

Quasi-heteroepitaxial growth of β -Ga₂O₃ on off-angled sapphire (0001) substrates

by Halide Vapor Phase Epitaxy

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Abstract

We demonstrate the high-speed growth of β -Ga₂O₃ quasi-heteroepilayers on off-angled sapphire (0001) substrates by halide vapor phase epitaxy (HVPE). ($\bar{2}01$) oriented β -Ga₂O₃ layers were successfully grown using GaCl and O₂ as source gases. The growth rate monotonically increased with increasing the partial pressures of the source gases, reaching over 250 $\mu\text{m/h}$. This rate is over two orders of magnitude larger than those of conventional vapor phase epitaxial growth techniques such as molecular beam epitaxy or metalorganic vapor phase epitaxy. X-ray pole figure measurements indicated the presence of six in-plane rotational domains, in accordance with the substrate symmetry, plus some minor (310) domains. By the use of off-angled substrates and thick layer overgrowth, one of the in-plane orientations was strongly favored and the (310) residuals effectively suppressed, so that quasi-heteroepitaxial growth was

achieved. Therefore, these results indicate the high-potential of the HVPE technique for the growth of thick and thin β -Ga₂O₃ layers for the cost-effective production of β -Ga₂O₃ based devices.

Keywords: A3. halide vapor phase epitaxy, B1. Oxides, B2. Semiconducting gallium compounds

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1. Introduction

β -Ga₂O₃ is the most transparent conductive oxide, with a band gap as large as 4.8 eV [1]. At present, β -Ga₂O₃ investigations point towards three groups of practical applications: UV emission/detection devices for disinfection purposes and solar-blind sensor, substrate for high-brightness vertically-structured and flip-chip GaN-LEDs [2-4], and high-power devices, because the large band gap of β -Ga₂O₃ in comparison with those of the counterparts SiC and GaN is advantageous for the realization of high-efficiency transistors [5-8].

One of the great advantages of β -Ga₂O₃ over other wide band gap semiconductors is

that high-quality single crystal wafers can be produced from melt by the floating zone (FZ) or the edge-defined film-fed growth (EFG) technique [9,10]. At present, EFG-grown 2-inch β -Ga₂O₃ wafers are commercially available. The EFG growth of β -Ga₂O₃ from melt, however, requires the use of very expensive Ir-crucibles. One of the solutions for this drawback is the realization of heteroepitaxial β -Ga₂O₃ film on large-area foreign substrates, such as sapphire. However, there is no successful report on the growth of such heteroepitaxial layers.

So far, several epitaxial growth techniques of β -Ga₂O₃, such as molecular beam epitaxy (MBE) [11-13], metalorganic vapor phase epitaxy (MOPVE) [14,15], and pulsed laser deposition (PLD) [16,17], have been reported. Among them, MBE is mainly used for the study of β -Ga₂O₃ power devices [5-8]. In order to ensure the sufficient break down voltage, relatively thick layers need to be grown. However, the growth rates achieved by those conventional techniques are pretty small, i.e., below 1 μ m/h in most cases.

Therefore, in order to guarantee a cost-effective production of β -Ga₂O₃ devices, it is necessary to investigate, on the one hand, which epitaxial growth technique can produce β -Ga₂O₃ epilayers with controlled thickness and electrical conductivity at a sufficient growth rate, and on the other hand, which foreign substrate is the most suitable for the

heteroepitaxial growth.

In this work, we have employed the halide vapor phase epitaxy (HVPE) technique to grow β -Ga₂O₃ layers. HVPE is a non-organic chemical vapor deposition (CVD) technique, which is characterized by a fast growth rate and the high crystalline quality of resulting layers. Yoshida *et al.* have reported the high-speed HVPE growth of GaN up to approximately 2 mm/h with no degradation of the crystal quality [18]. The first report which is related to the HVPE of β -Ga₂O₃ was made by Matsumoto *et al.* in 1974 [19]. They synthesized β -Ga₂O₃ by the reaction between GaCl gas and O₂ at 1100 - 1150°C. They did not use any single crystal substrates, but obtained small flakes or needle-like crystals on the inner wall of the quartz reactor. Recently, Nomura *et al.* have reported the results on the thermodynamic analysis of the HVPE growth of β -Ga₂O₃ using GaCl and O₂ as precursors. The theoretical estimations agreed well with their experimental results on the homoepitaxial growth, indicating that the HVPE of β -Ga₂O₃ can be thermodynamically controlled [20].

