Chapter 11

Title: **Halide Vapor Phase Epitaxy of α- and ε-Ga_2O_3**

Author: Yuichi Oshima
Affiliation: Optical Single Crystals Group, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
E-mail address: OSHIMA.Yuichi@nims.go.jp
Phone number: +81-29-860-4750

Abstract

Halide vapor phase epitaxy of metastable α- and ε-Ga_2O_3 is reviewed. The both polymorphs were grown using GaCl and O_2 as precursors. Phase-pure α-Ga_2O_3 was heteroepitaxially grown on (0001) sapphire at temperatures of approximately 550°C or lower. The n-type electrical conductivity was controlled by Ge doping using $GeCl_4$ as the dopant source, and very low resistivity of 8.6 mΩcm was achieved. Epitaxial lateral overgrowth was shown to be effective in improving the crystal quality, and the dislocation density was reduced from 10^{10} cm^{-2} to less than 5×10^6 cm^{-2} in the laterally grown wing region. Morphology of α-Ga_2O_3 islands was controlled such that inclined facets well develop, and dislocation density above mask openings remarkably decreased due to dislocation bending caused by the inclined facets. ε-Ga_2O_3 was grown on (0001) GaN and (0001) AlN using virtually the same growth recipe as that used for α-Ga_2O_3. Fundamental material properties of ε-Ga_2O_3, such as the optical bandgap energy, thermal stability, and thermal expansion coefficient, were investigated using the epitaxial film.

1. Introduction

Ga_2O_3 has been reported to crystalize into five different polymorphs: α-, β-, δ-, ε-, and γ-phases [1]. Among these polymorphs, the β-phase is thermodynamically the most stable at atmospheric pressure, and melt-grown high-quality single crystal substrates are available [2-4]. Accordingly, high-quality homoepitaxial growth is possible, and promising β-Ga_2O_3-based power devices have been demonstrated [5-7].

On the other hand, other polymorphs are metastable and transform into the β-phase at high temperatures beyond specific thresholds. Among the metastable Ga_2O_3 phases, the α-phase and ε-phase, which are the target materials of this review, have attracted great attention as wide-bandgap semiconductors. These materials are promising for power device applications because of their superior properties, including their larger bandgaps compared with that of β-Ga_2O_3, the ease of growing $(Al_xIn_yGa_{1-x-y})_2O_3$ solid solutions, and spontaneous polarization.

To fabricate α-/ε-Ga_2O_3 devices, it is essential to establish a thin-film growth technique. Unfortunately, the melt-grown native substrates are not available for α- or ε-Ga_2O_3. Accordingly, these materials must be grown heteroepitaxially. However, the development of such heteroepitaxial growth techniques remains in its infancy. To obtain high-quality phase-pure films with controlled electrical properties, we must overcome many technical challenges such as the selection of appropriate growth methods and substrates, nucleation control, defect control, and doping control. Moreover, it is desirable to establish a high-speed epitaxial technique for thick film growth, which will be useful for the growth of drift layers in power devices or the fabrication of freestanding α-/ε-Ga_2O_3 substrates. We have employed halide vapor phase epitaxy (HVPE) as the growth method and reported the first HVPE growth of α- and ε-Ga_2O_3 [8, 9].

Table I summarizes the HVPE growth conditions and resulting polymorphs [8-10]. The key points for the phase selection are the growth temperature and substrate. For example, α-Ga_2O_3 grows on sapphire at low temperatures, whereas β-Ga_2O_3 grows on the same substrate at high temperatures under the same gas supply conditions. If GaN is used instead of sapphire as the substrate under the same growth conditions for α-Ga_2O_3, then ε-Ga_2O_3 grows. Note that this tendency may not be universal and may be dependent on the growth method. Further study is required to clarify the essential factors for phase selection. In this chapter, we describe our HVPE technologies for α-/ε-Ga_2O_3 and the properties of the grown epilayers.

Table 1. Polymorphs of Ga_2O_3 and HVPE growth conditions.

Polymorph	β-Ga_2O_3	α-Ga_2O_3	ε-Ga_2O_3
Substrate	(0001) Sapphire		(0001) GaN, etc.
Typical growth temperature	1050°C	550°C	

2. HVPE of α-Ga_2O_3

2.1 Features of α-Ga_2O_3

α-Ga_2O_3 is a corundum-structured wide-bandgap semiconductor with a reported bandgap energy of 5.2–5.3 eV [8, 11], which is even larger than that of β-Ga_2O_3 (4.5–4.9 eV). The crystal structure is the same as that of sapphire (α-Al_2O_3); therefore, α-Ga_2O_3 can be grown on sapphire epitaxially. It is possible to grow α-$(Al_xGa_{1-x})_2O_3$ solid solutions without compositional limitation, which is useful for band engineering and the fabrication of high-performance hetero-structured devices [12]. In addition, α-Ir_2O_3 and α-Rh_2O_3 have been shown to exhibit clear p-type conduction; therefore, hetero-pn-junction bi-polar devices can be expected [13, 14]. Hence, α-Ga_2O_3 is a promising wide-bandgap semiconductor for power device applications. Indeed, Schottky barrier diodes with very low on-resistance and normally off metal-oxide semiconductor field-effect transistors (MOSFETs) using a hetero-pn-junction have already been demonstrated [15, 16]. See Chapter 39 for details.

The first epitaxial growth of α-Ga_2O_3 was demonstrated by Shinohara and Fujita using the mist chemical vapor deposition (CVD) technique [11]. The mist CVD technique also enables n-type conductivity control [17-20] and growth of α-$(Al_xIn_yGa_{1-x-y})_2O_3$ solid solutions [12]. These achievements of the mist CVD technique enabled the fabrication of the α-Ga_2O_3–based devices described above. See Chapter 12 for details. The first HVPE of α-Ga_2O_3 was demonstrated by Oshima et al. [8]. In the following sections, we provide an outline of the HVPE of α-Ga_2O_3, the properties of the epilayers, conductivity control, and technologies for crystal quality improvement.

