Orientation control of $\beta$-NaGaO$_2$ thin film: a precursor for $\beta$-CuGaO$_2$ as a thin-film solar cell absorber

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The $\beta$-NaGaO$_2$ thin film is a precursor film for the fabrication of a $\beta$-CuGaO$_2$ thin film by ion exchange, which is expected to be applicable to a thin film solar cell. The $\beta$-NaGaO$_2$ thin films were fabricated by electron beam evaporation, and they showed substrate dependence of the crystal orientation, which is in contrast to the recently reported $\beta$-NaGaO$_2$ films obtained by sputtering that exhibited no substrate dependence. The difference observed for evaporation and sputtering was discussed based on the kinetic energy of the particles impinging on the substrate during the deposition. An appropriate orientation of the $\beta$-NaGaO$_2$ film for ion exchange was discussed in terms of the in-plane shrinkage generated during the ion exchange from $\beta$-NaGaO$_2$ to $\beta$-CuGaO$_2$.

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1. Introduction

$\beta$-CuGaO$_2$ is an exclusive oxide semiconductor and can be applied as a thin-film solar cell absorber that realizes high conversion efficiency and is highly competitive against chalcogenide semiconductors, such as CdTe and Cu(In,Ga)Se$_2$. $\beta$-CuGaO$_2$ has a direct band gap of 1.47 eV and exhibits strong light absorption near the band edge. $\beta$-CuGaO$_2$ is a metastable phase that can only be obtained through ion exchange of Na$^+$ ions in precursor $\beta$-NaGaO$_2$ with Cu$^+$ ions. Recently, the ion exchange was applied to the $\beta$-NaGaO$_2$ thin films using CuCl vapor as a Cu$^+$ ion source, and $\beta$-CuGaO$_2$ thin films were successfully obtained. As the crystal orientation of the films before and after ion exchange are the same, it was shown that the ion exchange from $\beta$-NaGaO$_2$ to $\beta$-CuGaO$_2$ develops preserving the structural framework and the crystal orientation; that is, the reaction develops topotactically. Although $\beta$-CuGaO$_2$ thin films were obtained in the previous study, the following challenges to improve the quality of the films still remained: (i) Only the (110)-oriented precursor $\beta$-NaGaO$_2$ films were obtained by sputtering regardless of the substrates. Because in-plane shrinkage occurred during the ion exchange, which is caused by the size difference between Na$^+$ and Cu$^+$ ions, is large in the (110)-oriented film, a lot of in-plane cracks were generated in the obtained $\beta$-CuGaO$_2$ film after ion exchange. (ii) The composition of the precursor $\beta$-NaGaO$_2$ films that were deposited by magnetron sputtering deviated from the stoichiometry and exhibited a 10% Na-poor composition, $X_{Na}X_{Ga} = 0.91$. This resulted in a nonstoichiometric and 10% Cu-poor $\beta$-CuGaO$_2$ thin film since the number of Cu$^+$ ions introduced into the film by ion exchange is determined by the number of Na$^+$ ions originally existing in the precursor film. Therefore, control of the crystal orientation and adjusting the stoichiometry of the precursor $\beta$-NaGaO$_2$ thin films are essential to obtain stoichiometric $\beta$-CuGaO$_2$ thin films that are free of cracks.

Here, we fabricated a $\beta$-NaGaO$_2$ thin film by electron beam evaporation on Al$_2$O$_3$ single crystal substrates with various crystal orientations. The obtained $\beta$-NaGaO$_2$ films exhibited various crystal orientations depending on the substrates, although a previous study on the deposition by sputtering resulted in (110)-oriented films regardless of the substrates. The reason why the orientation of the films deposited by electron beam evaporation depended on the orientation of the substrates in contrast to the films obtained by sputtering is discussed in terms of the kinetic energy of the particles impinging on the surface of the substrate. The orientation of the $\beta$-NaGaO$_2$ films suitable to fabricate crack-free $\beta$-CuGaO$_2$ films is discussed based on the shrinkage introduced during the ion exchange. The composition of the $\beta$-NaGaO$_2$ films obtained was unfortunately not stoichiometric but Na-poor, similar to the films deposited by sputtering. A method to obtain stoichiometric $\beta$-NaGaO$_2$ thin films is also discussed.

