1. Introduction

Over the past decade, Ga₂O₃ has gained much attention as a wide-band gap semiconductor. Monoclinic β-Ga₂O₃ possesses an ultra-wide band gap of ~4.7 eV, and it has been the most studied phase owing to its thermal stability and the availability of large-area, native, semi-insulating, and conductive substrates. To further increase its band gap, growth and the low formation energy of defects may cause insulating are unknown, the thermodynamics during MBE growth window, and (iii) reduced out-of-lane mosaic spread when MOCATAXY is employed for the growth of α-Ga₂O₃. Through the use of intermediate catalyst growth processes during the growth of Ga₂O₃ thin films since the Ga-rich growth regimes lead to higher V_Ga formation energies, resulting in lower V_Ga densities within the Ga₂O₃ layers.

One approach to address these issues is through the use of metal–oxide-catalyzed epitaxy (MOCATAXY). This is a growth process where a catalytic element (e.g. In) is introduced to the growth system and results in metal-exchange catalysis. This growth mode has been observed for β-(Al,Ga)₂O₃ on different substrates and surface orientations, as well as for different epitaxial growth techniques.

Many benefits arise from using MOCATAXY during the growth of Ga₂O₃. For example: (i) it can improve the surface morphologies of β-Ga₂O₃-based films, (ii) the synthesis of Ga₂O₃ can occur in previously inaccessible kinetic and thermodynamic growth regimes (e.g. in highly metal-rich regimes) which can be beneficial for the suppression of undesired point defects (such as V_Ga) effects in Ga₂O₃, (iii) The formation of thermodynamically unstable Ga₂O₃ phases becomes energetically favorable, e.g. the formation of the χ-phase of Ga₂O₃, which has enabled novel χ-Ga₂O₃-based heterostructures, (iv) The growth rate (Γ), possible growth temperatures (T_G), and crystalline quality of β-(Al,Ga)₂O₃-based thin films can be vastly enhanced.

In this work, we introduce the growth of α-Ga₂O₃ by MOCATAXY, resulting in an expansion of the α-Ga₂O₃ growth window combined with an increased Γ and an improvement in its out-of-plane mosaic spread. It is the first demonstration of a catalytic growth process during the growth of α-Ga₂O₃.
2. Experimental

Samples were grown in a Veeco GEN930 plasma MBE system with standard Ga and In effusion cells. For all samples, the substrates were cleaned in acetone and isopropanol for 10 min and the \( \alpha\)-Ga\(_2\)O\(_3\) samples were grown for 60 min. The growth temperature \((T_G)\) was measured by a thermocouple located within the substrate heater. The Ga flux \((\phi_{Ga})\) and In flux \((\phi_{In})\) were monitored by beam equivalent pressure (BEP) chamber readings. For conventional MBE and MOCATAXY, the O\(_2\) flux \((\phi_O)\) was measured in standard cubic centimeters per min (SCCM) and a radio-frequency plasma power of 250 W was employed during all growths.

To convert the measured values of \(\phi_{Ga}\) (BEP), \(\phi_{In}\) (BEP), and \(\phi_O\) (SCCM) into units of \(\text{nm}^2\text{s}^{-1}\), conversion factors are taken from Ref. 25. Note, when using In-mediated catalysis, the available \(\phi_O\) for Ga to Ga\(_2\)O\(_3\) oxidation is about 2.8 times larger than for Ga oxidation in the absence of In.\(^{16,19}\)

For samples grown by conventional MBE and MOCATAXY, the impact of \(\phi_{In}\) and \(T_G\) is studied. In the case of MOCATAXY growth, the impact of \(\phi_{In}\) is also investigated. All the growth parameters used in this work are collected in Table I. For scanning transmission electron microscopy (STEM), samples were prepared using a Thermo Fisher Helios G4 UX Focused Ion Beam with a final milling step of 5 keV to minimize damage. Carbon and Au–Pd layers were sputtered to reduce charging during sample preparation. Carbon and platinum protective layers were also deposited to minimize ion-beam damage. STEM measurements were taken with an aberration-corrected Thermo Fisher Spectra 300 CFEG operated at 300 keV.

3. Results and discussion

Figure 1 shows the growth-rate-diagram of \(\alpha\)-Ga\(_2\)O\(_3\)\((10\bar{1}0)\) grown on \(\alpha\)-Al\(_2\)O\(_3\)\((10\bar{1}0)\) by conventional MBE (the gray shaded area) and MOCATAXY (the purple shaded area). For conventionally grown samples two distinct growth regimes are observed: (i) the O-rich regime where O adsorbates are in excess over Ga adsorbates (i.e. the Ga flux limited regime), and (ii) the \(\Gamma\)-plateau regime (i.e. the Ga\(_2\)O desorption limited regime). The O-rich regime is characterized by an increasing \(\Gamma\) with increasing \(\phi_{Ga}\), whereas the plateau regime is characterized by a constant \(\Gamma\), being independent of \(\phi_{Ga}\). Within this regime, however, \(\Gamma\) may decrease with increasing \(T_G\) (see inset in Fig. 1) as the desorption of the volatile suboxide Ga\(_2\)O becomes thermally more active.\(^{26}\) The data in the inset of Fig. 1 plots \(\Gamma\) as a function of \(T_G\) for (i) \(\alpha\)-Ga\(_2\)O\(_3\) grown on the O-rich regime and (ii) \(\alpha\)-Ga\(_2\)O\(_3\) grown in the \(\Gamma\)-plateau regime.