2.2 Growth apparatus and growth conditions

In this section, a brief description of the growth apparatus and basic growth conditions is presented. See Chapter 10 for a detailed explanation of the principle of HVPE and its thermodynamical basis.

We used a lab-made horizontal quartz reactor for the HVPE of α-Ga_2O_3. The growth was performed on (0001) sapphire under atmospheric pressure at 430°C–650°C using GaCl and O_2 as precursors. Figure 1 presents a schematic illustration of the HVPE reactor. GaCl was synthesized upstream in the reactor via the chemical reaction between metal Ga (> 99.99999% pure) and HCl gas (> 99.999% pure). The reaction temperature was fixed at 570°C unless otherwise stated. The GaCl and O_2 were transferred together with N_2 carrier gas, and injected on the substrate located downstream in the reactor. The partial pressures of the GaCl and O_2 supply were 4×10^{-2} to 7.5×10^{-1} kPa and 0.5–6.0 kPa, respectively. The growth was performed directly on sapphire without any buffer layer or slow growth.

2.3 HVPE growth characteristics of α-Ga_2O_3

Figure 2 shows the relative growth rate of α-Ga_2O_3 as a function of growth temperature T_g under a constant supply of the precursors. The growth rate increased with increasing temperature, which indicates that HVPE of α-Ga_2O_3 occurs in the chemical-reaction-limited regime. Nonetheless, it is possible to achieve a high growth rate by increasing the supply of precursors. Figure 3 shows the growth rate at 550°C as a function of the partial pressures of the supply of precursors. The growth rate increased monotonically with increasing precursor supply, reaching over 100 μm/h.

2.4. Properties of HVPE-grown α-Ga_2O_3

In this section, we describe the properties of a typical HVPE-grown α-Ga_2O_3 film on (0001) sapphire.

(1) Phase purity and growth temperature T_g

Figures 4 (a)–(d) present photographs of Ga_2O_3 films grown at various temperatures under the same precursor supply conditions. For T_g = 650°C, the film was translucent (Fig. 4 (a)). The fraction of the specular part increased with decreasing T_g, and became mirror-like throughout the wafer when T_g was less than 575°C (Fig. 4 (d)).

Figures 5 (a) and (b) present X-ray diffraction (XRD) 2θ–ω scan profiles of an α-Ga_2O_3 film grown at 550°C. Only diffraction peaks from the *c*-plane of α-Ga_2O_3 are observed except for those from the substrate. In contrast, diffraction peaks from β-Ga_2O_3 were dominant for T_g = 650°C (not shown). Thus, phase-pure α-Ga_2O_3 can be grown at appropriately low temperatures.

Figures 6 (a) and (b) present surface and cross-sectional scanning electron microscopy (SEM) images of an α-Ga_2O_3 film grown at 550°C, respectively. The surface was smooth. The film thickness was 3.6 μm for 7-min growth; therefore, the growth rate was approximately 30 μm/h.

(2) Crystal orientation

Figures 7 (a) and (b) present XRD pole figures of an α-Ga_2O_3 film and the sapphire substrate, respectively. Only three diffraction spots are observed in the pole figure, which were expected for the single-crystalline corundum structure. The epitaxial relationships were $[10\bar{1}0]_{\alpha\text{-}Ga_2O_3} \| [10\bar{1}0]_{\alpha\text{-}Al_2O_3}$ and $(0001)_{\alpha\text{-}Ga_2O_3} \| (0001)_{\alpha\text{-}Al_2O_3}$.

(3) Crystal quality

α-Ga_2O_3 epilayers grown on sapphire exhibit large mosaicity (represented by tilting of the *c*-plane and twisting around the *c*-axis) because of the large lattice mismatch (Δa/a = 4.5%, Δc/c = 3.3%). The mosaicity was estimated using the full-width half-maximum (FWHM) values of X-ray rocking curves (XRCs) of the *0006* and $10\bar{1}2$ diffractions measured in symmetric and skew-symmetric geometry, respectively (Fig. 8). In most cases, both the tilt angle and twist angles were broad. The tilt angle was sometimes very narrow (less than 100 arcsec). In this case, the twist angle tended to be very broad. Thus, the tilt and twist angles appear to have a trade-off relationship. Therefore, both the tilt and twist angles must be measured to estimate the crystal quality of α-Ga_2O_3 layers.

Figures 9 (a) and (b) present cross-sectional and plan-view transmission electron microscopy (TEM) images of an α-Ga_2O_3 film, respectively. A high density of dislocations along [0001] was observed, and the density was on the order of 10^{10} cm^{-2}.

(4) Impurity analysis

Table 2 summarizes the results of impurity analysis of an undoped α-Ga_2O_3 film performed using secondary mass spectrometry (SIMS). The concentrations were below the detection limits except for [Cl]. The chlorine impurity source would be GaCl. We speculate that the low growth temperature led to the incomplete dissociation of the Ga–Cl bond.

Table 2. Impurity concentrations in α-Ga_2O_3 measured by SIMS.

Element	Concentration [cm^{-3}]	Element	Concentration [cm^{-3}]
H	$< 6 \times 10^{16}$	Al	$< 6 \times 10^{16}$
C	$< 6 \times 10^{16}$	Cr	$< 1 \times 10^{14}$
Si	$< 3 \times 10^{15}$	Fe	$< 4 \times 10^{14}$
Cl	1×10^{16}	Ni	$< 3 \times 10^{14}$
S	$< 3 \times 10^{15}$	Mo	$< 1 \times 10^{15}$

(5) Optical bandgap

Figure 10 presents an optical transmittance spectrum of an α-Ga_2O_3 film. Although the transition type of α-Ga_2O_3 remains under discussion, the fitting result was better when direct transition was assumed (inset of Fig. 10). The optical bandgap energy was determined to be 5.15 eV, which is close to the value reported for mist-CVD-grown material [11].

