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Combinatorial approach to solution-processed InGaO$_3$(ZnO)$_m$ superlattice films: Growth mechanisms and their thermoelectric properties

Sung Woon Cho$^a$, Myoungho Jeong$^{b,c}$, Jun Hyeon Kim$^a$, Yong Hun Kwon$^a$, Hyoungsub Kim$^a$, Jeong Yong Lee$^{b,c}$ and Hyung Koun Cho$^a$

Multicomponent amorphous InGaZnO thin films with several metal cations have been synthesized with flexible chemical composition control based on a sol-gel process, and a combinatorial approach through sol-gel process enable us to perform systematic survey to fluently find the best film properties. Contrary to amorphous films, crystalline InGaO$_3$(ZnO)$_m$ requires refined chemical composition ratio among metal cations. These ratios are expected to affect the growth evolution and thermoelectric properties of two-dimensional InGaO$_3$(ZnO)$_m$ superlattice structures with various compositional combinations. Here, we explore a combinatorial approach to the ratio of metal cations using various mole fractions of metal precursors in InGaZnO sol for amorphous InGaZnO films fabricated on epitaxial ZnO buffer layer, and then they were crystallized with various chemical compositions. The crystallized InGaO$_3$(ZnO)$_m$ films can be classified as strong single-phase InGaO$_3$(ZnO)$_m$, double-phase InGaO$_3$(ZnO)$_m$/InGaO$_3$(ZnO)$_m$, and weak single-phase InGaO$_3$(ZnO)$_m$ with excess metal ions. Among them, the strong single-phase InGaO$_3$(ZnO)$_m$ films with superlattice structures showed superior thermoelectric power factors. The detailed microstructural growth evolution of single- and double-phase InGaO$_3$(ZnO)$_m$ films were investigated using transmission electron microscopy.

1. Introduction

Hosono et al. proposed a novel oxide semiconductor composed of single crystalline InGaO$_3$(ZnO)$_m$ with a two-dimensional periodic superlattice structure and have fabricated oxide-based thick film transistors (TFTs) with high mobility (~ 80 cm$^2$ V$^{-1}$ s$^{-1}$) due to reduced effective mass of electrons by quantum confinement effect. However, a subsequent and more innovative approach using low process temperature was suggested by the same group for amorphous In-Ga-Zn-O (InGaZnO) alloying compounds, which have been actively employed as channel layers for flat panel displays, as an alternative to existing Si-based TFTs such as amorphous Si and low-temperature polycrystalline Si.

Thus, significant attention has been paid to the development of amorphous oxide semiconductors, and technical interest in the single crystalline InGaO$_3$(ZnO)$_m$ films almost disappeared due to the high temperature process (~ 1400 °C) and unconfirmed application field.

Until recently, semiconducting or semi-insulating superlattice films were widely accepted as novel active structures due to the observation of quantum confinement effects and excellent physical properties. Firstly, an example of specifying a superlattice structure is the III-V compounds semiconductors such as InGaAlP, InGaN, and AlGaAsP alloys. These superlattice-based III-V thin films have been utilized as active layers in applications such as giant magnetoresistance, laser diodes, and light-emitting diodes. Next, several groups reported dramatically enhanced thermoelectric performance by introducing various superlattices in traditional thermoelectric complex materials such as Bi$_2$Te$_3$/Bi$_2$Se$_3$ and PbTe/PbSe. Their thermoelectric properties were effectively modified by controlling the thickness of each layer in superlattice structure. Anisotropic superlattice structures can improve thermoelectric figure of merit (ZT) values by taking advantage of the sharp electron density of states function due to quantum confinement effect for Seebeck coefficient, and frequent interface scattering of the phonons for thermal transport. Furthermore, oxide materials based on superlattice structures such as Bi$_2$O$_3$/Cu$_2$Se$_2$ and SrTi$_1$-$x$Nb$_x$O$_3$/SrTiO$_3$ have also exhibited enhanced Seebeck coefficient and ZT values compared with their bulk materials.

