1. Introduction

Sodium is one of the most attractive elements for use in materials because it is nontoxic, environment friendly, and abundant. Although elemental sodium and simple sodium-containing compounds such as sodium oxide cannot be used directly because they are highly reactive to moisture and carbon dioxide and are unstable in the atmosphere, they can be used as constituents in materials including soda-lime silicate glass for windows [1–3]. In addition to these conventional applications, various sodium-containing complex oxides have recently attracted attention for application as functional material in thermoelectric devices [4–6], photocatalysts [7–9], sensors [10–12], and rechargeable batteries [13–18]. The usage of sodium for future material development will continue to increase because of its above-mentioned desirable properties.

Functional materials need to be grown as thin films for application in devices. However, in the case of sodium-containing complex oxides, the physical vapor deposition (PVD) techniques, commonly applied for the growth of thin oxide films, is unsuitable because the sodium concentration in the resultant films is smaller than desired [19,20]. This is because of the high vapor pressure of Na and Na2O at the growth temperatures (PNa of approximately 10^4 Pa at 700°C [19] and PNa2O of approximately 5.0 × 10^2 Pa at 1300°C [21,22]). Consequently, the development of a safe and facile thin-film growth technique that enables control of the sodium concentration is invaluable for promoting the use of sodium in materials.

β-NaGaO2 thin film is an important precursor material for obtaining β-CuGaO2 thin films [23,24] that are expected to be used as absorber material [25–32] in safe and environment-friendly thin-film solar cells. Because the β-CuGaO2 is a metastable and cannot be obtained by any method other than ion-exchange of Na⁺ ions in β-Na2GaO3 with Cu²⁺ ions. The sodium concentration in the precursor β-NaGaO2 thin film determines the copper concentration in the β-CuGaO2 thin film because this thin film is fabricated through the ion-exchange of sodium ions in the precursor β-Na2GaO3 thin film with monovalent copper ions [20]; therefore, the concentration of sodium in β-NaGaO2 is crucial for controlling the electrical and optical properties of β-CuGaO2. However, the previous RF-sputtering [20] and electron beam evaporation techniques [33] resulted in highly off-stoichiometric β-Na1.8Ga2O4 thin films with δ ≥ 0.1, due to the above-mentioned factors.

Herein, we report the growth of β-Na2GaO3 thin films using the ultrasonic spray pyrolysis technique [34–36] where the chemical composition of the obtained films can be controlled by changing the chemical composition of the precursor solution. The spray pyrolysis thin-film growth technique is environment friendly because it is performed at atmospheric pressure and has a comparatively lower deposition temperature than...
the PVD methods. Furthermore, to make it completely environment friendly, we employed an aqueous solution of Ga$_2$O$_3$ and NaOH or an aqueous solution of β-NaGaO$_2$ as the precursor solution in this study, resulting in no other byproduct except water [36]. This is in contrast to common spray pyrolysis thin-film growth, where organometallic compounds, nitrates, and chlorides are used as starting materials; such processes exhaust CO$_2$, NO$_x$, Cl$_2$, and HCl gases, which are unsafe for humans and the environment. Subsequently, the chemical composition and morphology of the obtained films are determined.

2. Experimental

β-NaGaO$_2$ thin films were grown using a homebuilt ultrasonic spray pyrolysis system, as illustrated in Figure 1. The precursor solution was atomized at a frequency of 2.4 MHz using an ultrasonic atomizer (HM-2412, Honda Electronics, Japan) and supplied to the deposition chamber by a carrier gas. The deposition-upward configuration was employed in this study to minimize disruption of the flow of the precursor solution droplets floating in the carrier gas through thermal convection on the substrate surface. The substrate was heated using a ceramic heater plate (25 x 25 mm$^2$) equipped with a built-in thermocouple for temperature control (MS-1000 R, Sakaguchi E.H Voc Corp, Japan). A nichrome wire was wound around the outer surface of the inlet nozzle to enable preheating of the precursor solution droplets floating in the carrier gas.