(6) Thermal stability and thermal expansion coefficients

High-temperature XRD measurements were performed under air to estimate the thermal stability of an HVPE-grown α-Ga_2O_3 film. Each 2θ–ω scan was performed at constant temperature after 30 min to allow for temperature stabilization, and the temperature was elevated stepwise from room temperature (RT). Figure 11 presents the results. Apart from the diffraction peaks of the Pt sample holder and sapphire substrate, only the *0006* peak of α-Ga_2O_3 was observed from RT to 500°C. When the temperature reached 525°C, the *401* peak of β-Ga_2O_3 appeared, and the peak intensity of the *401* peak increased with increasing temperature while that of *0006* of α-Ga_2O_3 decreased. This result indicates that α-Ga_2O_3 is thermally stable up to approximately 500°C. Note that this threshold would be dependent on the crystal quality and strain, and the intrinsic threshold could be much higher. Indeed, it has been reported that α-Ga_2O_3 grown under special conditions using mist CVD was stable up to 800°C. See Chapter 12 for further details.

It is possible to calculate the thermal expansion coefficients (TECs) from the peak shift values in Fig. 11. The TECs for α-Ga_2O_3 and sapphire along [0001] were 1.1×10^{-5} K^{-1} and 8.6×10^{-6} K^{-1}, respectively. The value for α-Ga_2O_3 was in excellent agreement with that reported for powder material (1.1×10^{-5} K^{-1}) [22]. The values reported for sapphire range from 7.7×10^{-6} K^{-1} to 9.06×10^{-6} K^{-1}[23], and our value is in this range. Note that these values may not be exactly the same as those for freestanding materials because of the thermal stress resulting from the difference in TECs between α-Ga_2O_3 and sapphire.

2.5 n-type doping control

2.5.1 Motivation

It is essential to establish electrical conductivity control of α-Ga_2O_3 to utilize this material for semiconductor device applications. n-type doping control of α-Ga_2O_3 has been reported for mist-CVD-grown materials using Sn or Si as the dopant [17-20]. n-type conductivity control by HVPE has been demonstrated recently by Oshima et al. using Ge as the dopant [24]. In this section, we describe the current state of n-type doping control of α-Ga_2O_3 by HVPE.

2.5.2 Experimental methods

(1) Selection of dopant element

We selected Ge as the dopant. n-type doping of α-Ga_2O_3 was performed by substituting Ga sites with group IV materials, such as Si, Ge, or Sn. Of these materials, the ionic radius of Ge should be the closest to that of Ga. Accordingly, the use of Ge could minimize the negative impacts of the doping, such as increasing strain and decreasing thermal conductivity, especially upon heavy doping.

(2) Experimental methods

$GeCl_4$ (> 99.999% pure) was used as the dopant source. $GeCl_4$ is a liquid phase near RT (melting point: −50°C), and the bubbling technique using N_2 was used to transport the vapor into the HVPE reactor. The HVPE growth conditions of α-Ga_2O_3 were similar to those described in section 2.2. The temperatures of the Ga source and substrate were both 560°C. The partial pressures of the GaCl and O_2 supplies were 0.25 and 1.0 kPa, respectively.

The impurity concentrations idn Ge-doped α-Ga_2O_3 were estimated using SIMS. The effect of Ge doping on the crystal quality was investigated using XRC measurements. The electrical properties at both RT and elevated temperatures were investigated using Hall measurements and the van der Pauw method.

2.5.3 Properties of Ge-doped α-Ga_2O_3

(1) SIMS results

Figure. 12 presents a SIMS depth profile of a Ge-doped α-Ga_2O_3 film. An undoped thin layer was grown on the sapphire substrate first, and then Ge doping was performed on the undoped layer. [Ge] rose steeply, and no significant doping delay or diffusion was observed. [Cl] also increased at the same time. The source of the chlorine impurity is most likely $GeCl_4$. [Ge] was below the detection limit in a sample grown directly after the growth with the highest $GeCl_4$ supply, indicating that the memory effect of $GeCl_4$ was not significant. [Ge] could be linearly controlled by adjusting the $GeCl_4$ bubbling rate, as shown in Fig. 13.

(2) Effect of Ge doping on crystal quality

XRC measurements of the Ge-doped samples were performed, and the results were compared with those for an undoped reference sample to assess the effect of the Ge doping on the structural quality. The Ge doping had no significant effect on the tilt or twist angle.

(3) Hall measurements

Figure 14 (a) and (b) present the results of Hall measurements at RT. The carrier concentration first increased and then decreased at a $GeCl_4$ bubbling rate of 6 sccm, most likely because of the increase in the point defect density. The carrier mobility decreased monotonically with increasing $GeCl_4$ supply. Figure 14 (c) shows the relationship between the carrier mobility and carrier concentration. Data for Sn-doped α-Ga_2O_3 grown using mist CVD are also shown for comparison [20]. The electron mobility in this work was much greater than previously reported values. The lowest resistivity was 8.6 mΩcm, which is less than half of that of typical commercially available conductive SiC wafers.

Figures 15 (a) and (b) present the results of the Hall measurements at elevated temperatures. The ionization energy of Ge in α-Ga_2O_3 was determined to be 18 meV from the slope of the temperature dependence of the carrier concentration (Fig. 15 (a)); this value is similar to that for Sn [20]. The carrier mobility decreased monotonically with increasing temperature, most likely because of the scattering by both optical phonons and ionized donors. To clarify the detailed scattering mechanism, the low-temperature behavior must also be investigated.

2.6 Improvement of crystal quality by epitaxial lateral overgrowth

2.6.1 Motivation

(1) Need for improvement of crystal quality

As described in Section 2.4, heteroepitaxial α-Ga_2O_3 films contain high density of crystal defects. Accordingly, the crystal quality should be improved because such defects could lead to deterioration of the device performance.