Growth of β -Ga₂O₃ on foreign substrates has been reported on sapphire [11,-14,16,17], MgO [11,15], etc. These β -Ga₂O₃ thin-films are highly textured, exhibiting single out-of-plane orientations. These films are characterized by the formation of in-plane rotational domains that reflect the substrate symmetry. For

example, $(\bar{2}01)$ oriented $\beta\text{-Ga}_2\text{O}_3$ layers on sapphire (0001) consist of six in-plane rotational domains with six-fold symmetry in accordance with the substrate symmetry [11,14,16]. Similarly, (100) and $(\bar{1}02)$ oriented $\beta\text{-Ga}_2\text{O}_3$ layers are obtained on MgO (100) and (110) with four- and two-fold symmetric in-plane rotational domains, respectively [11, 15]. If $\beta\text{-Ga}_2\text{O}_3$ is grown on a substrate with no in-plane rotational symmetry, then the formation of such rotational domains can be suppressed. However, there are no such past reports. In this work, we employed sapphire (0001) substrates. The substrates have two great advantages. One is that the in-plane arrangement of oxygen atoms is similar to that of $\beta\text{-Ga}_2\text{O}_3$ ($\bar{2}01$), and therefore ($\bar{2}01$)-oriented $\beta\text{-Ga}_2\text{O}_3$ layers are readily achieved. The other advantage is that large diameter substrates are available with reasonable price. However, as stated above, there is a problem, *i.e.*, the formation of the in-plane rotational domains. Therefore, we introduced off-angles to sapphire (0001) substrates in order to reduce the in-plane symmetry of the substrates.

Summarizing the stated above, the establishment of a high-speed epitaxial growth technique and the epitaxial growth of $\beta\text{-Ga}_2\text{O}_3$ on foreign cheap substrates will be essential for the fabrication of cost-competitive devices based on $\beta\text{-Ga}_2\text{O}_3$. Accordingly, this work is focused on the demonstration of high-speed growth of $\beta\text{-Ga}_2\text{O}_3$ by the

HVPE technique, and the deposition of β -Ga₂O₃ quasi-heteroepilayers on off-angled sapphire (0001) substrates.

2. Experimental

β -Ga₂O₃ HVPE was carried out using GaCl and O₂ (> 99.99995% pure) in an atmospheric horizontal reactor. The GaCl was formed upstream in the reactor by the reaction between Ga metal (> 99.99999% pure) and HCl gas (> 99.999% pure). The partial pressures of the HCl ($P(\text{HCl})$) and O₂ ($P(\text{O}_2)$) were varied between 0.1-1.25 kPa and 0.5-5 kPa, respectively, both being constant for each single deposition. HCl was introduced just during the deposition at high temperature, while O₂ was flown from the beginning of the heating till the end of the cooling process. N₂ was flown (> 99.9999% pure) as carrier gas. The temperature in the reactor was kept constant at 1050°C. We used off-angled epi-ready sapphire (0001) substrates with off-angles between 0°-10° and a typical RMS value of 0.1 nm. The β -Ga₂O₃ films were directly grown on each substrate without any buffer layer to compensate for lattice mismatch.

The surface morphology of the HVPE-grown β -Ga₂O₃ films was observed by means of scanning electron microscopy (SEM). The growth rate was determined by the interference thickness meter. The orientation of the films was investigated by X-ray diffraction (XRD) ω -2 θ scan and pole figure measurements.

3. Results and discussion

3.1 Orientation of β -Ga₂O₃ film grown on non-off-angled substrates

Figure 1 shows the XRD ω -2 θ profile of the grown layer on a sapphire substrate with no off-angle. Besides the diffraction peaks of the substrate, the XRD profile presents only the reflections from the $\{\bar{2}01\}$ plane family, except a tiny peak at $2\theta \approx 79.5^\circ$, which can be assigned to the (620) reflection. This confirms that $(\bar{2}01)$ oriented β -Ga₂O₃ layers are also obtained by HVPE. ϕ -Scan profile of the β -Ga₂O₃ layer and the sapphire substrate in skew-symmetric geometry (not shown) indicated the existence of six rotational β -Ga₂O₃ domains and the following epitaxial relationship, which is the same as those in the past reports of other epitaxial growth techniques [11-14,17]:

$$(\bar{2}01) \beta\text{-Ga}_2\text{O}_3 \parallel (0001) \text{ sapphire, and } \langle 102 \rangle \beta\text{-Ga}_2\text{O}_3 \parallel \langle 11\bar{2}0 \rangle \text{ sapphire}$$