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Generally, the homogenous crystallization of InGaO$_3$(ZnO)$_m$ film with a natural superlattice structure, where InO$_2$ and GaO$^+$ (ZnO)$_m$ layers are alternatively stacked along the c-axis, has required high temperature to guarantee poly (> 700 °C) and single (> 1400 °C) crystal phases. In contrast, we have already reported the formation of single crystalline InGaO$_3$(ZnO)$_m$ films heterogeneously crystallized using ZnO buffer layers at reduced temperatures (900 °C). These buffer layers are helpful for reducing the critical energy required for the crystallization of InGaO$_3$(ZnO)$_m$ films by considerably decreasing the lattice mismatch between the InGaO$_3$(ZnO)$_m$ and substrate. In our first approach, we used epitaxial ZnO films and a sputtered InGaZnO target, and the resulting sample was thermally annealed for crystallization at 900 °C, resulting in the formation of single crystalline InGaO$_3$(ZnO)$_m$. Next, we have used amorphous InGaZnO (a-InGaZnO) films prepared via wet-based spin coating instead of sputtering InGaZnO films. Furthermore, it is identified that single crystalline InGaO$_3$(ZnO)$_m$ film with specific m value (m = 2) and superlattice structure shows two-fold increased Seebeck coefficient and dramatically low thermal conductivity (1.11 W m$^{-1}$ K$^{-1}$) compared to those of ZnO and In$_2$O$_3$ with three-dimensional structure. Contrary to amorphous films, crystalline InGaO$_3$(ZnO)$_m$ requires ideal stoichiometric composition ratio among metal cations. While the thickness of the InO$_2$ layer in crystalline InGaO$_3$(ZnO)$_m$ remains unchanged, the thickness of the GaO$^+$ (ZnO)$_m$ layer is varied through the selection of m. The m value of GaO$^+$ (ZnO)$_m$ layer is naturally determined by the compositional ratio of metal ions in InGaO$_3$(ZnO)$_m$ superlattice. Thus, we believe that the microstructural and thermoelectric properties of the InGaO$_3$(ZnO)$_m$ superlattice can dramatically be influenced by the compositional ratio of metal ions, as complex or other oxide thermoelectric materials with superlattice structure. However, combinatorial approach about various compositional ratios of metal ions in InGaO$_3$(ZnO)$_m$ superlattice films have not been performed due to the difficulties of composition control on previous vacuum-based and high temperature process.

In this study, we prepared various a-InGaZnO films with various metal cation ratios on the ZnO buffer layers through combinatorial approach using sol-gel process which easily and fluently can control chemical composition, like the solution-processed a-InGaZnO channels in the oxide TFTs. Following thermal treatment, we obtained crystallized InGaO$_3$(ZnO)$_m$ films with superlattice structures, and compared the compositional and microstructural changes via thermal annealing of these films. The basic thermoelectric properties (Seebeck coefficient, electrical resistivity, and power factors) of these InGaO$_3$(ZnO)$_m$ products were analyzed. Furthermore, we investigated detailed microstructural evolution during the thermal annealing process and the formation of superlattice structures using transmission electron microscopy (TEM).

2. Experimental

The entire sub-sequential process to prepare crystalline InGaO$_3$(ZnO)$_m$ films with various chemical compositions was designed with three steps: i) an epitaxial ZnO buffer layer (sputtering), ii) the a-InGaZnO layer (sol-gel), and iii) the
formation of the InGaO$_3$(ZnO)$_m$ superlattice (high temperature annealing), as shown in Fig. 1.

**Step 1 : Epitaxial ZnO buffer layer deposition (sputtering)**

The c-plane sapphire substrate was cleaned via sequential sonication for 10 min each in acetone, ethanol, and deionized water, and then dried in an oven at 70 °C for 1 hour. The ZnO buffer layers were epitaxially prepared on sapphire substrates via radio frequency magnetron sputtering to suppress lattice mismatch between the sapphire substrate and InGaO$_3$(ZnO)$_m$ crystals, as well as to provide seed sites for solid phase epitaxy at relatively reduced temperatures. The ZnO buffer layers were deposited at 700 °C and under a mixed gas atmosphere (15 mTorr) of Ar/O$_2$ (20/10 sccm). The thickness of the ZnO was fixed at 50 nm, since it was expected to affect the crystal phase and composition of the crystallized InGaO$_3$(ZnO)$_m$ films.

**Step 2 : a-InGaZnO layer deposition (sol-gel)**

Preferentially, metal precursors of various combinatorial ratios (In : Ga : Zn = X : Y : Z) among In, Ga, and Zn cations were dissolved in 2-methoxyethanol (2-ME, C$_7$H$_{14}$O$_2$) solvent of 10 mL to 0.2 M total metal concentration in a glove box under a nitrogen atmosphere and low moisture. Indium nitrate hydrate [In(NO$_3$)$_3$·xH$_2$O, Aldrich], gallium nitrate hydrate [Ga(NO$_3$)$_3$·xH$_2$O, Aldrich], and zinc acetate dehydrate [Zn(CH$_3$COO)$_2$·2H$_2$O, Aldrich] were used as metal precursors of In, Ga, and Zn, respectively. 0.3 M monoethanolamin (MEA, C$_2$H$_7$NOH) was also added as a stabilizer to improve solubility and produce a homogeneous InGaZnO mixing solution. Constant magnetic stirring at 400 rpm on a 70 °C hot plate for 1 hour ensured that each metal precursor (indium nitrate hydrate, gallium nitrate hydrate, and zinc acetate dehydrate) was homogeneously decomposed to M-OH (M = In, Ga and Zn) through hydrolysis, as in the following reactions:

\[
\text{In(NO}_3\text{)}_3\cdot 3\text{H}_2\text{O} \rightarrow \text{In(OH)}_3 + 3\text{HNO}_3
\]

\[
\text{Ga(NO}_3\text{)}_3\cdot 3\text{H}_2\text{O} \rightarrow \text{Ga(OH)}_3 + 3\text{HNO}_3
\]

\[
2\text{Zn(}\text{CH}_3\text{COO)}_2\cdot 2\text{H}_2\text{O} \rightarrow 2\text{Zn(OH)}_2 + 4\text{CH}_3\text{COOH}
\]

Homogeneous solutions were aged for 24 hours to yield a stable InGaZnO sol, which was spin coated onto 50 nm ZnO buffer layers at 3000 rpm for 30 s and dried for 10 min at 250 °C per one spin-coating. The In-O, Ga-O, and Zn-O were formed via water and alcohol condensation reaction [M-OH to M-O-M (M = In, Ga, and Zn)] at 230-250 °C as in the following reaction:

\[
\text{xln(OH)}_2 + y\text{Ga(OH)}_3 + z\text{Zn(OH)}_2 \rightarrow \text{In}_x\text{Ga}_y\text{Zn}_z\text{O}_m + b\text{H}_2\text{O}
\]

The thickness of a-InGaZnO films (500 nm) was controlled via repeated spin-coatings and drying processes (10 times).

**Step 3 : Formation of InGaO$_3$(ZnO)$_m$ superlattice (high-temperature annealing)**

The 500 nm a-InGaZnO films with various chemical compositions (In : Ga : Zn = X : Y : Z) on 50 nm epitaxial ZnO buffer layers were crystallized via post-annealing at 900 °C for 9 hours under air ambient in furnace. The 200 nm crystallized InGaO$_3$(ZnO)$_m$ films with superlattice structure were produced and consisted of single or double phases depending on the mole fraction of the metal cations.

**Characterization**

The compositional and microstructural characteristics of the crystallized samples were investigated via x-ray diffraction (XRD) (Bruker D8 DISCOVER) with Cu Kα radiation (λ = 1.54 Å) and transmission electron microscopy (TEM) (JEOL) with a LaB$_6$ electron source operating at 200 kV. Bright field (BF), high-resolution electron microscopy (HRTEM) images, and selected area diffraction patterns (SADPs) were observed. Cross-sectional TEM specimens were prepared via mechanical polishing and Ar ion milling. Less developed crystalline InGaO$_3$(ZnO)$_m$ films were coated with carbon to protect their intrinsic microstructure during mechanical polishing and ion milling, since they consist of small-sized crystals and include some voids. To investigate the effect of compositional and microstructural characteristics on the thermoelectric properties of the crystallized samples, electrical resistivity (ρ) was evaluated using a Hall-effect measurement system (Ecopia, HMS-3000) and the Seebeck coefficient (S) is measured at the 325 K with an in-plane configuration. In contrast, the thermal conductivity was evaluated in the out-of-plane configuration with a metal strip of 60 μm at 325 K via 3ω method. Thus, we provided power factor and thermal conductivity separately, due to different carrier flow directions.

3. Results and discussion

3.1 The synthesis of InGaO$_3$(ZnO)$_m$ superlattice films

In this experiment, we have observed three distinguishable categories for the final crystallized InGaO$_3$(ZnO)$_m$ products depending on the mole fraction of metal precursors in InGaZnO sol for 500 nm amorphous InGaZnO films fabricated on the 50 nm ZnO buffer layers. Firstly, the a-InGaZnO films synthesized via spin coating with a mole fraction of In:Ga:Zn (1:1:Z, where Z = integer) in sol precursors produced single-phase InGaO$_3$(ZnO)$_m$ crystals after the buffer-assisted crystallization process at a high temperature of 900 °C in all samples with different Z integers (Z = 0, 1, and 2). In particular, the 50 nm ZnO leads to the contribution of an additional ZnO mole fraction of exactly 1 to the InGaO$_3$(ZnO)$_m$ films. Consequently, as shown in Fig. 2a-c, the mole fractions of 1:1:0, 1:1:1, and 1:1:2 (In:Ga:Zn) in metal precursors result in single-phase InGaO$_3$(ZnO)$_m$ films with m values of 1, 2, and 3, respectively, which indicates the relationship of m = Z + 1 in the 50 nm ZnO buffer and 500 nm a-InGaZnO film before thermal annealing. These final InGaO$_3$(ZnO)$_m$ films show the absence of ZnO-related peaks at 900 °C annealing, indicating complete intermixing between the ZnO buffer and a-InGaZnO. Also, these crystallized samples exhibit very clear and intense periodic satellite peaks originating from atomically well-aligned arrangement along the c-axis, which was introduced in a previous study. The positions of satellite peaks are exactly matched with theoretically-expected crystal planes corresponding to the (0001) of the InGaO$_3$(ZnO)$_m$ based on JCPDS cards (No. 38-1104, 40-0252, and 40-0253). The InGaO$_3$(ZnO)$_2$ phase shows diffraction peaks at 2θ = 10.2, 20.4, and 30.9° corresponding to (0003), (0006), and (0009) planes, respectively. The InGaO$_3$(ZnO)$_2$ phase exhibits diffraction peaks...
Fig. 2. θ-2θ XRD scans of strong single- (Z = integer) and double- (Z = non-integer) phase InGaO$_3$(ZnO)$_m$ films using mixing solution with specific mole fractions [In:Ga:Zn = 1:1:Z] among metal precursors; (a) Z = 0, (b) Z = 1, (c) Z = 2, (d) Z = 0.5, and (e) Z = 1.5.