(2) Principle of epitaxial lateral overgrowth technique

To improve the crystal quality of heteroepitaxial films, a technique called epitaxial lateral overgrowth (ELO) has been established mainly for III–V semiconductors such as GaN. Figures 16 (a)–(f) show the steps in the ELO process. First, a seed layer of the target material is grown on a substrate, and photolithography is used to fabricate periodic masks on the template (Fig. 16 (a)). SiO_x and SiN_x are used as the mask material in many cases. The mask dimensions are typically on the micro-meter scale, and a stripe- or dot-patterned mask is usually employed. Next, the regrowth process is performed on the template. The regrowth process begins selectively from the windows of the mask, and isolated stripes or islands of the target crystal are formed (Fig. 16 (b)). These crystals grow vertically and laterally and coalesce (Fig. 16 (c), (d)), finally forming a flat surface (Fig. 16 (e)). During the regrowth process, dislocations in the seed layer propagate into the regrown crystal only through the mask windows; therefore, the dislocation density in the laterally grown wing region is very low. In addition, to minimize the elastic strain energy, dislocations in the window area bend toward the lateral direction when the stripes or islands are grown such that they have inclined facets on the top by controlling the regrowth condition. As a result, the dislocation density above the windows can also be reduced (Fig. 16 (f)). This type of ELO is called facet-initiated ELO (FIELO) [25].

The ELO technique was first proposed as a method to produce mesa structures of electronic devices of Si or GaAs [26, 27], and later, the technique was used by Nishinaga et al. to improve the crystal quality of GaAs [28]. Usui et al. applied this technique to GaN on sapphire and established the FIELO technique [25]. Today, the FIELO technique is recognized as an essential technique for the production of high-quality freestanding GaN wafers [25, 29, 30].

The effectiveness of the ELO technique for α-Ga_2O_3 has already been demonstrated [31]. In the demonstration, α-Ga_2O_3 was grown on a (0001) sapphire substrate using mist CVD with stripe-patterned SiO_2 masks (mask/window = 2 μm/2 μm) on the surface. Although coalescence of α-Ga_2O_3 was not reported, cross-sectional TEM analysis revealed that no dislocations present in the wing region.

(3) Purpose of the study

To reduce the dislocation density effectively, it is desirable to use a mask pattern with a small mask fill factor, i.e., a small window size and wide window spacing. In that case, however, island coalescence requires thick film growth. Accordingly, it is preferable to employ a high-speed epitaxial technique from the viewpoint of cost effectiveness. We thus used HVPE as the growth method for ELO of α-Ga_2O_3. In the following parts, we describe the current state of the development of the ELO technique using HVPE.

2.6.2 Experimental methods

A (0001) α-Ga_2O_3 template grown on a sapphire substrate was used as the seed substrate for the investigation. Dot- or stripe-patterned SiO_x masks were prepared on the template using RF sputtering and conventional photolithography. The dot-patterned mask was designed such that 5-μm-diameter circular windows formed a triangular lattice pattern. The window spacing (the distance between the mask edges of the nearest windows) was 5 μm unless otherwise specified. The widths of the mask/window of the stripe-patterned mask were 5 μm/5 μm.

The HVPE growth conditions used for this investigation are described in Section 2.2. The partial pressures of the GaCl and O_2 supplies were 1.25×10^{-1} and 1.25 kPa, respectively, unless otherwise mentioned.

The morphology of the grown samples was examined using SEM, the mosaicity was estimated using XRC, and the behavior of the dislocations was investigated using TEM.

2.6.3 Morphological characterization of ELO-grown α-Ga_2O_3

(1) Effect of window spacing and growth rate

Figures 17 (a)–(c) present SEM images of the samples grown under the same conditions on a dot-patterned mask with a window spacing of 5–20 μm. For the spacing of 5 μm, α-Ga_2O_3 islands were selectively grown at the mask openings, forming a regular array (Fig. 17 (a)). When the spacing was wider, however, additional crystal grains appeared around each α-Ga_2O_3 island (Fig. 17 (b), (c)). In this type of selective area growth, the precursors are consumed virtually only in the window regions. Therefore, the effective precursor supply increases with increasing window spacing and decreasing window density. Indeed, the island size increases with increasing window spacing. It is likely that this increase in the driving force for the growth resulted in the undesired nucleation. To confirm this speculation, slower growth was performed on the 20-μm-wide mask by decreasing only the GaCl supply such that the nominal growth rates (growth rate for flat films) decreased from 12 to 7 and 5 μm/h. As a result, nucleation of additional crystal grains was markedly suppressed, as observed in Figs. 18 (a) and (b).

(2) Effect of growth temperature T_g

Figures 19 (a)–(c) present SEM images of the samples grown at 540°C, 500°C, and 460°C. For T_g = 540°C, the island morphology is primarily a hexagonal pillar with a well-developed *c*-plane and inclined $(10\bar{1}1)$ planes cutting off the top edge (Fig. 19 (a)). When T_g was decreased to 500°C, $(10\bar{1}1)$ planes developed well, whereas the (0001) plane become unstable (Fig. 19 (b)). When T_g was further decreased to 460°C, the (0001) plane disappeared and $(10\bar{1}4)$ planes appeared instead (Fig. 19 (c)). Thus, the island morphology is sensitive to the growth temperature and can be controlled. This nature is essential to perform the FIELO process, as described in section 2.6.1. (2).

(3) Time evolution of the growth

Figures 20 (a)–(d) show the time evolution of the ELO process of α-Ga_2O_3. The degree of growth is indicated by the nominal thickness (thickness for a flat film). At the beginning of the regrowth, the shape of each island was similar to that of a circular window (Fig. 20 (a)). Then, the crystal habit became clear, and hexagonal pillars were formed (Fig. 20 (b)). Under these growth conditions, vertical growth was faster than lateral growth. Island coalescence started at the bottom of the islands (Fig. 20 (c), (d)), and finally, a flat film was obtained.

