaCuOCh has a layered natural MQW structure, composed of $(\text{La}_2\text{O}_2)^{2+}$ and $(\text{Cu}_2\text{Ch}_2)^{2-}$ layers alternatively stacked along the c -axis (Fig. 6).^{34),35)} The covalent $(\text{Cu}_2\text{Ch}_2)^{2-}$ layers, in which Cu is tetrahedrally coordinated by four Ch^{2-} ions, dominantly contribute to the top of the valence band, working as conduction paths for hole carriers (well).³⁶⁾ On the other hand, the ionic $(\text{La}_2\text{O}_2)^{2+}$ layers acting as a barrier layer to

Fig. 5. Cross-sectional HRTEM images of the amorphous $\text{InGaO}_3(\text{ZnO})_5$ /epi-ZnO bilayer after annealing at different temperatures ((a) without heating, (b) after heated at 800°C , (c) after heated at 1000°C , and (d) after heated at 1400°C).

confine positive holes in the two-dimensional $(\text{Cu}_2\text{Ch}_2)^{2-}$ layers and preserve transparency in the visible range. The electrical conductivity of the material is controllable by doping of divalent ions Mg^{2+} , which act as acceptors by substituting La^{3+} ions.³⁷⁾ Sharp near-UV photoluminescence peak associated with exciton is observed around the fundamental absorption edge even at room temperature.^{38)–40)} Further, we successfully controlled the bandgap of the oxychalcogenide by the formation of a complete alloy between LaCuOS and LaCuOSe .⁴¹⁾ The bandgap of $\text{LaCuOS}_{1-x}\text{Se}_x$ systematically varies from 3.1 eV to 2.8 eV with an increase in x from $x=0.0$ to 1.0. Therefore, epitaxial film growth is of critical importance for the fabrication of LaCuOCh -based optoelectronic devices such as near UV-LEDs and LDs.

We have engaged in intensive efforts to grow epitaxial LaCuOS films at high temperatures by conventional PLD method on YSZ or MgO substrates. Films deposited at temperatures below $\sim 500^\circ\text{C}$ in H_2S atmosphere were always amorphous, and no crystallization occurred below $\sim 500^\circ\text{C}$. When substrate temperatures were increased up to 800°C , the resulting polycrystalline films were composed of a mixture of LaCuOS , La_2O_3 and $\text{La}_2\text{O}_2\text{S}$, irrespective of varying several deposition parameters.

In order to fabricate epitaxial films of LaCuOCh , we applied R-SPE method (Fig. 7).⁷⁾ 5-nm-thick Cu layer was deposited at 400°C under a vacuum ($\sim 10^{-5}$ Pa), and amorphous LaCuOS (a- LaCuOS , hereafter) layer was deposited at

25°C in a H_2S atmosphere ($\text{H}_2\text{S}/\text{Ar}=25\%$, 0.5 Pa). Then, the bilayer films were covered with YSZ plates and annealed at 1000°C . All the thermal-annealing treatments were performed in evacuated SiO_2 glass tubes with a small amount of LaCuOS powder. The YSZ plate and the LaCuOS powders are crucial for maintaining the stoichiometric composition of the films during annealing.

Figure 8(a) shows a cross-sectional HRTEM image of the LaCuOS film on a YSZ substrate by the R-SPE method. Layered patterns due to (00 l) planes of LaCuOS are stacked parallel to the substrate surface over the whole area of the film. Square shaped domains with atomically flat terraces and steps are observed in the topographic AFM image of the LaCuOS film (Fig. 8(b)). These results clearly demonstrate that the resultant LaCuOS film was high-quality epitaxial film.

In order to clarify the growth mechanism in the R-SPE method, we have investigated the change in the crystallographic orientation of the bilayer films grown on the (001)-YSZ substrate during thermal annealing using HRTEM.⁴²⁾ Figure 9 shows cross-sectional HRTEM images of a- $\text{LaCuOS}/\text{Cu}/(001)\text{-YSZ}$ samples as-deposited (a) and annealed at 500°C (b), 800°C (c), and 1000°C (d). Island structures are formed at the a- LaCuOS -YSZ substrate interface in the as-deposited sample (Fig. 9(a)). When annealed at 500°C (Fig. 9(b)), thin (~ 10 nm) crystallites, exhibiting a layered structure, are observed at the interface. The number density of this crystal-

Fig. 6

Fig. 7

Fig. 6. Schematic crystal structure of LaCuOCh ($\text{Ch} = \text{S}$ or Se). Crystal symmetry: tetragonal, space group: $P4/nmm$. Each layer is constituted by edge-shared La_4O and CuCh_4 tetrahedra. The c -axis length of LaCuOS is 0.853 nm.