At 2θ = 7.9, 15.8, 23.8, and 31.9°, corresponding to the (0002), (0004), and (0008) planes, respectively. Furthermore, the InGaO$_3$(ZnO)$_0$ phase discloses diffraction peaks at 2θ = 6.5, 12.9, 19.2, 25.7, and 32.3° corresponding to the (0003), (0006), (0009), (00012), and (00015) planes, respectively. For the metal precursor without Zn content (In:Ga:Zn = 1:1:0), the final composition is 1:1:1 and also satisfies the relation of m = Z + 1 in the 50 nm buffer ZnO samples. The low m values of 1, 2, and 3 can be simply produced at relatively low temperature, because high m values have high formation energy and require higher thermal temperature. However, high annealing temperatures lead to the uncontrollable evaporation of metallic In, Ga, and Zn elements, resulting in inhomogeneous final products. Thus, generally low m values are obtained in the crystallized InGaO$_3$(ZnO)$_m$ films fabricated from ZnO buffer and a-InGaZnO. Thick ZnO buffer layers cause failure in the formation of crystallized InGaO$_3$(ZnO)$_m$ films due to high m values. As a result, the thickness ratio of 50 nm epitaxial ZnO to 500 nm a-InGaZnO is currently appropriate for the formation of single-phase InGaO$_3$(ZnO)$_m$ films with superlattice structures. When compared the in-plane lattice parameter ([a$_{InGaO_3(ZnO)_m}$-a$_{ZnO}$] / a$_{ZnO}$) between InGaO$_3$(ZnO)$_m$ and ZnO, the high m value of 3 showed reduced lattice mismatch and it is expected that the crystallization process is more active due to low ΔG$_{strain}$. Nevertheless, all satellite peaks from different InGaO$_3$(ZnO)$_m$ crystals exhibit similar intensity due to small differences in lattice mismatch: 1.29, 1.19, and 1.07 % in m values of 1, 2, and 3, respectively.

Secondly, we synthesized a-InGaZnO films with the mole fraction In:Ga:Zn (1:1:Z, where Z = non integer) on a ZnO buffer, and produced crystallized InGaO$_3$(ZnO)$_m$ layers via thermal treatment at 900 °C. These InGaO$_3$(ZnO)$_m$ films also exhibit crystal diffraction peaks and periodic satellite peaks, as shown in Fig. 2d and e; however, these samples exhibit a blend of two crystal phases, even when given sufficient annealing time. The crystal InGaO$_3$(ZnO)$_m$ films obtained from Z = 0.5 and 1.5 consisted of two phases corresponding to m = 1 and 2, and m = 2 and 3, respectively, considering the positions of satellite peaks. Also, the intensity of the peaks is relatively weak, but still exhibits distinguishable periodic peaks, indicating that exact control of metal precursors for the formation of single phase InGaO$_3$(ZnO)$_m$ crystal film is necessary, unlike in a-InGaZnO films.