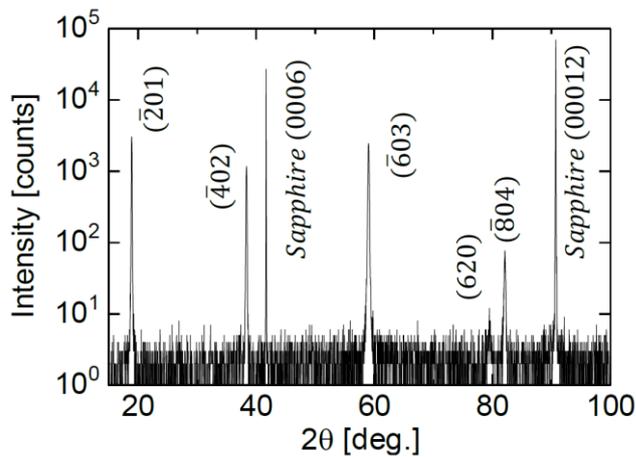


Figure 1. XRD ω -2 θ profile of a β -Ga₂O₃ layer grown on a sapphire (0001) substrate with no off-angle.

3.2 Growth rate of β -Ga₂O₃

Figure 2 shows the growth rate of β -Ga₂O₃ on sapphire (0001) substrates with no off-angle as a function of the partial pressures of (a) $P(\text{HCl})$ and (b) $P(\text{O}_2)$. The growth rate increases almost linearly with increasing $P(\text{HCl})$, showing a slight saturating tendency around $P(\text{HCl}) = 1.25$ kPa. The growth rate reaches over 250 $\mu\text{m}/\text{h}$, which is over two orders of magnitude greater than those of other epitaxial growth techniques. The dependence on $P(\text{O}_2)$ shows a similar behavior, becoming saturated at about $P(\text{O}_2) = 5$ kPa. The saturation in Fig. 2(a) is likely to be caused by the decrease in conversion efficiency of HCl into GaCl, and/or the insufficient mixing of GaCl and O₂. In the case of Fig. 2(b) it is probably due to the shortage of GaCl.

In the following sections, we describe the results of the growth on off-angled substrates. We applied the same growth recipe for each deposition, i.e., $P(\text{HCl}) = 0.1$ kPa and $P(\text{O}_2) = 5$ kPa.

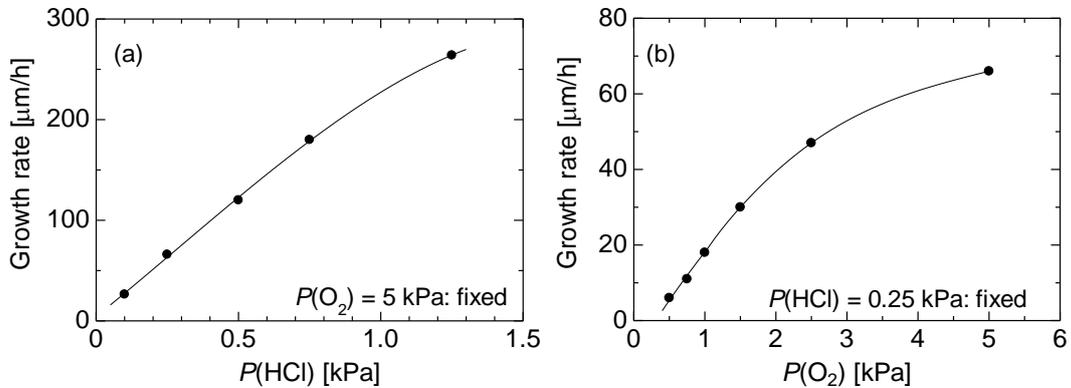


Figure 2. Growth rate of β -Ga₂O₃ as a function of (a) HCl partial pressure, (b) O₂ partial pressure.