Fig. 7. Fabrication procedure for epitaxial films of LaCuOCh ($\text{Ch} = \text{S}$ or Se) by the R-SPE method. *Step 1*: 5-nm-thick Cu metal is deposited by PLD at 500°C on a substrate. *Step 2*: amorphous LaCuOS or LaCuOSe layer was deposited on the Cu layer using a sintered LaCuOS or LaCuOSe target at room temperature. *Step 3*: The resultant bilayer film is fully covered by placing a YSZ plate ($10\text{ mm} \times 10\text{ mm} \times 0.5\text{ mm}^t$) on the film surface. *Step 4*: The bilayer film is annealed at 1000°C in an evacuated SiO_2 glass tube.

Fig. 8. (a) Cross-sectional HRTEM image of the R-SPE grown LaCuOS on (001)-face of YSZ substrate. (b) Topographic AFM image of the LaCuOS epitaxial film. Square shaped domains with atomically flat terraces and steps are observed.

lite is similar to that of the Cu island observed in Fig. 9(a), suggesting that the Cu island is converted to the crystallite without coagulating. Figure 9(c) shows that the crystallite serves as a seed for growing large grained epitaxial layers at temperatures $\geq 500^\circ\text{C}$. However, nonoriented polycrystalline LaCuOS are still seen in the film surface region. Finally at 1000°C , a LaCuOS epitaxial crystal grows in the entire area, as seen in Fig. 9(d). From these observations, the R-SPE process is summarized as follows: The thin metallic Cu layer deposited between a- LaCuOS and YSZ (Fig. 9(a)) works as an initiator to form epitaxial LaCuOS seeds at temperatures $\geq 500^\circ\text{C}$. Single-crystalline grain growth proceeds from the epitaxial LaCuOS seeds toward the top of film surface at 800°C to 1000°C .

Very recently we have successfully demonstrated the room temperature operation of blue light emitting diode (blue LED) using a p - n heterojunction composed of a wide bandgap p -type oxychalcogenide LaCuOSe epitaxial film, and an n -type amorphous In-Ga-Zn-O (In/Ga/Zn atomic ratio $\sim 1/1/5$).⁴³⁾ A blue electroluminescence (EL) peaking at $\lambda \sim 430\text{ nm}$ and associated with the intrinsic exciton of LaCuOSe , is observed at room temperature by applying a forward bias voltage above $\sim 8\text{ V}$. The successful operation of

the LED device at room temperature indicates that layered oxychalcogenides LnCuOCh ($\text{Ln} = \text{lanthanide}$, $\text{Ch} = \text{chalcogen}$) have a substantial potential as the light-emitting layer in optoelectronics devices that operate in the blue-ultraviolet region.

4. Layered Sodium Cobaltite, Na_xCoO_2 ($x \sim 0.8$)⁹⁾

Recently, sodium cobalt-oxide, Na_xCoO_2 ($x = 0.5\text{--}0.9$, hexagonal lattice, space group: $P6_3/mmc$, $a = 0.284\text{ nm}$, $c = 1.081\text{ nm}$ ⁴⁴⁾) (Fig. 10) has attracted emerging attention toward the realization of oxide-based thermoelectric energy conversion (TE) devices, such as a thermoelectric generator and Peltier cooler, because they have potential advantages over conventional TE devices, such as Bi_2Te_3 -based TE devices, with respect to thermal stability and environmental compatibility.^{45)–49)} This material also attracts much attention because it can be converted into a superconductor (transition temperature, $T_c = 4.7\text{ K}$) by introducing H_2O molecules into a layer between the two adjacent CoO_2^- layers.^{50),51)} Although a number of TE properties for bulk single crystal^{45),46)} and sintered polycrystalline Na_xCoO_2 ^{47)–49)} have been reported to date, those of thin films have not been reported so far. High-quality epitaxial film of Na_xCoO_2 is obviously preferable for high-performance thin film TE devices, primarily because epitaxial films exhibit intrinsic electrical properties as bulk single crystal.