Next, we synthesized a-InGaZnO films from metal precursors with the mole fraction of In:Ga:Zn = X:Y:1 (X≠Y), where the In/Ga ratio deviated from 1. As shown in Fig. 3, the crystallized In$_x$Ga$_y$O$_3$(ZnO)$_m$ films produced from these 500 nm a-InGaZnO films and 50 nm ZnO buffer also feature superlattice structures with periodic satellite peaks, though their diffraction peaks have relatively broad and asymmetric shoulders and low intensity, indicating a less developed superlattice structure in the In$_x$Ga$_y$O$_3$(ZnO)$_m$ films. The a-InGaZnO films fabricated using a solution process can have various composition ratios due to their amorphous bonding structure with short range
order, and their compositions are strongly dependent on only the content of the metal precursors. The stable \(\text{In}_x\text{Ga}_y\text{O}_3(ZnO)_m\) crystal phases are generally reported to exist as solely \(\text{In:Ga} = 1:1\), regardless of \(m\) values. From the position of the satellite peaks, we found that the \(\text{InGaO}_3(ZnO)_2\) and \(\text{InGaO}_3(ZnO)_3\) crystal phases were formed in the In+Ga of 2.5 and 1.5, respectively, with respect to Zn = 1. In addition, excess metal ions deviated from the In:Ga = 1:1 ratio are expected to hinder the formation of perfect superlattice structures. Consequently, to produce \(\text{InGaO}_3(ZnO)_m\) crystal films with highly-ordered atomic arrangement along the c-axis, a mole fraction of metal solution precursors with a narrow window is a prerequisite, and the 500 nm a-InGaZnO films on the 50 nm ZnO buffer layers should be synthesized with a In:Ga:Zn ratio of 1:1: (integer 0, 1, and 2). Table 1 features a summary of the phase formation of our \(\text{InGaO}_3(ZnO)_m\) crystal thin films produced by 500 nm a-InGaZnO with various metal mole fractions and a 50 nm ZnO buffer. When ignoring the contribution of structural factors to diffraction intensity in the samples with various \(m\) values, we can estimate the fraction of crystal phase from the diffraction peaks with the strongest intensity, as shown in Table 1.

### Table 1: A summary of the phase formation and compositional contents of \(\text{InGa:Zn:ZnO}_m\) superlattice films produced via 500 nm a-InGaZnO synthesized using InGaZnO sol with various mole fractions of metal precursors and a 50 nm ZnO buffer.

<table>
<thead>
<tr>
<th>Metal cation ratio in InGaZnO sol &amp; a InGaZnO (In : Ga : Zn)</th>
<th>Crystalline (\text{InGaO}_3(ZnO)_m) (Crystallized a-InGaZnO with epi-ZnO : a-InGaZnO + epi-ZnO)</th>
<th>Total metal cation ratio [In : Ga : Zn] &amp; phase category</th>
<th>Partial metal cation ratio [In : Ga : Zn] &amp; actual phase</th>
<th>Phase fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 : 1 : 1) (Z = integer)</td>
<td>1 : 1 : 1</td>
<td>Strong single-phase (\text{InGaO}_3(ZnO)_2)</td>
<td>1 : 1 : 1</td>
<td>(\text{InGaO}_3(ZnO)_2)</td>
</tr>
<tr>
<td>(1 : 1 : 1)</td>
<td>1 : 1 : 2</td>
<td></td>
<td>1 : 1 : 2</td>
<td>(\text{InGaO}_3(ZnO)_2)</td>
</tr>
<tr>
<td>(1 : 1 : 1)</td>
<td>1 : 1 : 3</td>
<td></td>
<td>1 : 1 : 3</td>
<td>(\text{InGaO}_3(ZnO)_2)</td>
</tr>
<tr>
<td>(1 : 1 : 0.5) (Z = Non-integer)</td>
<td>1 : 1 : 1.5</td>
<td>Double-phase (\text{InGaO}_3(ZnO)_2)</td>
<td>0.5 : 0.5 : 0.5</td>
<td>(\text{InGaO}_3(ZnO)_2)</td>
</tr>
<tr>
<td>(1 : 1 : 1.5)</td>
<td>1 : 1 : 2.5</td>
<td></td>
<td>0.5 : 0.5 : 1</td>
<td>(\text{InGaO}_3(ZnO)_2)</td>
</tr>
<tr>
<td>(0.5 : 0.5 : 0.5)</td>
<td></td>
<td></td>
<td>0.5 : 0.5 : 1</td>
<td>(\text{InGaO}_3(ZnO)_2)</td>
</tr>
<tr>
<td>(X : Y : 1) (X + Y)</td>
<td>1 : 0.5 : 1</td>
<td>Weak single-phase (\text{InGaO}_3(ZnO)_2)</td>
<td>0.5 : 0.5 : 1.5</td>
<td>(\text{InGaO}_3(ZnO)_2)</td>
</tr>
<tr>
<td>(0.5 : 1 : 1)</td>
<td>0.5 : 1 : 2</td>
<td></td>
<td>0.5 : 0.5 : 1.5</td>
<td>(\text{InGaO}_3(ZnO)_2)</td>
</tr>
<tr>
<td>(0.5 : 0.5 : 0.5)</td>
<td></td>
<td></td>
<td>0.5 : 0.5 : 1.5</td>
<td>(\text{InGaO}_3(ZnO)_2)</td>
</tr>
<tr>
<td>(1 : 1.5 : 1)</td>
<td>1 : 1.5 : 2</td>
<td></td>
<td>1 : 1.5 : 2</td>
<td>(\text{InGaO}_3(ZnO)_2)</td>
</tr>
<tr>
<td>(0 : 0.5 : 0)</td>
<td></td>
<td></td>
<td>0.5 : 0 : 0</td>
<td>(\text{Ga}^{+})</td>
</tr>
<tr>
<td>(1.5 : 1 : 1)</td>
<td>1.5 : 1 : 2</td>
<td></td>
<td>1 : 1 : 2</td>
<td>(\text{InGaO}_3(ZnO)_2)</td>
</tr>
<tr>
<td>(0.5 : 0 : 0)</td>
<td></td>
<td></td>
<td>0 : 0 : 0</td>
<td>(\text{Ga}^{+})</td>
</tr>
</tbody>
</table>