2. Experimental procedure

The evaporation sources of $\beta$-NaGaO$_2$ were prepared by a conventional solid-state reaction of Na$_2$CO$_3$ (99.8%; Wako Pure Chemical Industries, Japan) and Ga$_2$O$_3$ (99.99%; Kojundo Chemical Laboratory, Japan). Na$_2$CO$_3$ and Ga$_2$O$_3$ were weighed and mixed, and then pressed into 17.2 mm diameter disks at 100 MPa. The disks were calcined at 1013 K for 14 h in air. The calcined disks were crushed and pressed into 9 mm diameter disks, and then it was sintered at 1173 K for 20 h in air.

$\beta$-NaGaO$_2$ thin films were deposited by electron beam evaporation (Kenix Co., Ltd., KB-200, Japan). The substrates used were c-plane (0001)-Al$_2$O$_3$, a-plane (1120)-Al$_2$O$_3$ and r-plane...
(1102)-Al2O3 single crystals and SiO2-glass substrates for comparison. The film thickness and deposition rate were monitored by a quartz crystal oscillator during the deposition. The thickness of the obtained films was approximately 450 nm. The other conditions employed are summarized in Table 1.

The crystal phase and orientation of the obtained thin films were identified by θ-2θ X-ray diffraction (XRD) (Rigaku, RINT2500, Cu Kα radiation). During XRD measurement, the β-NaGaO2 thin films were exposed to a dry air flow at 500 cm3 min⁻¹ to prevent water absorption of the films, because β-NaGaO2 is highly hygroscopic.31 The chemical compositions of the films were determined by energy-dispersive X-ray spectroscopy (JEOL Ltd., JED-2300, Japan).

3. Results and discussion
3.1 Deposition and characterization of β-NaGaO2 films on various substrates

Figure 1 shows θ-2θ XRD profiles of the β-NaGaO2 films deposited on various substrates by electron beam evaporation. On the (0001)-Al2O3 substrate, only a peak attributed to a (110) diffraction of β-NaGaO2 appeared indicating that a (110)-oriented β-NaGaO2 film was obtained. On the (1120)-Al2O3 and (1102)-Al2O3 substrates, (121) and (200) diffractions were respectively greater than the other diffractions compared with β-NaGaO2 powder indicating that (121)- and (100)-oriented films were respectively obtained. The β-NaGaO2 film deposited on SiO2-glass substrate did not exhibit distinct diffractions indicating that the film was in an amorphous form.

β-NaGaO2 has the β-NaFeO2-type structure, which is one of the wurtzite-derived structures. The thin films of wurtzite-type ZnO typically exhibit (0001)-orientation on (0001)- and (1120)-Al2O3 substrates (Table 2). Other wurtzite-type and β-NaFeO2-type materials, such as GaN,7 BeO8 and β-AgGaO2,9 also exhibit (0001)-orientation on a (0001)-Al2O3 substrate. The reason why only β-NaGaO2 films show different orientations from the other wurtzite-related materials is still unclear. Larger structural distortion of β-NaGaO2 from the ideal wurtzite structure10 may play a role in these unique orientations.

In contrast to the crystal orientation observed in the present study, β-NaGaO2 films deposited by sputtering were always (110)-oriented regardless of the substrates8 (Table 2). The difference between electron beam evaporation and sputtering can be explained as follows. According to the previous study on the deposition of ZnO thin films,11 a higher kinetic energy of the particles impinging on the surface of the substrate during deposition leads to the exposure of the crystal plane having a lower surface energy [(0001) plane in the case of ZnO] in the nucleation stage by promoting atomic migration on the top surface of the growing film, while a lower kinetic energy of the particles tends to increase the possibility of exposure of planes having higher surface energy [(1120) and (1010) planes in the case of ZnO]. Taking into account the fact that the kinetic energy of particles impinging on the substrate by the sputtering method is much higher (5–10 eV) than that by evaporation (~0.2 eV),12 it is supposed that the (110) plane of β-NaGaO2 has the lowest surface energy and the exposure of this plane is more promoted by sputtering than electron beam evaporation.

It is known that the kinetic energy of the particles impinging on the surface is an important factor in determining whether the film would be crystalline or amorphous, for example, as was reported for TiO2 film deposition where the film exhibited crystalline form by sputtering (higher kinetic energy) and amorphous form by evaporation (lower kinetic energy).13 Therefore, the deposition of an amorphous film on SiO2 glass by electron beam evaporation [Fig. 1(e)] arises from the low kinetic energy of the evaporated particles.