2.6.4 Structural characterization of ELO-grown α-Ga_2O_3

(1) XRC-FWHM

XRC measurements of the ELO-grown samples were performed to verify the effectiveness on the improvement of the crystal quality. Figure 21 plots the tilt and twist angles as functions of the nominal thickness. Both the tilt and twist angles decreased with increasing nominal thickness, which indicates the increase of the high-quality area during the 3D growth. Figure 22 presents XRC profiles of the sample with a nominal thickness of 12 μm. Multiple peaks were not observed for the *0006* diffraction in contrast to the case for the ELO-grown GaN. It has been reported that the out-of-plane XRC of ELO-grown GaN contains multiple peaks because of the formation of small-angle grain boundaries [32, 33]. This inclination of the laterally grown wing region was attributed to the edge dislocation array formed above the mask edge, which was clearly visible in the cross-sectional TEM image [32]. Accordingly, the absence of peak splitting for ELO-grown α-Ga_2O_3 indicates that the character of the dislocations and their response to crystal strain in ELO-grown α-Ga_2O_3 can be different from those in GaN.

(2) Effect of island morphology on the behavior of crystal defects

Figures 23 (a) and (b) present cross-sectional TEM images of α-Ga_2O_3 islands grown at 540°C and 460°C; the corresponding SEM images are presented in Fig. 19 (a) and (c), respectively. The 540°C-grown island had a well-developed (0001) plane on the top, whereas the 460°C-grown island had well-developed inclined facets. In both cases, dislocations in the seed layer propagated into the island through the window. For T_g = 540°C, the dislocation density in the wing area was clearly lower than that in the seed layer; however, the dislocations in the window area extended to the island top (Fig. 23 (a)). However, dislocations in the 460°C-grown island bent such that the dislocation line was nearly normal to the free surface (Fig. 23 (b)). Thus, the FIELO process can be used not only for GaN but also for α-Ga_2O_3. To estimate the dislocation density in the wing region, plan-view TEM analysis was performed for a sample grown on a stripe-patterned mask under growth conditions similar to those used for the 540°C-grown sample. Figure 24 presents the results. The α-Ga_2O_3 stripes did not coalesce with each other yet, and low-dislocation-density regions were observed on both sides of the gap. No dislocations were observed in the low-dislocation-density regions of approximately 22 μm^2; therefore, the dislocation density should be less than 5×10^6 cm^{-2}.

(3) Behavior of crystal defects in a coalesced film

Cross-sectional TEM analysis was performed on a coalesced film to clarify the behavior of dislocations in an ELO-grown continuous film. The sample was grown for 2 h at 520°C; therefore, the film should have been formed through inclined facet growth. Figure 25 (a) presents a plan-view SEM image of the sample. The surface was still bumpy, with the protruding parts corresponding to the window areas. Figure 25 (b) presents a schematic illustration of the sample cross-section. TEM analysis was performed in the dashed-line rectangle area. Figure 25 (c) presents the TEM image. The dislocations above the window bent because of the faceted growth, and the dislocation density of the top part was much lower than that of the seed layer. No dislocation array was observed above the mask edge, which was observed for ELO-GaN. This result is consistent with the XRC results described in 2.6.4. (1). At the coalesced boundary, we can see the dislocation contrast in the vicinity of the mask. The density decreased in the upper part, and no dislocation contrast was observed in the top part. Thus, ELO of α-Ga_2O_3 by HVPE is promising for improvement of the crystal quality. It would be possible to further reduce the dislocation density by increasing the duration of the 3D growth. Double-ELO would be also effective if the second mask is aligned to cover the window positions of the first mask. Note that in general, acceptable defect density is strongly dependent on the material, device structure, and driving condition. Accordingly, it is desirable to simultaneously perform device investigations to clarify the effect of crystal defects and to specify the target quality.

3. HVPE of ε-Ga_2O_3

3.1 Features and potential applications of ε-Ga_2O_3

ε-Ga_2O_3 is a metastable phase of Ga_2O_3 as well as α-Ga_2O_3. The first synthesis of ε-Ga_2O_3 was reported by Roy et al. [1]. They obtained a mixture powder of ε-Ga_2O_3 and β-Ga_2O_3 through annealing of $Ga(NO_3)_3$. The first synthesis of ε-Ga_2O_3 with high phase purity and its epitaxial growth was demonstrated by HVPE, and the band gap energy was reported to be 4.9 eV [9]. Detailed structural analysis of ε-Ga_2O_3 was performed by Playford et al., and they identified the crystal structure with space group $P6_3mc$ (PDF# 01–082-3196) [34]. The crystal structure of ε-Ga_2O_3 does not have inversion symmetry along the *c*-axis. Spontaneous polarization is therefore expected [35], and ferroelectric behavior was observed [36]. The existence of polarization would lead to the formation of a high concentration of two-dimensional electron gas [35]. Thus, ε-Ga_2O_3 is also a promising material for power device applications.

To fabricate ε-Ga_2O_3 devices, it is essential to establish epitaxial growth techniques. As described above, the epitaxial technique of ε-Ga_2O_3 was first demonstrated by HVPE, and then other techniques, such as MOCVD and mist CVD, were also shown to be effective [37, 38]. In this section, HVPE of ε-Ga_2O_3 and the characteristics of the grown layers are presented.

3.2 Growth methods and conditions of ε-Ga_2O_3

The HVPE apparatus used in this study is described in section 2.2, and the growth conditions were also similar. The growth temperature was 550°C, and the partial pressures of GaCl and O_2 were 0.25 and 1.0 kPa, respectively. (0001) GaN and (0001) AlN were used as the substrates. GaN and AlN belong to $P6_3mc$ as well as ε-Ga_2O_3. The in-plane lattice mismatches between ε-Ga_2O_3 and these substrates are summarized in Table 3.

Table 3. Lattice constants of ε-Ga_2O_3 and its substrates and lattice mismatches between them.