3.3 Surface morphology of $\beta\text{-Ga}_2\text{O}_3$ layers grown on off-angled substrates

Figure 3 shows the surface SEM images of the $\beta\text{-Ga}_2\text{O}_3$ layers grown on sapphire (0001) substrates with various off-angles toward $\langle 11\bar{2}0 \rangle$ (Δ_a). In the case of $\Delta_a = 0^\circ$, we can see a domain-like morphology, which might be correlated with the in-plane rotational domains. When Δ_a is not zero, the domain-like pattern becomes unclear, and a stripe-like pattern along $\langle 10\bar{1}0 \rangle$ of sapphire develops as the Δ_a increases, i.e., as the density of surface steps along sapphire $\langle 10\bar{1}0 \rangle$ rises. This transformation of the surface morphology is indicative of the change in the crystal orientation, which is elucidated in the following section 3.4.

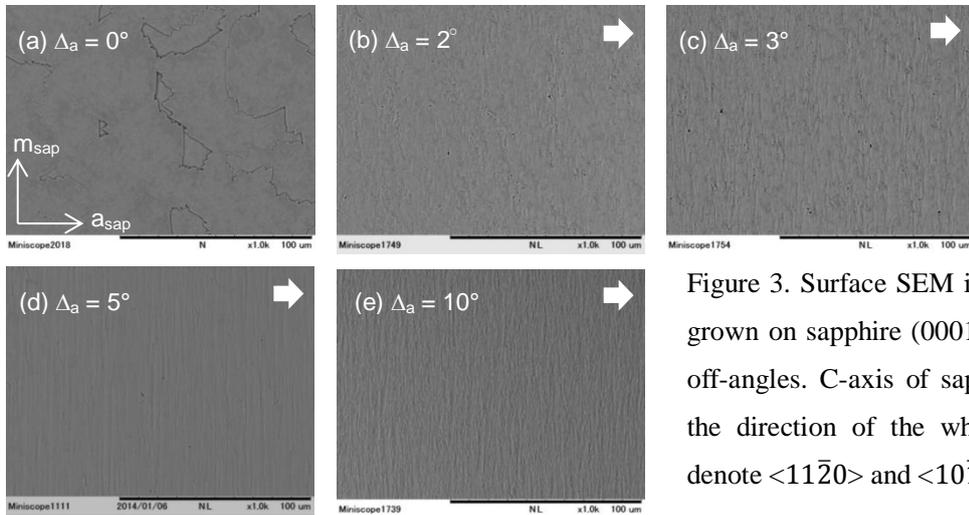


Figure 3. Surface SEM images of $\beta\text{-Ga}_2\text{O}_3$ layers grown on sapphire (0001) substrates with various off-angles. C-axis of sapphire is inclined toward the direction of the white arrow. a_{sap} and m_{sap} denote $\langle 11\bar{2}0 \rangle$ and $\langle 10\bar{1}0 \rangle$, respectively.

3.4 Orientation control of $\beta\text{-Ga}_2\text{O}_3$ layers by the use of off-angled substrates

In order to clarify the effect of the off-angle on the orientation of $\beta\text{-Ga}_2\text{O}_3$ layers, X-ray pole figure measurements were carried out. First of all, we show the (002) pole

figure of an EFG-grown single crystal $\beta\text{-Ga}_2\text{O}_3$ ($\bar{2}01$) wafer in Fig. 4(a) for comparison. Only one (002) peak appears in the pole figure, since the crystal structure of $\beta\text{-Ga}_2\text{O}_3$ does not have rotational symmetry around the axis normal to the ($\bar{2}01$) plane. Note that the ($\bar{2}02$) peak also appears because the (001) and ($\bar{1}01$) planes have almost the same spacing and thus the same Bragg angle. On the other hand, the pole figure of the HVPE-grown $\beta\text{-Ga}_2\text{O}_3$ layer on sapphire (0001) substrate with no off-angle exhibits six (002) peaks (Fig. 4(b)). However, once off-angled sapphire (0001) substrates are utilized, the in-plane orientation of the $\beta\text{-Ga}_2\text{O}_3$ layers changes dramatically. The gradual change that takes place with increasing off-angle is shown in Figs. 4(c)-(e). Only a small off-angle of $\Delta_a = 2^\circ$ results in the decrease of the number of (002) peaks from six to three. In addition, the intensity of the (002) peak along the off-direction is enhanced, while other two diminish. This trend is further promoted with increasing Δ_a . When Δ_a is 5° or more, the appearance of the pole figure is indistinguishable from that of the single crystal $\beta\text{-Ga}_2\text{O}_3$ wafer, Fig. 4(a).