#### 3.2 A phase diagram showing the thermoelectric properties of \(\text{InGaO}_3(ZnO)_m\) superlattice films

Fig. 4a shows a combinatorial diagram mapped as a ternary phase diagram of In-Ga-Zn metal ions for crystallized \(\text{InGaO}_3(ZnO)_m\) film, in which 500 nm a-InGaZnO films deposited on 50 nm ZnO buffer layers were sufficiently post-annealed, and where the strong single-phase, double-phase, and weak single-phase crystals are indicated by “★”, “□”, and “○”, respectively. In Fig. 4b-d, the Seebeck coefficient (S), electrical resistivity (\(\rho\)), and power factor (P.F. = \(S^2/\rho\)) are designated in the corresponding compositions of In-Ga-Zn metal ions in crystallized \(\text{InGaO}_3(ZnO)_m\) films. Interestingly, the \(\text{InGaO}_3(ZnO)_m\) crystal phases located along the normal center line with an In:Ga ratio of 1:1 show enhanced Seebeck coefficients. These films corresponded to the strong single-phase and double-phase \(\text{InGaO}_3(ZnO)_m\) crystals with c-axis ordered structures and consist of stoichiometric crystal phases without excess metal ions. Furthermore, the electrical resistivity from the strong single-phase \(\text{InGaO}_3(ZnO)_m\) films showed extremely low values, below 10 m\(\Omega\) cm, while double-phase and weak single-phase (excess metals) \(\text{InGaO}_3(ZnO)_m\) films showed > 100 m\(\Omega\) cm. The strong single-phase \(\text{InGaO}_3(ZnO)_m\) film is anticipated to have reduced grain boundaries, while the weak single-phase (excess metals) samples are expected to induce frequent interface scattering for electron charge transport from the boundaries between various phases. Also, the excess metal ions in the less crystallized single-phase hinder the charge transport efficiency. Thus, the defect-related charge scattering from phase boundaries and impurities led to suddenly increased electrical resistivity. Finally, the thermoelectric power factor, \(S^2/\rho\), can be obtained from these values, as shown in Fig. 4d. The higher value of S and lower value of \(\rho\) in the strong single-phase \(\text{InGaO}_3(ZnO)_m\) films leads to an enhanced power factor. According to previous surveys, the bulk ZnO and \(\text{In}_2\text{O}_3\) based...
oxides have shown lower Seebeck coefficients (\( \sim -100 \, \mu \text{V} \, \text{K}^{-1} \)) and power factor values (\( \sim 10^{-2} \, \text{mW} \, \text{m}^{-1} \, \text{K}^{-2} \)), while well-engineered nano-inclusion, nano-grain, and preferred orientation induced improved Seebeck coefficient (> -200 \( \mu \text{V} \, \text{K}^{-1} \)) and power factor (> 10\(^{-1}\) \( \text{mW} \, \text{m}^{-1} \, \text{K}^{-2} \)) as our strong single-phase InGaO\(_3\)(ZnO)\(_m\) films. The thermal conductivity which is another principal factor to evaluate thermoelectric performance was measured from strong single-phase InGaO\(_3\)(ZnO)\(_m\) superlattice films. Interestingly, their thermal conductivities exhibited low values (0.72 ~ 1.84 \( \text{W} \, \text{m}^{-1} \, \text{K}^{-1} \) at 325 K) due to dramatically increased phonon scattering from the In\(_2\)/GaO\(_3\)/ZnO\(_m\)/InO\(_2\) interfaces, compared to those of typical bulk In\(_2\)O\(_3\) and ZnO-based oxides (\( > 10 \, \text{W} \, \text{m}^{-1} \, \text{K}^{-1} \)). Among those samples, the InGaO\(_3\)(ZnO)\(_m\) film produced from the 500 nm a-InGaZnO with reduced Zn fraction and a 50 nm ZnO buffer has a larger power factor than the other samples. The largest power factor was 0.155 \( \text{mW} \, \text{m}^{-1} \, \text{K}^{-2} \). These results inform us that the InGaO\(_3\)(ZnO)\(_m\) films for the thermoelectric application must simultaneously feature a strong single crystallized phase and a well-ordered c-axis structure.