Two precursor solutions, an aqueous solution of Ga$_2$O$_3$ and NaOH, and an aqueous solution of β-NaGaO$_2$, were prepared as described below. For the Ga$_2$O$_3$ and NaOH aqueous solution, a saturated solution of Ga$_2$O$_3$ to 1 M NaOH was prepared by sealing 3.75 g of Ga$_2$O$_3$ powder (99.99%, Kojundo Chemical Laboratory, Co., Ltd, Japan) in a Teflon-lined stainless-steel autoclave (50 mL capacity) with 40 mL of 1 M NaOH aqueous solution (Fujifilm Wako, Japan) and heated to 220°C for 5 h under autogenous pressure. The resulting solution, in which the residual solids were removed through filtration, was diluted ten-fold or two-fold and used as precursor solutions A and B, respectively. For the β-NaGaO$_2$ aqueous solution, 5.0 g of β-NaGaO$_2$ powder prepared through the standard solid-state reaction of Ga$_2$O$_3$ and Na$_2$CO$_3$ (99.8%, Fujifilm Wako, Japan) [37,38] was sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity) with 40 mL ultrapure water and heated to 220°C for 5 h under autogenous pressure. The residual solids were removed through filtration, and the clear solution was diluted two-fold and used as precursor solution C. The concentrations of Na and Ga in the precursor solutions that were determined through inductively coupled plasma atomic emission spectroscopy (ICP-AES; ARCOS EOP130, SPECTRO, Germany) are summarized in Table 1. The atomized precursor solution was supplied to the growth chamber through carrier O$_2$ gas. The flow rate of the carrier gas was 1 L min$^{-1}$ corresponding to a supply rate of 0.14 mL min$^{-1}$ of the source solution. The growth time was fixed to 10 min. A (1120)-Al$_2$O$_3$ single crystal with a thickness of 0.43 mm was used as the substrate. Before thin-film growth, the substrate was preheated at 900°C for 5 min in air in the deposition chamber for surface cleaning. The growth temperature, i.e. the substrate temperature, was set to 200°C or 400°C, and the precursor solution droplets floating in the carrier gas were preheated at 200°C or 400°C before spraying.

The crystalline phases of the obtained films were determined through X-ray diffraction (XRD; Cu Kα radiation, SmartLab, Rigaku, Japan). The morphologies of the surfaces and cross-sections of the films

Table 1. Concentrations of Na and Ga in the precursor solutions.

| Solution | Na concentration/mmol$^{-1}$ | Ga concentration/mmol$^{-1}$ |
|----------|-------------------------------|------------------------------|
| A        | 0.11                          | 0.067                        |
| B        | 0.55                          | 0.34                         |
| C        | 0.48                          | 0.45                         |

![Figure 1. Illustration of the (a) ultrasonic spray pyrolysis system and (b) growth chamber used in this study.](image)
were observed using a field emission scanning electron microscope (FE-SEM; SU6600, Hitachi, Japan). The film compositions were evaluated through ICP-AES and/or an electron probe microanalyzer (EPMA; JXA-8530F, JEOL Ltd.) at an acceleration voltage of 15 kV.

Thermo-fluid dynamics simulation was performed to evaluate the velocity and temperature distribution in the deposition chamber. The calculation was based on the finite element technique in computational fluid dynamics (CFD) using COMSOL Multiphysics ver. 5.5 software (COMSOL AB Inc., Denmark), involving the CFD module and heat transfer module. The geometries shown in Figure 1(b) were used as the simulated CFD models. The assumptions, boundary conditions, and parameters employed in the computation are summarized in Table 2.

### Table 2. Assumptions, boundary conditions and parameters used in the CFD simulation model.

| Assumptions | Boundary Conditions | Parameters |
|-------------|---------------------|------------|
| 1 The gas species are 79% N₂, and 21% O₂ (air). | 2 The gas is a Newtonian fluid with a weak compressible flow. | 3 The gas flow is calculated using Navier-Stokes equations. |
| 4 There is no slip on the wall surfaces. | 5 Gravity is the loading in the vertical direction of the deposition system. | 6 The applied pressure in the system is 1 atm at the outlet. |
| 7 The volume flow rate at the inlet is 1 Lmin⁻¹. | 8 The temperatures are 20°C at the inlet, 400°C on the substrate, and 20°C as the ambient. |

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3. Results and discussion

Figure 2(a) displays the XRD patterns of the films grown on a substrate at 400°C from precursor solution A where the concentrations of Ga and Na are 0.067 and 0.11 molL⁻¹, respectively. The diffractions observed in the growth without preheating the precursor solution droplets are identified as those of β-NaGaO₂ [39]. Although the intensity of the 002 diffraction is slightly higher, the relative intensities of the respective diffractions are almost identical to those of powdered β-NaGaO₂ (bottom panel of Figure 2(a)), indicating almost no preferential orientation in the film. The SEM images (Figure 2(b)) indicate that the obtained film is an aggregate of small particles isolated from each other without forming a continuous film. This observation is consistent with the XRD pattern indicating almost powdered β-NaGaO₂. For growth involving preheating of the precursor solution droplets at 200°C, the XRD pattern of the film is almost the same as that of powdered β-NaGaO₂; the particles are slightly larger and exhibit a slightly cylindrical shape compared to that without preheating the precursor solution droplets. However, the particles do not form continuous films. When the precursor solution is preheated at 400°C, the intensity of the 002 diffraction is significantly higher than those of the other diffractions, indicating that the β-NaGaO₂ crystals in the film exhibit preferential orientation along the [00 l] direction. In the

![Figure 2](image-url)
cross-sectional SEM image, an approximately 0.5-μm-thick layer and cylindrical particles (2 – 3 μm of diameter and 5 – 6 μm of lengths) on the top surface of the layer is observed.