The position of the each peaks shifted according to the off-angle, and the epitaxial relationship shown in section 3.1 seems to be approximately conserved. However, there is still a possibility that ($\bar{2}01$) of $\beta\text{-Ga}_2\text{O}_3$ are a bit inclined from (0001) of sapphire. Unfortunately, such inclination could not be confirmed since the off-angled sapphire

substrates we used for the experiment exhibited some peak-split in XRD profile.

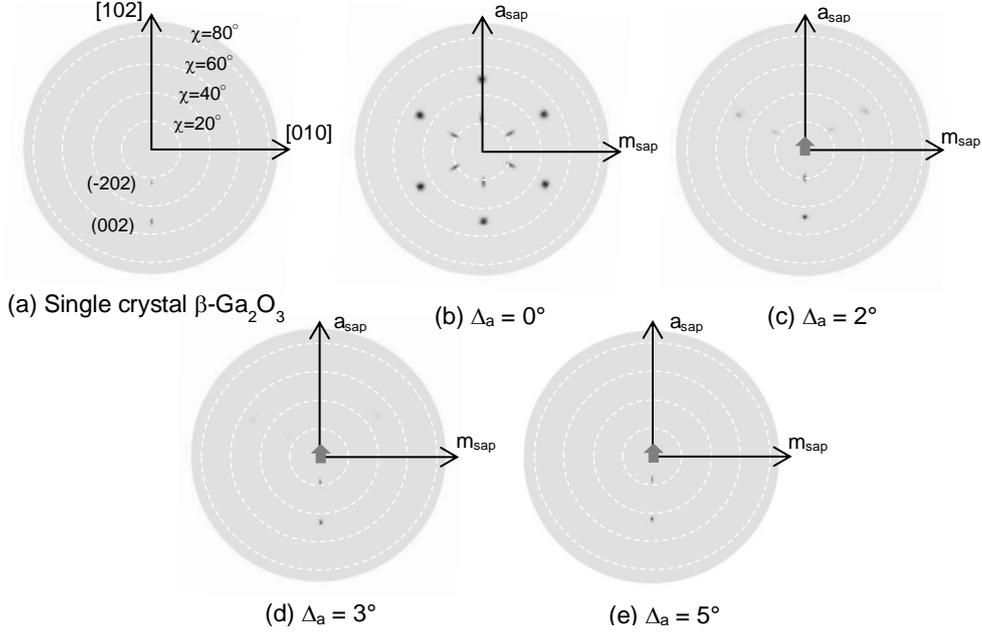


Figure 4. (002) pole figures of (a) single crystal $\beta\text{-Ga}_2\text{O}_3$ wafer, (b)-(e) $\beta\text{-Ga}_2\text{O}_3$ layers grown on sapphire (0001) substrates with various off-angles Δ_a . Gray arrows show the direction of off-angle.

In order to evaluate the variation of the in-plane orientation, we consider the ratio $I(002)_{\max} / I(002)_{\text{total}}$, where $I(002)_{\max}$ is the intensity of the highest (002) peak, and $I(002)_{\text{total}}$ is the sum of all (002) peak intensities. This ratio is a measure of the heteroepitaxial quality and it varies between 1/6 for $\Delta_a = 0^\circ$, when of six (002) peaks appear with the same intensity, and 1, in the case of the ideal single crystal. The variation of $I(002)_{\max} / I(002)_{\text{total}}$ is shown as a function of Δ_a in Fig. 5 (a). The in-plane orientation improves rapidly up to around $\Delta_a = 3^\circ$, at $\Delta_a = 5^\circ$ is already very close to 1, and at $\Delta_a = 10^\circ$ no further improvement is observed. It should be noted that this ratio is

simply calculated from the height of each peak. Various factors, such as the difference in peak width and its anisotropy, defocus correction for inclined incidence of X-ray, X-ray absorptive correction, etc., are not taken into consideration. Therefore, it does not reflect the domain volume ratios with accuracy.