### 3.3 The microstructural growth evolution of InGaO\(_3\)(ZnO)\(_m\) superlattice films

Although the XRD patterns provided helpful information on the formation of superlattice structures in the crystallized InGaO\(_3\)(ZnO)\(_m\) films, we cannot clearly understand the precise microstructural difference and distribution of crystal phases. Thus, we have performed TEM observation of the InGaO\(_3\)(ZnO)\(_m\) films with double-phase crystals (Fig. 5 and 6) and strong single-phase crystals (Fig. 7). The sample consisting of double-phase crystals was produced by 500 nm a-InGaZnO with an In:Ga:Zn ratio of 1:1:1.5 and 50 nm ZnO, and the final crystal phases consisted of InGaO\(_3\)(ZnO)\(_2\) and InGaO\(_3\)(ZnO)\(_3\). The bright-field image using \( g = 000l \) shows the absence of vertically-aligned grain boundaries, and it appears as a single crystalline phase like the epitaxial ZnO/sapphire and GaN/sapphire, even though the InGaO\(_3\)(ZnO)\(_m\) film consists of two phases with similar XRD intensities. It is noticeable that the selective area diffraction patterns (SADPs) from the top and bottom regions are not identical, as shown in Fig. 5b and c. Fig. 5c is a traditional SADP from the InGaO\(_3\)(ZnO)\(_m\) crystals with superlattice structures along the c-axis on a sapphire substrate, and the distance between diffraction peaks indicates that this crystal is InGaO\(_3\)(ZnO)\(_m\). However, we can detect additional patterns of InGaO\(_3\)(ZnO)\(_2\) indicated by blue arrows in top region, as shown in Fig. 5b. These spots were also distributed with a periodic distance along the c-axis. We obtained high-resolution TEM images for distinct analysis of microstructural changes (Fig. 5d and e). While the bottom...
region shows a homogenous atomic arrangement corresponding to the InGaO₃(ZnO)₃ phase, the crystal structure in the middle region of the InGaO₃(ZnO)₃ film was transferred from InGaO₃(ZnO)₃ to InGaO₃(ZnO)₂ with an InO₂⁻/GaO₂⁻/(ZnO)₂/InO₂⁻ stacking sequence, as shown in Fig. 5e. These TEM images inform us that the InGaO₃(ZnO)₃ in the bottom region features a higher Zn composition of m = 3 and that the top region features a reduced Zn mole fraction of m = 2. This is attributed to the difference in the degree of diffusion from the ZnO buffer layers, considering a determined total Zn mole fraction and a possible crystal structure. Consequently, these results reveal that the double-phase crystal was distributed in vertical stacks like a double layer, and thus there is an absence of vertically-aligned grain boundaries.

We investigated the detailed microstructural evolution of InGaO₃(ZnO)₃ with double-phase crystals prepared at various annealing times. Fig. 6 shows XRD patterns, TEM images, and SADPs for the InGaO₃(ZnO)₃ films with double-phase crystals annealed for as-dep, 0.5, 3, 6, and 9 hours. In the sample with as-deposited a-InGaZnO/ZnO buffer structure, only the ZnO-related (0002)ZnO peak is observed except the substrate. After thermal annealing for 0.5 h at 900 °C, weak and broad

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**Fig. 6.** (a) The growth evolution of double phase InGaO₃(ZnO)₃/InGaO₃(ZnO)₂ superlattice film. 0-20 XRD scans of double phase InGaO₃(ZnO)₃/InGaO₃(ZnO)₂, based on various post-annealing times: as-dep, (a-InGaZnO), 0.5 h, 3 h, 6 h, and 9 h. Their bright field images and selective area diffraction patterns: (b-e) 0.5 h, (f, g) 3 h, and (h, i) 9 h.