The observed variation in the morphology of the film depending on the preheating temperature can be reasonably understood based on the common understanding of crystal precipitation and morphology in the spray pyrolysis process [34,35]. The precursor solution droplets vary from leaving the nozzle to approaching the substrate, as depicted in Figure 3. A more detailed explanation of the spray pyrolysis reaction based on the Leidenfrost phenomenon has recently been proposed [40], and the Leidenfrost phenomenon during Ga2O3 thin-film deposition has been directly observed by high-speed camera very recently [41]. The difference between the conventional explanation as shown in Figure 3 and the explanation based on the Leidenfrost phenomenon is whether the precursor solution completely evaporates or not. In the following discussion, we explained the variation of the morphology of the thin films dependent on the preheating temperature based on the conventional explanation as shown in Figure 3. In general, (i) powdered precipitates are deposited on the substrate when the droplet splashes on it because of the evaporation of the solvent and decomposition of the solute on the substrate (Figure 3(a)). (ii) Films that continuously cover the substrate surface are deposited when the solvent evaporates, and the solute vaporizes or sublimes before approaching the substrate because the solute vapor diffuses onto the substrate and undergoes a heterogeneous precipitation reaction on the substrate (Figure 3(b)). (iii) Fine powders are deposited when the solvent evaporates, the solute vaporizes or sublimes, and the homogeneous precipitation reaction completes before approaching the substrate because the fine solid particles precipitated from the solute vapor reach the substrate (Figure 3(c)). As the substrate heated at high temperatures is the only thermal source for heating the floating droplets in the conventional spray pyrolysis system [34,35], variation of the morphology depending on the substrate temperature has been reported [42–45]. In addition, the distance between the nozzle and substrate, which determines the heating duration of the floating droplets by the hot substrate, strongly affects the morphology of the precipitates [35]. In the spray pyrolysis system utilized in this study, a heating wire was wound around the outer surface of the nozzle, enabling direct control of the heat input to the droplet without changing the substrate temperature or the distance between the nozzle and substrate. Consequently, the source materials in the precursor solution transform into vapor, as shown in Figure 3(b), when the precursor solution is preheated at 400°C. As a result, a film covering the substrate surface is formed, as depicted in the bottom panel of Figure 2(b). In the growth without and with preheating of the precursor solution droplets at 200°C, the deposited particles with diameters of 1.5 – 3 μm and lengths of 2–5 μm are not simple spherical shapes. When a 4.0-μm diameter droplet generated by the

Figure 3. Illustration of the deposition process with different heat input to the droplets: (a) low heat input, (b) medium heat input, and (c) high heat input.
ultrasonic atomizer experiences evaporative dryness, a spherical β-NaGaO₂ particle with a diameter of 0.8 μm is formed based on the concentration of the precursor solution A. This indicates that β-NaGaO₂ particles grew during deposition regardless of whether the precursor solution droplets are preheated at 200°C. In particular, the particles grow along a direction perpendicular to the substrate and are cylindrical-shaped in the growth involving preheating of the precursor solution at 200°C, as observed in the middle panel of Figure 2(b). These observations suggest that the heat input is insufficient for continuous film growth, but a portion of the solute is vaporized and consumed for particle growth. This situation can be considered as the intermediate condition between those depicted in Figure 3(a,b).

The growth of cylindrical-shaped crystals and not continuous film in the growth involving preheating of the precursor solutions implies small number of heterogeneous nucleation site during growth; therefore, growth was performed using the five-fold concentrated precursor solution B instead of precursor solution A. Figure 4(a) displays the XRD patterns of the films grown on a substrate at 400°C using precursor solution B. In contrast to the growth using dilute precursor solution A, the β-NaGaO₂ crystals in the film exhibit preferential orientation along the [00 l] direction in the growth without as well as with preheating of the precursor solution droplets at 200°C.