Although the concrete mechanism of the in-plane orientation improvement is not clear at present, we can state some parallelisms from the crystallographical point of view. The crystal structure of sapphire has a three-fold rotational symmetry around the c-axis, and a six-fold one if only the arrangement of oxygen atoms is considered. Non-off-angled layers present six-fold rotational domains in accordance with the oxygen in-plane arrangement. Instead, the domains in off-angled layers are reduced to three, when the in-plane symmetry reflects the bulk symmetry. With increasing off-angle the density of surface steps increases and the domain growing along the tilted direction is largely favored over the other two. As the result, the in-plane orientation of β -Ga₂O₃ converges to one preferable direction.

Figure 5 (b) shows the relationship between $I(002)_{\max} / I(002)_{\text{total}}$ and the film thickness in the case of $\Delta_a = 10^\circ$. It was found that the in-plane orientation does not improve by thick film growth. Since the in-plane rotational domains have nearly the same out-of-plane orientation, they all grow at the same rate and no domain overgrowth

can take place. Therefore, other growth parameter should be optimized for further improvement of the in-plane orientation.

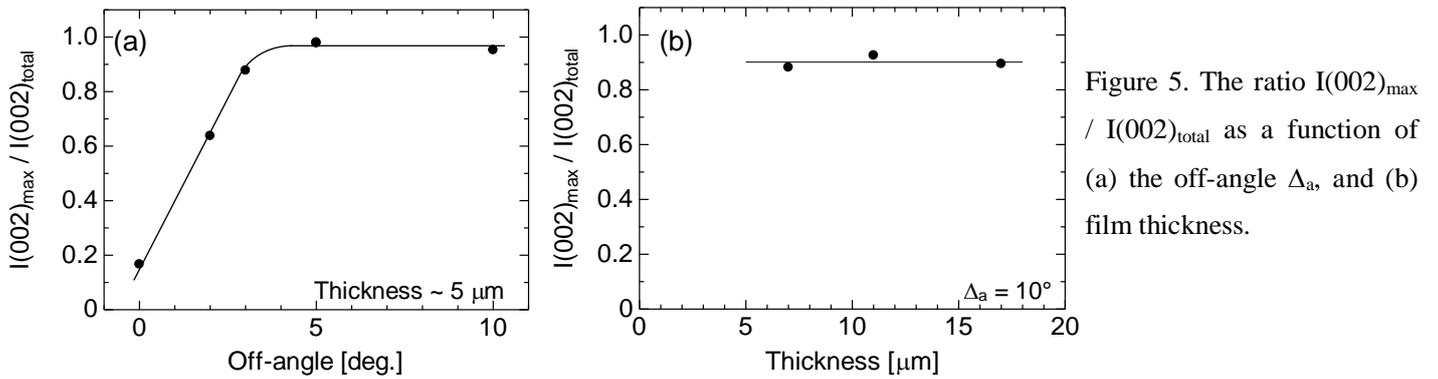


Figure 5. The ratio $I(002)_{\max} / I(002)_{\text{total}}$ as a function of (a) the off-angle Δ_a , and (b) film thickness.

For the sake of comparison, a sapphire (0001) substrate with an off-angle of $\Delta_m = 2^\circ$ toward the $\langle 10\bar{1}0 \rangle$ direction, i.e. perpendicular to previous tilting, was utilized. Interestingly, the result obtained is quite different. Figure 6 shows the (002) $\beta\text{-Ga}_2\text{O}_3$ pole figure. In contrast to previous case, the amount of domains did not reduce to three; It continued being a set of six but with uneven peak intensities. The origin of this difference is not clear at this point, and further detailed investigations at the atomic level will be needed to clarify it.

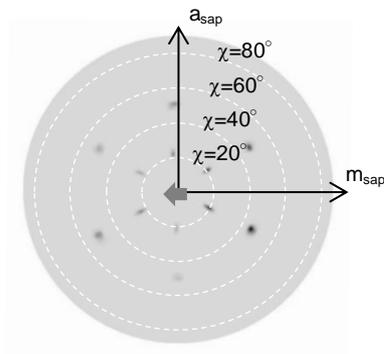


Figure 6. (002) pole figure of a $\beta\text{-Ga}_2\text{O}_3$ layer grown on sapphire (0001) substrates with an off-angle $\Delta_m = 2^\circ$. The gray arrow shows the direction of the off-angle.