We applied R-SPE technique to the growth of Na_xCoO_2 epitaxial film. Figure 11 schematically illustrates the R-SPE procedure for the growth of epitaxial Na_xCoO_2 films.⁹⁾ *Step 1*: High-quality epitaxial film of (111)-oriented CoO was deposited on a (0001)-face of $\alpha\text{-Al}_2\text{O}_3$ substrate ($10\text{ mm} \times 10\text{ mm} \times 0.5\text{ mm}^t$) at 700°C by PLD using a Co_3O_4 sintered disk as a target. *Step 2*: surface of the PLD-deposited CoO film was fully capped by YSZ single-crystalline plate ($10\text{ mm} \times 10\text{ mm} \times 0.5\text{ mm}^t$) to keep the surface clean. *Step 3*: NaHCO_3 powder was put on the YSZ plate. *Step 4*: The sandwich specimen was annealed at 700°C for 1 h in air.

Figure 12 shows out-of-plane (a) and in-plane (b) X-ray Bragg diffraction patterns of the Na_xCoO_2 film grown on (0001)-face of $\alpha\text{-Al}_2\text{O}_3$ substrate by the R-SPE method. Only intense Bragg diffraction peaks of 0001 Na_xCoO_2 are observed

Fig. 9. Cross-sectional HRTEM images of annealed a-LaCuOS/Cu/(001)-YSZ at various temperatures. (a) As-deposited (nonannealed), (b) 500°C, (c) 800°C, and (d) 1000°C. The incident direction of the electron beam is $[010]$ of YSZ substrate.

Fig. 10

Fig. 11

Fig. 10. Schematic crystal structure of Na_xCoO_2 ($x \sim 0.8$). Crystal symmetry: hexagonal, space group: $P6_3/mmc$.

Fig. 11. Fabrication procedure for epitaxial films of Na_xCoO_2 ($x \sim 0.8$) by the R-SPE method. *Step 1*: Pulsed-laser-deposition of highly (111)-oriented epitaxial film of CoO on a (0001)-oriented $\alpha\text{-Al}_2\text{O}_3$ substrate. *Step 2*: Surface capping by YSZ single-crystalline plate to keep the film surface clean. *Step 3*: Putting NaHCO_3 powder on the YSZ plate. *Step 4*: Thermal annealing at 700°C in air.

together with 0006 $\alpha\text{-Al}_2\text{O}_3$ (Fig. 12(a)), indicating that the film was highly c -axis oriented. On the other hand, only intense Bragg peak of 11–20 Na_xCoO_2 is seen together with 3–300 $\alpha\text{-Al}_2\text{O}_3$ (Fig. 12(b)), indicating that heteroepitaxial growth occurred with the following epitaxial relationship: (0001) $[11\bar{2}0]$ $\text{Na}_x\text{CoO}_2 \parallel$ (0001) $[1\bar{1}00]$ $\alpha\text{-Al}_2\text{O}_3$. Intense streak RHEED pattern of the film (inset) also support this conclusion. Topographic AFM image of the Na_xCoO_2 epitaxial film is shown in Fig. 12(c). A step-like structure composed of several flake-like domains is seen. The step increment was approximately 3 nm, which is three times as long as that of the c -axis length of Na_xCoO_2 , suggesting that step bunching occurred during the annealing at 700°C. The chemical composition of the resultant film was evaluated to be $\text{Na}_{0.83}\text{CoO}_2$ by X-ray fluorescence (XRF) measurement. Electrical conductivity (σ), carrier concentration (n), Hall mobility (μ), and Seebeck coefficient (S), and power factor ($S^2\sigma$) of the $\text{Na}_{0.83}\text{CoO}_2$ epitaxial film were 1160 S cm^{-1} , $3.8 \times 10^{21} \text{ cm}^{-3}$, 1.9

$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $+117 \mu\text{V K}^{-1}$, and $1.6 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$, respectively, which are comparable to those of bulk single-crystalline Na_xCoO_2 . These results suggest that the $\text{Na}_{0.83}\text{CoO}_2$ film grown by the R-SPE was high-quality epitaxial film.