Material	Lattice constant [nm]	Mismatch [%]
(0001) ε-Ga_2O_3	$a = 0.2904$	-
(0001) GaN	$a = 0.3189$	8.8
(0001) AlN	$a = 0.3112$	6.6

3.3 Properties of HVPE-grown ε-Ga_2O_3

(1) XRD analysis of HVPE-grown Ga_2O_3 films

Figures 26 (a) and (b) present XRD 2θ–ω scan profiles of the films grown by HVPE on the two types of substrates. In the both cases, only diffraction peaks from the *c*-plane of ε-Ga_2O_3 were observed in addition to those from the substrates. The peak positions were in good agreement with those reported by Playford et al. [34]. Thus, ε-Ga_2O_3 with no contamination by β-Ga_2O_3 was obtained.

(2) SEM analysis of typical films

Figures 27 (a)–(d) present plan-view SEM images of the ε-Ga_2O_3 films. The sample surfaces were specular to human eyes; however, 3D grains are visible in the SEM images. The grain size was uniform on each sample. The density of the grains did not change by increasing the growth time, although the grain size increased. These results indicate that the grains nucleate at a certain moment during the growth. Figures 28 (a) and (b) present cross-sectional SEM images of the ε-Ga_2O_3 films grown for 2 and 7 min, respectively. From these images, the growth rate was estimated to be approximately 20 μm/h. Figure 28 (b) shows that the grain nucleated at the film/substrate boundary. Accordingly, growth optimization is necessary at the beginning of the growth to suppress the grain nucleation.

(3) Crystal orientation

Figure 29 (a) and (b) show the XRD pole figures of ε-Ga_2O_3 and the GaN substrate, respectively. The pole figures for ε-Ga_2O_3 (Fig. 29 (a)) and (0001) GaN (Fig. 29 (b)) exhibited six-fold symmetry, indicating that (0001) ε-Ga_2O_3 was grown epitaxially. The result for ε-Ga_2O_3 grown on (0001) AlN was similar (not shown).

(4) Crystal quality

The mosaicity of the HVPE-grown ε-Ga_2O_3 films were estimated from XRC measurements of *0004* and $10\bar{1}1$ diffractions in symmetric and skew-symmetric geometry. Figures 30 (a) and (b) present XRC profiles of the ε-Ga_2O_3 films grown on (0001) GaN and (0001) AlN, respectively. The FWHMs tended to be narrow when the in-plane lattice mismatch, which is summarized in Table 3, was small. However, for all the cases, the mosaicity was very large. Accordingly, the crystal quality should be improved by optimizing the growth conditions, introducing buffer layers, and/or utilizing the ELO technique.

(5) Impurity analysis

Table 4 summarizes the impurity analysis results obtained using SIMS of an HVPE-grown ε-Ga_2O_3 film. Although the growth conditions for ε-Ga_2O_3 were similar to those for α-Ga_2O_3, the concentrations of H and Cl were much higher than those in α-Ga_2O_3. Further study is necessary to clarify the reason for this difference, which likely originates from the difference in the surface structures of these polymorphs.

Table 4. Impurity concentrations in ε-Ga_2O_3 measured by SIMS.

Element	Concentration [cm^{-3}]
H	1×10^{18}
C	$< 6 \times 10^{16}$
N	$< 5 \times 10^{16}$

Si	$< 1 \times 10^{16}$
Cl	2×10^{18}
Al	$< 3 \times 10^{15}$
Cr	$< 4 \times 10^{14}$
Fe	$< 8 \times 10^{14}$
Ni	$< 3 \times 10^{15}$

(6) Optical bandgap of ε-Ga_2O_3

Until recently, ε-Ga_2O_3 was obtained only as the mixture powder with β-Ga_2O_3; therefore, the optical bandgap was unknown. Now ε-Ga_2O_3 with high phase purity has been successfully grown epitaxially, and the optical bandgap energy was estimated for the first time using transmittance measurements. Figure 31 presents the optical transmittance of ε-Ga_2O_3 grown by HVPE on (0001) AlN. Although the optical transition type of ε-Ga_2O_3 remains under discussion, better fitting was obtained when direct transition was assumed (inset of Fig. 31). The optical band gap energy was estimated to be 4.9 eV, which is close to the value for β-Ga_2O_3.

(7) Thermal stability, TEC

ε-Ga_2O_3 is a metastable phase and should transform into β-Ga_2O_3 above a certain threshold temperature. The thermal stability of ε-Ga_2O_3 was investigated using the same high-temperature XRD system described in Section 2.6 (2). Figure 32 presents the result for ε-Ga_2O_3 grown on (0001) GaN. Apart from the diffraction peaks of the Pt sample holder and GaN substrate, only the *0004* peak of ε-Ga_2O_3 was observed from RT to 700°C. When the temperature reached 725°C, the *401* peak of β-Ga_2O_3 appeared, and the peak intensity increased with increasing temperature, whereas that of *0004* of ε-Ga_2O_3 decreased. This result indicates that ε-Ga_2O_3 is thermally stable up to approximately 700°C. It is possible to calculate the TECs from the peak shift values in Fig. 32. The TECs along [0001] for ε-Ga_2O_3 grown on (0001) GaN was determined to be 1.1×10^{-5} K^{-1}. Again, note that the value may not be the same as that for freestanding materials because of the thermal stress resulting from the difference in TECs between ε-Ga_2O_3 and the substrates.

4. Summary and future prospects

The current state of HVPE technologies for α-Ga_2O_3 and ε-Ga_2O_3 were reviewed.

Regarding α-Ga_2O_3, the device technology is developing steadily. SBDs with very low R_{on} are almost ready for sample shipment, and a normally off MOSFET was recently demonstrated. To further improve the device performance, the establishment of growth technologies to obtain high-quality α-Ga_2O_3 and the realization of conductive freestanding α-Ga_2O_3 wafers are indispensable. The techniques described in this chapter, such as high-speed growth, conductivity control, and the ELO technique, will be essential in achieving these objectives. Further development of these techniques is required, and study of scientific fundamentals of the related phenomena is also necessary.