The substrate dependence of the orientation of the films obtained by electron beam evaporation clearly indicates that the interaction between the substrate and the particles arriving on the

Table 1. Conditions used for electron beam evaporation of β-NaGaO2 thin films

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure</td>
<td>&lt;9 × 10⁻⁵ Pa</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>823 K</td>
</tr>
<tr>
<td>Accelerating voltage of electron beam</td>
<td>3.5–4 kV</td>
</tr>
<tr>
<td>Emission current</td>
<td>~10 mA</td>
</tr>
<tr>
<td>Pressure during deposition</td>
<td>~5 × 10⁻⁴ Pa</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>9 nm min⁻¹</td>
</tr>
<tr>
<td>Deposition time</td>
<td>50 min</td>
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</tbody>
</table>

Table 2. Orientations of β-NaGaO2 thin films fabricated by sputtering and electron beam evaporation on various substrates together with ZnO thin films

<table>
<thead>
<tr>
<th>Substrate</th>
<th>β-NaGaO2 (evaporation)</th>
<th>ZnO (sputtering)</th>
<th>β-NaGaO2 (sputtering)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0001)-Al2O3</td>
<td>(110)</td>
<td>(0001)/(001)</td>
<td>(110)</td>
</tr>
<tr>
<td>(1120)-Al2O3</td>
<td>(121)</td>
<td>(0001)/(001)</td>
<td>(110)</td>
</tr>
<tr>
<td>(1102)-Al2O3</td>
<td>(100)</td>
<td>(1120)/(010)</td>
<td>(110)</td>
</tr>
<tr>
<td>SiO2-glass</td>
<td>amorphous</td>
<td>typically (0001)/(001)</td>
<td>(110)</td>
</tr>
</tbody>
</table>

Fig. 1. XRD profiles of (a) β-NaGaO2 powder and β-NaGaO2 films deposited by electron beam evaporation on various substrates: (b) (0001)-Al2O3, (c) (1120)-Al2O3, (d) (1102)-Al2O3 and (e) SiO2-glass substrate. The peaks marked with asterisks are diffractions of the Al2O3 single crystal.
substrate worked as the driving force for the oriented crystallization. The possible relationships of the atomic arrangements between the surfaces of the Al2O3 substrates and β-NaGaO2 are shown in Fig. 2. Owing to the large lattice mismatch of larger than 10%, epitaxial growth does not develop under such a large mismatch. A detailed relationship needs to be determined that should include the possibility of higher order epitaxy similar to that of the epitaxial ZnO film on a (0001)-Al2O3 substrate with a lattice mismatch of as large as 18.3%.15)

3.2 Suitable orientation of a β-NaGaO2 precursor film for the fabrication of a crack-free β-CuGaO2 thin film

It has previously been reported that many in-plane cracks were generated inside the film during the ion exchange from β-NaGaO2 to β-CuGaO2 when the (110)-oriented β-NaGaO2 thin film was used as a precursor. This is because of the large in-plane shrinkage, which occurs during the ion exchange of large Na+ ions in β-NaGaO2 films with small Cu+ ions. Figure 3 shows the in-plane shrinkage generated during ion exchange for various orientations. Among the orientations obtained in this work [Fig. 3(a)–(c)], the (121)-oriented film exhibited the smallest line and area shrinkage of 2.9 and 4.7%, respectively [Fig. 3(b)]. This area shrinkage of 4.7% was ~1% smaller than that of the previously obtained (110)-oriented film; furthermore, the shrinkage was more isotropic in the (121)-oriented film than in the (110)-oriented film; that is, the largest in-plane shrinkage in (121)-oriented film was 2.9%, which is significantly smaller than that in (110)-oriented film of 5.4%. Therefore, the crack formation during ion exchange might be suppressed when the (121)-oriented β-NaGaO2 film is subjected to the ion exchange. The area shrinkage of the (010)-oriented film should be the smallest of 1.1% based on the assumption [Fig. 3(d)]; therefore, the (010)-oriented β-NaGaO2 film is the ideal precursor film for the fabrication of β-CuGaO2 films, even though the (010)-oriented β-NaGaO2 films are yet to be obtained.