3.5 Reduction of (310) domains

Figure 7 shows the (020) pole figures of $\beta\text{-Ga}_2\text{O}_3$ layers grown on sapphire substrates with $\Delta_a = 0^\circ$ and 3° . In both cases, (020) peaks appeared at around $\chi=37.5^\circ$. This cannot happen if the layers consist of only $(\bar{2}01)$ oriented domains, since the (020) plane is perpendicular to the $(\bar{2}01)$ one. Therefore, this result indicated the existence of additional secondary domains with an out-of-plane orientation different from $(\bar{2}01)$. From the peak positions in (020) and (400) pole figures (not shown), it was elucidated that those (020) peaks have the same origin as the (620) reflection in Fig.1. The epitaxial relationship between the (310) oriented $\beta\text{-Ga}_2\text{O}_3$ domains and sapphire is as follows:

$$(310) \beta\text{-Ga}_2\text{O}_3 \parallel (0001) \text{ sapphire, and } \langle 001 \rangle \beta\text{-Ga}_2\text{O}_3 \parallel \langle 10\bar{1}0 \rangle \text{ sapphire}$$

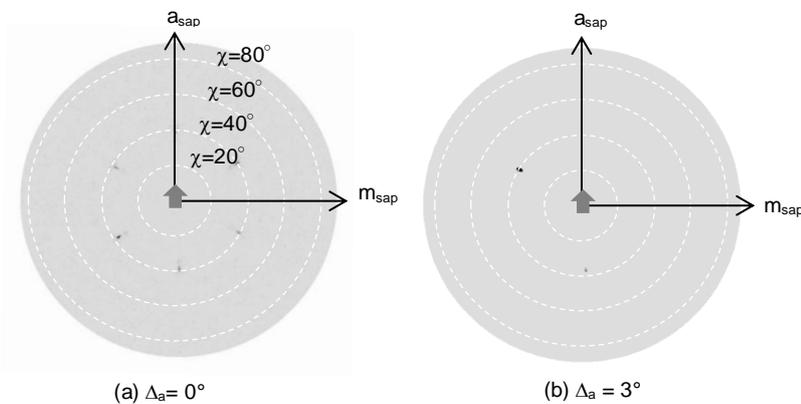


Figure 7. (020) pole figures of $\beta\text{-Ga}_2\text{O}_3$ layers grown on sapphire (0001) substrates with off-angles of (a) $\Delta_a = 0^\circ$, and (b) $\Delta_a = 3^\circ$. Gray arrows at the center show the direction of the off-angle.

In order to analyze the degree of coexistence between primary and secondary domains, we use the ratio $I(020)_{\text{total}} / I(002)_{\text{total}}$, where $I(020)_{\text{total}}$ and $I(002)_{\text{total}}$ are the sum of all (020) or (002) peaks, respectively. Again, note that this ratio is just orientational, simply calculated from the peaks height, its value being zero when (310) domains are not present. The variation of $I(020)_{\text{total}} / I(002)_{\text{total}}$ is shown as a function of Δ_a in Fig. 8 (a). The ratio increases with increasing Δ_a up to 3° , and then it turns to decrease so that at $\Delta_a = 10^\circ$ the value is even smaller than that at $\Delta_a = 0^\circ$. Additionally, Fig. 8 (b) shows the relationship between the ratio $I(020)_{\text{total}} / I(002)_{\text{total}}$ and the film thickness in the case of $\Delta_a = 10^\circ$. It was found that in this case the ratio decreases rapidly with the increase of film thickness. This fact indicates that the existence of the (310) domains is confined near the interface between the $\beta\text{-Ga}_2\text{O}_3$ layer and the substrate. The mechanism of this dependence is unclear at present. However, it is plausible that the growth rate of the (310) domains are smaller than that of the $(\bar{2}01)$ ones, so that the growth of the (310) domains is hindered by the overgrowth of the $(\bar{2}01)$ domains.

As a means of the further suppression of the (310) domains, one might think that increasing Δ_a beyond 10° is promising. In reality, however, ternary domains with different out-of-plane orientation from both $(\bar{2}01)$ and (310) appeared when $\Delta_a = 15^\circ$

(the detail is not described in this paper). Hence, around $\Delta_a = 10^\circ$ seems to be the best off-angle under current growth conditions.