The XRD pattern of the film grown using the precursor solution preheated at 400°C indicates that the [00 l]-orientation is weakened, and an almost powder pattern is observed. The SEM images in Figure 4(b) show that a continuous film is grown using precursor solutions without and with preheating at 200°C. For growth using the precursor solution without preheating, the film surface exhibits slight undulation and the film thickness ranges from 3 to 5 μm, whereas for growth involving preheating of the precursor solution at 200°C, the surface is almost flat, and the film thickness is approximately 3 μm. Thus, β-NaGaO₂ thin films were successfully formed using the ultrasonic spray pyrolysis without byproducts other than water through a completely environment-friendly thin-film growth process. Growth using a precursor solution preheated at 400°C results in a very thick film (approximately 8 μm) with many cylindrical crystals on the top surface, indicating rapid crystal growth under this condition due to excess supply of the source material vapor.

The cross-sectional SEM images of all the films (Figure 4(b)) indicate that the film structure includes approximately 0.8-μm diameter columnar crystals. The XRD patterns (Figure 4(a)) show that the columnar crystals grow along the [00 l] direction. The c-axis of the β-NaGaO₂ crystal with a ternary wurtzite structure (β-NaFeO₂ structure) corresponds to the c-axis of a simple wurtzite structure [46,47]. Compounds with

![Figure 4](image_url)

**Figure 4.** Growth of β-NaGaO₂ from 0.17 molL⁻¹ Ga₂O₃ solution in 0.55 molL⁻¹ NaOH aqueous solution (solution B) without preheating and with preheating at 200 and 400°C, respectively, on a substrate at 400°C. (a) XRD patterns and photographic images and (b) surface and cross-sectional SEM images. The diffraction peaks indicated with triangles are related to those from the substrate.
wurtzite structures, such as ZnO, AlN, and GaN, preferentially grow along the [00 \bar{l}] direction [48–52]; thus, the ternary-wurtzite β-NaGaO₂ crystal has inherited the preferential growth direction from binary wurtzite-type compounds. We employed the (1120)-Al₂O₃ single crystal as substrates in the present study expecting [121]-oriented β-NaGaO₂ thin-film deposition [33] because [121]-oriented β-NaGaO₂ thin film exhibits relatively small area shrinkage during the ion-exchange to obtain β-CuGaO₂ thin film. Unfortunately, the orientation of thin films is determined by the kinetics or surface energy owing to the high deposition rate and not by the crystallographic orientation relationship between the substrate and film.

The films are obtained on a very small area on the substrate, as indicated by the dotted circle in the top panel in Figure 4(a) (approximately 5 mm diameter on an approximately 15 × 15 mm² substrate). The reason for film grown on such a small area of the substrate can be inferred from the CFD simulation results as follows: Figure 5(a,b) show the steady-state flow velocity and temperature distribution, respectively, of the gas flowing through the deposition chamber, evaluated through CFD simulation. In this simulation, the gas was not preheated when passing through the nozzle. The flow velocity and temperature distribution were symmetric and systematically varied, and as the deposition-upward configuration was applied, local turbulent flow and temperature fluctuation due to

Figure 5. (a) Steady-state flow velocity distribution and (b) temperature distribution of the gas flowing through the deposition chamber, evaluated through CFD simulation in the vertical cross-section of the chamber through the center of the substrate (upper panels) and in the horizontal cross-section of the chamber 0.5 mm from the substrate (lower panels). The dotted lines in the upper panels indicate the position of the horizontal cross-section shown in the lower panels. Simulation is performed without preheating the carrier gas. (c) Variation of the temperature of the center of the gas flow as a function of distance from the substrate surface.
disruption of the thermal convection were not observed. After leaving the nozzle, the gas flow was concentrated in the nozzle extension area, and it further spread slightly to the surrounding area before reaching the substrate (upper panel of Figure 5(a)). This indicates that the cluster of precursor droplets collides with the substrate while maintaining the cross-sectional shape of the nozzle. A small velocity due to deceleration induced by collision compared to the surrounding area was observed in a small area with a diameter of approximately 5 mm (lower panel of Figure 5(a)) in the horizontal cross-section of the chamber. With respect to the temperature distribution, in this small area, the temperature of the gas leaving the nozzle at 20°C increased to a temperature slightly lower than the substrate temperature (lower panel of Figure 5(b)). In addition, the temperature at the center of the gas flow is heated up to 350°C within 0.1 mm of the substrate even without preheating, as indicated in Figure 5(c), indicating that the splaying does not significantly affect the substrate temperature. Thus, the simulation indicated that only in the area where the continuous film was deposited (approximately 5 mm-diameter area), the β-NaGaO₂ source material was sufficiently supplied and remained for a sufficient duration, and the temperature was increased to a sufficient level.