Currently, ε-Ga_2O_3 is attracting considerable attention because of its unique properties, including spontaneous polarization, and is potentially useful for power device applications. However, research on ε-Ga_2O_3 remains in a very primitive stage, and further accumulation of fundamental knowledge is required.

Acknowledgements

Part of this work is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO). This work was also partly supported by a Grant-in-Aid for Scientific Research (C) Nos. 25420307 and 17K05047 from the Japan Society for the Promotion of Science (JSPS). The author would like to acknowledge K. Kawara, T. Shinohe, T. Hitora, Prof. M. Kasu, and Prof. S. Fujita for their contributions to the NEDO project. The author would also like to thank Drs. E. G. Villora, Y. Matsushita, S. Yamamoto, and K. Shimamura for their support in the JSPS projects.

References

1. R. Roy, V. G. Hill, and E. F. Osborn: J. Am. Chem. Soc. **74**, 719 (1952).
2. H. Aida, K. Nishiguchi, H. Takeda, N. Aota, K. Sunakawa, Y. Yaguchi: Jpn. J. Appl. Phys. **47**, 8506 (2008).
3. E.G. Víllora, K. Shimamura, Y. Yoshikawa, K. Aoki, N. Ichinose: J. Cryst. Growth **270**, 420 (2004).
4. Z. Galazka, K. Irmscher, R. Uecker, R. Bertram, M. Pietsch, A. Kwasniewski, M. Naumann, T. Schulz, R. Schewski, D. Klimm, and M. Bickermann: J. Cryst. Growth **404**, 184 (2014).
5. K. Sasaki, A. Kuramata, T. Masui, E.G. Víllora, K. Shimamura, and S. Yamakoshi, Appl. Phys. Express **5**, 035502 (2012).
6. M. Higashiwaki, K. Sasaki, A. Kuramata, T. Masui, S. Yamakoshi, Appl. Phys. Lett. **100**, 013504 (2012).
7. M. Higashiwaki, K. Sasaki, T. Kamimura, M.H. Wong, D. Krishnamurthy, A. Kuramata, T. Masui, S. Yamakoshi, Appl. Phys. Lett. **103**, 123511 (2013).
8. Y. Oshima, E. G. Villora, and K. Shimamura: Appl. Phys. Express **8**, 055501 (2015).
9. Y. Oshima, E. G. Villora, Y. Matsushita, S. Yamamoto, and K. Shimamura: J. Appl. Phys. **118**, 085301 (2015).
10. Y. Oshima, E. G. Villora, and K. Shimamura: J. Cryst. Growth **410**, 53 (2015).
11. D. Shinohara and S. Fujita: Jpn. J. Appl. Phys. **47**, 7311 (2008).
12. S. Fujita and K. Kaneko: J. Cryst. Growth **401**, 588 (2014).
13. K. Kaneko, S. Kan, T. Hitora, S. Fujita: The 64th JSAP Spring Meeting, 16p-P8-19 (2017) Yokohama, Japan.
14. K. Kaneko, S. Fujita, and T. Hitora: Jpn. J. Appl. Phys. **57**, 02CB18 (2018).
15. M. Oda, R. Tokuda, H. Kambara, T. Tanikawa, T. Sasaki, and T. Hitora: Appl. Phys. Express **9**, 021101 (2016).
16. FLOSFIA and Kyoto univ: News release, July 13 (2008). http://flosfia.com/20180713/
17. T. Kawaharamura, G. T. Dang, and M. Furuta: Jpn. J. Appl. Phys. **51**, 040207 (2012).
18. K. Akaiwa and S. Fujita: Jpn. J. Appl. Phys. **51**, 070203 (2012).
19. T. Uchida, R. Jinno, S. Takemoto, K. Kaneko, and S. Fujita: The 77th JSAP Autumn Meeting, 16a-A22-8 (2016) Niigata, Japan.
20. K. Akaiwa, K. Kaneko, K. Ichino, and S. Fujita: Jpn. J. Appl. Phys. **55**, 1202BA (2016).
21. Y. Oshima, K. Kawara, T. Shinohe, T. Hitora, M. Kasu, S. Fujita, “Epitaxial Lateral Overgrowth of α-Ga_2O_3 by Halide Vapor Phase Epitaxy” to be published in APL materials.
22. L. J. Eckert and R. C. Bradt: J. Amer. Cer. Soc. **56**, 229 (1973).
23. W. M. Yim and R. J. Paff: J. Appl. Phys. **45**, 1456 (1974).
24. Y. Oshima, K. Kawara, M. Kasu, T. Shinohe, T. Hitora: 60th Electronic Materials Conference, II02, (2018) Santa Barbara, USA.