The chemical compositions of the β-NaGaO2 thin films obtained were all on the Na-poor/Ga-rich side of the stoichiometry (Table 3) similar to the films deposited by sputtering (XNa/XGa = 0.9:1).5) When an evaporation source was continuously used for the deposition of two β-NaGaO2 thin films, the Na content in the film that was subsequently deposited was much smaller than that in the film deposited first (Table 3); this indicates that the Na2O component preferentially evaporates as compared with a Ga2O3 component, and the composition of the source itself changes to Na-poor during the evaporation. This results in the concentration of Na in particles impinging on the substrate surface being higher than that of Ga because of the preferential evaporation of the Na2O component from the evaporation source; however, Na2O is supposed to re-evaporate from the surface more preferentially than Ga2O3 because of the higher equilibrium total vapor pressure of Na2O16) than that of Ga2O3.17) As a result, the amount of the residual Na in the film deposited is smaller than that of Ga, although the concentration of the Na2O component in the particles impinging on the substrate surface is higher than that of Ga. This explanation is consistent with the previous studies where the thin films of stoichiometric β-LiGaO2 that possess the same structure as β-NaGaO2 were deposited by sputtering unlike β-

![Fig. 2. Schematic drawings of the atomic arrangements of β-NaGaO2 and the surface of Al2O3 substrates, and their mismatch. (a) (110)-β-NaGaO2 on (0001)-Al2O3, (b) (121)-β-NaGaO2 on (1120)-Al2O3 and (c) (100)-β-NaGaO2 on (102)-Al2O3. The distance labeled with “ave.” indicates the mean distance taking the anisotropy of the atomic arrangement into account.](image)

![Fig. 3. Schematic illustration of (110), (121), (100) and (010) planes in the orthorhombic wurtzite-derived structure. The values noted in red indicate the line and area shrinkages generated during ion exchange from β-NaGaO2 to β-CuGaO2. Line shrinkages were calculated as follows; |hkl|CuGaO2−|hkl|NaGaO2|/|hkl|NaGaO2.](image)

| Table 3. Chemical composition of the films deposited on (1120)-Al2O3. Evaporation source No.2 was used for two depositions in succession. | |
|---|---|---|
| Evaporation source | Cumulative deposition time | Film composition (Na/Ga) |
| No.1 | 0–28 min | 0.86 |
| No.2 | 28–42 min | 0.37 |
| No.2 | 0–50 min | 0.66 |
taking the three orders of magnitude lower equilibrium total vapor pressure of Li$_2$O than Na$_2$O into account. Based on these findings, it is difficult to obtain stoichiometric $\beta$-NaGaO$_2$ films by physical vapor deposition using $\beta$-NaGaO$_2$ as a source material, because Na$_2$O re-evaporates preferentially from the surface more than Ga$_2$O$_3$. The stoichiometric $\beta$-NaGaO$_2$ films are likely to be obtained by chemical vapor deposition.

4. Summary

We fabricated $\beta$-NaGaO$_2$ thin films by electron beam evaporation. The $\beta$-NaGaO$_2$ films deposited on (0001)-Al$_2$O$_3$, (1120)-Al$_2$O$_3$ (1102)-Al$_2$O$_3$ substrates respectively exhibited (110)-, (121)- and (100)-orientation, although the previous deposition by sputtering resulted in (110)-oriented films regardless of the substrates. The reason for the difference of the orientation in the film deposited between the electron beam evaporation and the sputter-evaporation, the (121)-oriented $\beta$-Ga$_2$O$_3$ thin films implies that it is difficult to obtain stoichiometric $\beta$-NaGaO$_2$ thin films regardless of the substrates and the vapor deposition program. Nevertheless, further study is required to obtain the ideal film expected to exhibit the smallest shrinkage, that is, the (010)-oriented $\beta$-NaGaO$_2$ thin film, which is yet to be obtained. The composition analysis of the obtained films implies that it is difficult to obtain stoichiometric $\beta$-NaGaO$_2$ films by physical vapor deposition using $\beta$-NaGaO$_2$ as a source material, because an extremely high vapor pressure of Na$_2$O preferentially promotes re-evaporation of Na$_2$O from the surface more than Ga$_2$O$_3$. The stoichiometric $\beta$-NaGaO$_2$ films are likely to be obtained by chemical vapor deposition.

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