Recently, columnar grain growth of Cs₂AgBiBr₆ was reported using ultrasonic mist deposition by Haruta et al. [53]. They explained the columnar growth by dissolution of pre-deposited crystals into the precursor solution and following recrystallization, based on the situation that the precursor solution reached the substrate surface maintaining the mist droplet state. In contrast to that situation, in our experimental setup, the temperature of the carrier gas is heated up to 350°C within 0.1 mm of the substrate even without preheating as shown in Figure 5(c). Because of this, the solvent water should evaporate completely before the precursor solution droplet arrived on the substrate surface. This suggests that the growth of the β-NaGaO₂ thin film is not described by the dissolution and recrystallization on the substrate but the direct growth shown in Figure 3(b).

ICP-AES analysis of the films indicates that the atomic ratio of the films grown using precursor solution B is C_{Na}:C_{Ga} = 1.0:0.58, which is almost identical to that of the precursor solution (C_{Na}:C_{Ga} = 1.0:0.61). This confirms that the sodium concentration in the film is controlled by that in the precursor solution when using the spray pyrolysis technique as the growth method because of the higher pressure of the growth atmosphere and lower growth temperature compared to the PVD method. Thus, we can conclude that spray pyrolysis is a suitable technique for growing films containing sodium.

Figure 6 shows the growth results using precursor solution C, where the concentrations of Na and Ga are 0.48 and 0.45 molL⁻¹, respectively, demonstrating that the film composition can be controlled by the composition of the precursor solution. The XRD pattern shows almost no preferential orientation in the film unlike the films obtained from the solution B (Figure 4); however, the obtained film continuously covers the substrate, and the surface is flat with a uniform thickness of approximately 5 μm. The atomic ratio of the film is C_{Na}:C_{Ga} = 1.0:0.91, which is identical to that of the precursor solution (C_{Na}:C_{Ga} = 1.0:0.94). This further confirms that the sodium concentration in the film is controlled by that in the precursor solution and clearly indicates that stoichiometric β-NaGaO₂ films can be grown using a precursor solution containing equimolar amounts of Na and Ga. The reason for the film shown in Figure 6 exhibited no preferential orientation in contrast to the film shown in Figure 4 exhibited [00 l]-orientation is plausibly attributed to the lower substrate temperature.
for the film shown in Figure 6 (200°C) than the film shown in Figure 4 (400°C). However, the compositions of the films, such as the concentrations of the Ga-vacancy and the oxygen vacancy, were different from each other, i.e. NaGa$_{0.58}$O$_{2.6}$ for the film shown in Figure 4 and NaGa$_{0.91}$O$_{2.6}$ for the film shown in Figure 6. We cannot exclude the composition difference as an origin of the orientation difference, because the composition difference generally causes the difference of diffusivity of component atoms in the crystal, resulting in the difference in crystal growth mode.

4. Conclusions

We studied the growth of β-NaGaO$_2$ thin films through ultrasonic spray pyrolysis and successfully formed [00 l]-oriented β-NaGaO$_2$ thin films at a high growth rate of 300–500 nm min$^{-1}$ from a precursor solution of Ga$_2$O$_3$ and NaOH in water and an aqueous solution of β-NaGaO$_2$. The atomic ratios of Na and Ga in the films were the same as those of the precursor solutions, indicating that the spray pyrolysis method could address the lack of the high-vapor-pressure sodium component in films owing to its lower deposition temperature and higher deposition pressure compared to PVD methods such as sputtering and evaporation. This suggests that the chemical composition of the film can be controlled by that of the precursor solution during spray pyrolysis deposition, as demonstrated in this study. Thus, the spray pyrolysis technique is a suitable thin-film deposition method, particularly for materials that include components with high vapor pressure, such as Na. The spray pyrolysis system used in this study enabled to preheat the droplet of the source solution. The morphology of the obtained films was strongly dependent on the preheating temperature, indicating that the preheating of the solution droplet is effective to control the morphology of the films. In addition, the spray pyrolysis method employed in the present study is very environment friendly because an aqueous solution of oxide and/or hydroxide was employed as the precursor solution, which does not produce any other byproduct other than water. This will be a big advantage in the future of materials manufacturing. Therefore, it is expected that the β-NaGaO$_2$ thin films formed through spray pyrolysis deposition can be used for fabricating β-CuGaO$_2$ thin films, which can be applied as absorber material in safe and environment friendly thin-film solar cells.

Disclosure statement

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