25. A. Usui, H. Sunakawa, A. Sakai, and A. A. Yamaguchi: Jpn. J. Appl. Phys. **36**, L899 (1997).
26. B. D. Joyce and J. A. Baldrey: Nature, **195**, 486, (1962).
27. F. W. Tausch, Jr., and A. G. Lapierre, III: J. Electrochem. Soc. **112,** 706 (1965).
28. T. Nishinaga, T. Nakano, and S. Zhang: Jpn. J. Appl. Phys. **27**, L964 (1988).
29. Y. Oshima, T. Eri, M. Shibata, H. Sunakawa, K. Kobayashi, T. Ichihashi, A. Usui: Jpn. J. Appl. Phys **42**, L1 (2003).
30. K. Motoki, T. Okahisa, N. Matsumoto, M. Matsushima, H. Kimura, H. Kasai, K. Takemoto, K. Uematsu, T. Hirano, M. Nakayama, S. Nakahata, M. Ueno, D. Hara, Y. Kumagai, A. Koukitu and H. Seki: Jpn. J. Appl. Phys. **40**, L140 (2001).
31. A. Takatsuka, M. Oda, K. Kaneko, S. Fujita, T. Hitora: The 62th JSAP Spring Meeting, 13a-P18-12 (2015) Hiratsuka, Japan.
32. A. Sakai, H. Sunakawa, and A. Usui: Appl. Phys. Lett. **73**, 481 (1998).
33. P. Fini, C. Thompson, G. B. Stephenson, J. A. Eastman, M.V. Ramana Murty, O. Auciello, L. Zhao, S. P. Denbaars and J. S. Speck: Appl. Phys. Lett. **76**, 3893 (2000).
34. H. Y. Playford, A. C. Hannon, E. R. Barney, and R. I. Walton: Chem. Eur. J **19**, 2803 (2013).
35. M. B. Maccioni and V. Fiorentini: Appl. Phys. Express **9**, 041102 (2016).
36. F. Mezzadri, G. Calestani, F. Boschi, D. Delmonte, M. Bosi, and R. Fornari: Inorg. Chem. **55**, 12079 (2016).
37. F. Boschi, M. Bosi, T. Berzina, E. Buffagni, C. Ferrari, R. Fornari: J. Cryst. Growth **443**, 25 (2016).
38. H. Nishinaka, D. Tahara, and M. Yoshimoto: Jpn, J. Appl. Phys. **55**, 1202BC (2016).

Figure captions

Figure 1. Schematic illustration of an HVPE reactor for Ga_2O_3.

Figure 2. Growth rate of α-Ga_2O_3 as a function of growth temperature.

Figure 3. Growth rate of α-Ga_2O_3 as functions of (a) O_2 partial pressure and (b) HCl partial pressure. [8]

Figure 4. Photographs of Ga_2O_3 films grown at (a) 650°C, (b) 600°C, (c) 575°C, and (d) 550°C.

Figure 5. XRD 2θ–ω profiles of an α-Ga_2O_3 layer: (a) wide-scan profile and (b) narrow-scan profile near *0006* diffraction. [8]

Figure 6. SEM images of an α-Ga_2O_3 layer: (a) surface image and (b) cross-sectional image. [8]

Figure 7. X-ray $10\bar{1}2$ pole figures (log scale) of (a) α-Ga_2O_3 layer and (b) sapphire substrate. [8]

Figure 8. XRCs of a conventional α-Ga_2O_3 film grown by HVPE. [21]

Figure 9. TEM images of a conventional α-Ga_2O_3 film grown by HVPE: (a) cross-sectional image and (b) plan-view image [21].

Figure 10. Transmittance spectra of α-Ga_2O_3. The inset shows the absorption coefficient in $(h\nu\alpha)^2$ vs. $h\nu$. [8]

Figure 11. XRD 2θ–ω scan profiles for an HVPE-grown α-Ga_2O_3 film measured at RT and elevated temperatures.

Figure 12. SIMS depth profile of a Ge-doped α-Ga_2O_3 film. The arrows indicate the detection limits.

Figure 13. Ge concentration in α-Ga_2O_3 as a function of $GeCl_4$ bubbling rate.

Figure 14. (a) Carrier concentration and (b) electron mobility at RT as functions of $GeCl_4$ bubbling rate. (c) Relationship between electron mobility and carrier concentration at RT for Ge-doped α-Ga_2O_3. Data from the literature [20] are also shown for comparison.

Figure 15. (a) Carrier concentration and (b) electron mobility as functions of temperature.

Figure 16. Procedure of FIELO technique.

Figure 17. SEM images of α-Ga_2O_3 islands grown on dot-patterned mask with window spacings of (a) 5 µm, (b) 10 µm, and (c) 20 µm (bird's eye view) [21].

Figure 18. SEM images of α-Ga_2O_3 islands grown at nominal growth rates of (a) 7 µm/h and (b) 5 µm/h (bird's eye view) [21].

Figure 19. SEM images of α-Ga_2O_3 islands grown at (a) 540°C, (b) 500°C, and (c) 460°C (bird's eye view) [21].

Figure 20. SEM images of α-Ga_2O_3 islands with nominal thickness of (a) 0.5 µm, (b) 1.6 µm, (c) 8 µm, and (d) 12 µm (plan-view and bird's eye view) [21].

Figure 21. XRC FWHMs of ELO-grown α-Ga_2O_3 as a function of nominal thickness [21].

Figure 22. XRC profiles of ELO-grown α-Ga_2O_3 with nominal thickness of 12 µm [21].

Figure 23. Cross-sectional TEM images of α-Ga_2O_3 islands grown at (a) 540°C and (b) 460°C.

Figure 24. Plan-view TEM image of α-Ga_2O_3 stripes with well-developed (0001) plane [21].

Figure 25. (a) Plan-view SEM image of a coalesced α-Ga_2O_3 film. (b) Schematic illustration of the cross section. (c) Cross-sectional TEM image of the film [21].

Figure 26. XRD 2θ–ω scan profiles of ε-Ga_2O_3 layers grown on (a) (0001) GaN and (b) (0001) AlN [9].

Figure 27. Plan-view SEM images of ε-Ga_2O_3 layers grown on (0001) GaN and (0001) AlN with growth times of 2 and 7 min [9].

Figure 28. Cross-sectional SEM images of ε-Ga_2O_3 layers grown on (0001) GaN with growth times of (a) 2 min and (b) 7 min [9].

Figure 29. X-ray pole figures (log scale) of (a) ε-Ga_2O_3 $10\bar{1}4$ and (b) GaN $10\bar{1}2$ [9].

Figure 30. XRCs of ε-Ga_2O_3 layers grown on (a) (0001) GaN and (b) (0001) AlN [9].

Figure 31 Transmittance spectrum of ε-Ga_2O_3. The inset shows the absorption coefficient in $(h\nu\alpha)^2$ vs. $h\nu$ [9].

Figure 32. XRD 2θ–ω scan profiles for an HVPE-grown ε-Ga_2O_3 film measured at RT and elevated temperatures [9].