**Fig. 7.** The growth evolution of strong single-phase InGaO₃(ZnO)₂ superlattice film. (a) 0-20 XRD scans of strong single-phase InGaO₃(ZnO)₂ films with various post-annealing times (3, 6, and 9 h). Their bright field images and HRTEM image; (b) 3 h, (c) 6 h, and (d, e) 9 h.
crystallized peaks appear with periodic distances and the (0002)_{200} peak becomes weak. Here, the formed crystals are InGaO_{3}(ZnO)_{m} with higher Zn mole fractions, even though the as-deposited samples consisted of 500 nm a-InGaZnO with In:Ga:Zn = 1:1:1.5 and 50 nm ZnO. The well-developed crystal phases are preferentially observed in the bottom region of crystallized InGaO_{3}(ZnO)_{m} film near the ZnO buffer (Fig. 6b), and the top region is composed of randomly-arrayed crystal grains with small size; some voids are also observed (Fig. 6c). The sample annealed for 3 hours exhibits a disappearance of the ZnO-related peak, implying complete intermixing between a-InGaZnO and the ZnO buffer. In addition, the diffraction peaks from the crystal phases become strong and the superlattice-like SADPs are also observed (Fig. 6g). However, it is still poly-crystalline InGaO_{3}(ZnO)_{m} film including many crystal grains and several voids due to insufficient crystallization. As the annealing time increases, a double-phase crystal appears and the SADPs become distinctly intense. In particular, the final InGaO_{3}(ZnO)_{m} crystal film has relatively smooth surface morphology and high density without voids, as well as consists of two crystals of InGaO_{3}(ZnO)_{m} and InGaO_{3}(ZnO)_{1} (Fig. 6h and i). Here, the line defects located on the (0001) planes are stacking faults produced by thermal annealing and two phase boundaries.

The growth evolution on the InGaO_{3}(ZnO)_{m} film with the strong single-phase was also studied. Fig. 7 presents XRD results and TEM images showing microstructural evolution for the 200nm InGaO_{3}(ZnO)_{m} film produced from 500 nm a-InGaZnO with In:Ga:Zn = 1:1:0 and 50 nm ZnO buffer. Insufficient annealing time leads to a partially-crystallized film consisting of a complete crystal with high c-axis preferred orientation in the bottom and amorphous or less-developed crystals with random orientation in the top region, as shown in Fig. 7b and c. An enough annealing time of 9 hours produces single-phase InGaO_{3}(ZnO)_{m} as the final product, which can be confirmed from XRD patterns, TEM image, and HRTEM image. Fig. 7d and e shows similar TEM images obtained from single crystalline epitaxial ZnO films on the sapphire substrates, though this film still features stacking faults. In addition, its surface morphology is flat as the single crystalline domain, despite going through transition process with ruggered morphology in the insufficient annealing. Table 2 shows a summary of thermoelectric properties from these InGaO_{3}(ZnO)_{m} films based on annealing time. The sample synthesized under sufficient annealing time exhibits the highest Seebeck coefficient (-240 μV K^{-1}) and lowest electrical resistivity (3.7 mΩ cm), resulting in a high power factor (0.155 mW m^{-1} K^{-2}) due to the suppression of defect generation.

4. Conclusions

We have studied a combinatorial approach to the formation of crystallized InGaO_{3}(ZnO)_{m}, where a-InGaZnO films (500 nm) with various cation ratios (In:Ga:Zn = X:Y:Z) using a solution-based process (repeatedly spin-coating and drying) were produced on 50 nm epitaxial ZnO buffer layers. The crystallized InGaO_{3}(ZnO)_{m} films could be categorized as i) strong single-phase InGaO_{3}(ZnO)_{m} from a-InGaZnO of In:Ga:Zn = 1:1:Z (Z = integer), ii) double-phase InGaO_{3}(ZnO)_{m}/InGaO_{3}(ZnO)_{m+1} from In:Ga:Zn = 1:1:Z (Z = non-integer), and iii) weak single-phase InGaO_{3}(ZnO)_{m} with excess metal ions from In:Ga:Zn = X:Y:1 (X,Y). The final InGaO_{3}(ZnO)_{m} crystals showed the relationship of m = Z + 1 in the 50 nm ZnO buffer and 500 nm a-InGaZnO film due to the interdiffusion caused by high temperature annealing. Resultantly, the double-phase crystallized film was composed of InGaO_{3}(ZnO)_{m+1} in the bottom region and InGaO_{3}(ZnO)_{m} in the top region. The strong single-phase InGaO_{3}(ZnO)_{m} superlattice films showed the best thermoelectric power factors due to better Seebeck coefficients and excellent electrical conductivity. In particular, the single-phase InGaO_{3}(ZnO)_{m} superlattice films had no grain-boundary, high c-axis preferred orientation, and low stacking fault density, resulting in the most ideal thermoelectric properties [P.F. = 0.155 mW m^{-1} K^{-2}, Seebeck coefficient = -240 μV K^{-1}, electrical resistivity = 3.7 mΩ cm].

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Notes and references

Graphical abstract

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The strong single-phase among InGaO$_3$(ZnO)$_m$ films with superlattice structures showed superior thermoelectric power factors. The detailed microstructural growth evolution of single- and double-phase InGaO$_3$(ZnO)$_m$ films were investigated using transmission electron microscopy.