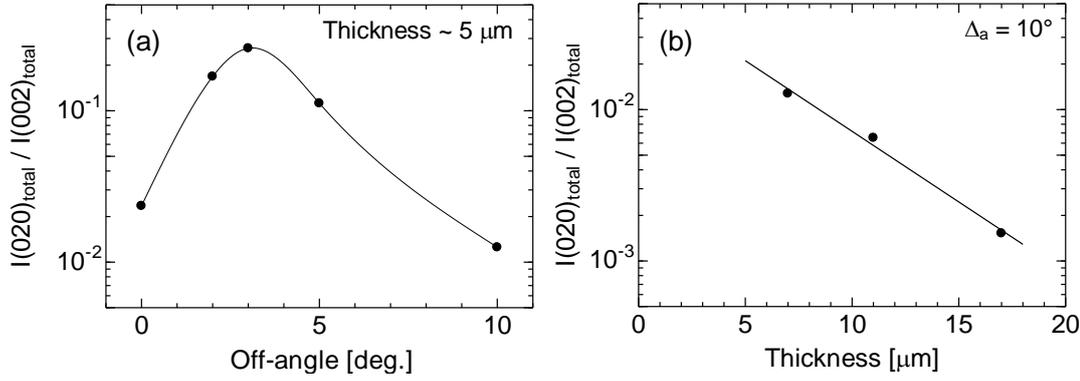


Figure 8. The ratio $I(020)_{\text{total}} / I(002)_{\text{total}}$ as a function of (a) the off-angle Δ_a , and (b) film thickness.

4. Conclusion

This work demonstrates the high-speed growth of $\beta\text{-Ga}_2\text{O}_3$ by HVPE, and the orientation control by utilizing off-angled sapphire (0001) substrates, obtaining quasi-heteroepilayers. The deposition rate monotonically increased with increasing the partial pressures of the source materials (GaCl and O_2), reaching a high growth rate over $250 \mu\text{m/h}$. Without off-normal angle, $(\bar{2}01)$ oriented $\beta\text{-Ga}_2\text{O}_3$ layers with six in-plane rotational domains were deposited in accordance with the substrate symmetry. On the other hand, on sapphire (0001) substrates off-angled toward $\langle 11\bar{2}0 \rangle$, the number of the rotational domains decreased from six to three, with one of the domains being strongly predominant with increasing off-angle. In contrast, when the off-angle was toward

$\langle 10\bar{1}0 \rangle$ of sapphire, still all six domains appeared with different X-ray intensities. It was also found that the $\beta\text{-Ga}_2\text{O}_3$ layers included a very minor quantity of (310) oriented domains, whose presence diminish with off-angles over 3° and with thick layer overgrowth. In conclusion, with an off-angle of $\Delta_a = 10^\circ$ the quasi-heteroepilayer growth is favored, since the in-plane orientation is strongly enhanced and the residual (310) domains drastically diminish.

Taking into account current results, we presume that it is possible to obtain $\beta\text{-Ga}_2\text{O}_3$ heteroepitaxial layers by further improving the growth conditions. In combination with the electrical conductivity control, which is our important future work, the cost-competitive production technique of such $\beta\text{-Ga}_2\text{O}_3$ epilayers can be established in the near future.

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Figure Captions

Figure 1. XRD ω - 2θ profile of a β -Ga₂O₃ layer grown on a sapphire (0001) substrate with no off-angle.

Figure 2. Growth rate of $\beta\text{-Ga}_2\text{O}_3$ as a function of (a) HCl partial pressure, (b) O_2 partial pressure.

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Figure 5. The ratio $I(002)_{\text{max}} / I(002)_{\text{total}}$ as a function of (a) the off-angle Δ_a , and (b) film thickness.

Figure 6. (002) pole figure of a $\beta\text{-Ga}_2\text{O}_3$ layer grown on sapphire (0001) substrates with an off-angle $\Delta_m = 2^\circ$. The gray arrow shows the direction of the off-angle.

Figure 7. (020) pole figures of $\beta\text{-Ga}_2\text{O}_3$ layers grown on sapphire (0001) substrates with off-angles of (a) $\Delta_a = 0^\circ$, and (b) $\Delta_a = 3^\circ$. Gray arrows at the center show the direction of the off-angle.

Figure 8. The ratio $I(020)_{\text{total}} / I(002)_{\text{total}}$ as a function of (a) the off-angle Δ_a , and (b) film thickness.