We then investigated the change in the crystalline phase of the CoO epitaxial film grown on the (0001)- $\alpha\text{-Al}_2\text{O}_3$ substrate during the thermal annealing using HR-XRD to clarify the growth mechanism. **Figure 13** (left) shows the out-of-plane XRD patterns of the CoO film after annealing at various temperatures. Only intense Bragg diffraction peak of 111 CoO is seen together with 0006 $\alpha\text{-Al}_2\text{O}_3$ at 25°C. After annealing at 300°C, 111 Co_3O_4 and 222 Co_3O_4 peaks are additionally seen. After annealing at 500°C, intensity of 111 Co_3O_4 and 222 Co_3O_4 peaks are increased, while 111 CoO peak intensity is decreased. The color of the film turned transparent (almost colorless) to brown. After annealing at 600°C, the periphery of the film turned black (Na_xCoO_2), while the center still remained transparent brown (Co_3O_4). Finally, after the sam-

Fig. 12. (a) Out-of-plane and (b) in-plane X-ray Bragg diffraction patterns of the R-SPE grown Na_xCoO_2 film. RHEED pattern of the Na_xCoO_2 film is also shown in (b). (c) Topographic AFM image of the Na_xCoO_2 epitaxial layer grown by the R-SPE method. Cross-sectional profile from **a** to **b** is also shown. Step-like structure composed of several flake-like domains is seen.

Fig. 13. (Left) Out-of-plane XRD pattern of CoO epitaxial layer after annealing with NaHCO_3 powders at different temperatures (without heating, after heated at 300°C, at 500°C, at 600°C, and at 700°C). (Right) Schematic illustration of growth mechanism of Na_xCoO_2 epitaxial layer by the R-SPE method. Thermal oxidation of the CoO film into Co_3O_4 occurred at lower temperature (300–500°C). Na_xCoO_2 epitaxial layer is formed at 600–700°C via lateral diffusion of Na^+ ion into Co_3O_4 layers.

ple was annealed at 700°C, only intense diffraction peaks of Na_xCoO_2 are seen together with 0006 $\alpha\text{-Al}_2\text{O}_3$. The growth mechanism for the Na_xCoO_2 by the R-SPE method is schematically illustrated in Fig. 13 (right). First, thermal oxidation of CoO into Co_3O_4 occurs at lower temperature (300–500°C). Then, the Na_xCoO_2 epitaxial layer is formed at 600–700°C via lateral diffusion of Na^+ ions together with oxide ions into Co_3O_4 layers.

There are two features in the present Na^+ -diffusions. First is the insertion is limited to lateral direction. Insertion of the top layer is not significant. This fact is evidenced by an observation that only periphery of the film was changed into Na_xCoO_2 when CoO film was annealed at 700°C for short time (~5 min). Another is that epitaxial thin film is retained after the Na^+ -diffusion is completed. In most cases, samples are broken into pieces by diffusion such as intercalation. It is considered that cracking due to Na^+ -diffusion and crack heal due to solid-state sintering are well-balanced at 600–700°C for

this material.

Thin film TE devices can be developed by using the R-SPE grown $\text{Na}_{0.83}\text{CoO}_2$ epitaxial film. In addition, this $\text{Na}_{0.83}\text{CoO}_2$ epitaxial film would be appropriate to study the mechanism of superconductivity for the water containing system, $\text{Na}_{0.35}\text{CoO}_2\cdot 1.3\text{H}_2\text{O}$. Very recently we have successfully fabricated $\text{Na}_{0.35}\text{CoO}_2\cdot 1.3\text{H}_2\text{O}$ epitaxial film by oxidation & hydration of $\text{Na}_{0.8}\text{CoO}_2$ epitaxial film grown by the R-SPE. The $\text{Na}_{0.35}\text{CoO}_2\cdot 1.3\text{H}_2\text{O}$ epitaxial film exhibited superconducting transition at the $T_c \sim 4\text{ K}$.

5. Summary

I reviewed high-quality epitaxial film growth of $\text{InGaO}_3(\text{ZnO})_m$ ($m=\text{integer}$), LaCuOCh ($\text{Ch}=\text{S}$ and Se) and Na_xCoO_2 ($x \sim 0.8$), which have natural MQW structure, by reactive solid-phase epitaxy (R-SPE). For the epitaxial film growths of the complex systems with a complicated layered crystal structure, it is essential to form an epitaxial template layer before the film deposition, followed by the thermal annealing of the bilayer films. The layers subsequently deposited on the template layer may be amorphous, polycrystalline or powder, which allows control of the epitaxially grown films in the R-SPE method.

The R-SPE method is considered to be a versatile technique for the epitaxial growth. It is not limited to layered oxides as described above, but applicable to various materials. It is particularly suited to the epitaxial growth of complex oxides with a layered structure.

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