To expand the accessible growth window of \(\alpha\)-Ga\(_2\)O\(_3\) to higher \(\phi_{Ga}\) and to higher \(T_G\), combined with increased \(\Gamma\) and improved crystalline quality, In-mediated catalysis was employed in the formation of \(\alpha\)-Ga\(_2\)O\(_3\).\(^{19}\) The red stars in Fig. 1 show the resulting \(\Gamma\) as a function of \(\phi_{Ga}\) at constant \(T_G\). The gray shaded and purple shaded areas in Fig. 1 depict model-based descriptions of \(\Gamma\) for \(\alpha\)-Ga\(_2\)O\(_3\) grown by conventional MBE and MOCATAXY, respectively. The maximum \(\Gamma\) obtained for each growth technique is \(\Gamma \approx 1.5 \text{ nm min}^{-1}\) and \(\Gamma \approx 3.3 \text{ nm min}^{-1}\), respectively. Using MOCATAXY, a more than 2-times increase in \(\Gamma\) for \(\alpha\)-Ga\(_2\)O\(_3\) at given growth conditions, as well as a shift far into the desorption-controlled regime (i.e. far into the Ga-rich flux regime) is observed. This direct comparison between the two growth types clearly shows the expanded growth window made possible with MOCATAXY, for example, enabling \(\Gamma \approx 1.8 \text{ nm min}^{-1}\) for \(\alpha\)-Ga\(_2\)O\(_3\) at \(\phi_{Ga} = 5.5 \text{ nm}^2\text{s}^{-1}\). In contrast, at these growth conditions, no growth of \(\alpha\)-Ga\(_2\)O\(_3\) is obtained by conventional MBE. The catalytic effect on \(\Gamma\) of \(\alpha\)-Ga\(_2\)O\(_3\) is modeled as a function of \(\phi_{O}\) within the supplemental section.\(^{27}\) We note that the depicted models use arbitrary kinetic parameters, based on kinetic parameters extracted for the growth of \(\beta\)-Ga\(_2\)O\(_3\).\(^{28}\)

Table I. Collected growth parameters used in this work, values of \(\phi_{Ga}\), \(\phi_{In}\), \(\phi_O\), and \(T_G\) for samples grown by conventional MBE and MOCATAXY are listed. The conversion for \(\phi_{Ga}\) and \(\phi_{In}\) from BEP to \(\text{nm min}^{-1}\) to \(\text{nm}^2\text{s}^{-1}\) are \(\phi_{Ga} = 2.5 \times 10^{-10} \text{Torr} \div 1.1 \text{ nm min}^{-1} = 1 \text{ nm}^2\text{s}^{-1}\) and \(\phi_{In} = 1.1 \times 10^{-10} \text{Torr} \div 6 \text{ nm}^2\text{s}^{-1}\), respectively.

<table>
<thead>
<tr>
<th>Growth parameters</th>
<th>Conventional MBE</th>
<th>MOCATAXY</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\phi_{Ga}) (\text{nm}^2\text{s}^{-1})</td>
<td>0.8–2.0</td>
<td>1.1–5.5</td>
</tr>
<tr>
<td>(\phi_{In}) (\text{nm}^2\text{s}^{-1})</td>
<td>0</td>
<td>2.6–2.8</td>
</tr>
<tr>
<td>(\phi_{O}) (SCCM)</td>
<td>1.4</td>
<td>0.7–1.0</td>
</tr>
<tr>
<td>(\phi_{O}) (\text{nm}^2\text{s}^{-1})</td>
<td>2.2</td>
<td>3.2–4.6</td>
</tr>
<tr>
<td>(T_G) (°C)</td>
<td>640–800</td>
<td>680</td>
</tr>
</tbody>
</table>
respective growth surface, facilitating the formation of the final Ga$_2$O$_3$ compound at much higher $\phi_{\text{Ga}}$ and $T_G$, which enables excellent crystal quality.\textsuperscript{16,19} We further note that the same factor of 2.8 was needed for modeling the MOCATAXY growth of $\beta$-Ga$_2$O$_3$ on different substrates and different surface orientations.\textsuperscript{16,19} We note, however, that for a quantitative extraction of all kinetic growth parameters more $\Gamma$-studies of $\alpha$-Ga$_2$O$_3$ are needed and are beyond the scope of this work. Nevertheless, the models help validate the $\Gamma$-data and provide insight into the growth regimes and growth mechanisms of $\alpha$-Ga$_2$O$_3$. For example, once $\phi_{\text{Ga}}$ exceeds the active O flux, i.e. $\phi_{\text{Ga}} > \phi_{\text{O}}$, the growth will enter the Ga-rich regime and $\Gamma$ will start to decrease, as shown by the gray shaded area in Fig. 1. Thus, this is the first direct indication that the growth of $\alpha$-Ga$_2$O$_3$ is limited by the formation and subsequent desorption of Ga$_2$O$_3$ like what is observed for $\beta$-Ga$_2$O$_3$ grown by conventional MBE.\textsuperscript{28}

Figure 2 directly compares the impact of both MBE growth techniques on the structural quality of the epitaxially grown films. In Fig. 2 (a), 2θ-ω XRD scans of two selected $\alpha$-Ga$_2$O$_3$ films are shown, one grown by conventional MBE (depicted as the blue trace) and one grown by MOCATAXY (depicted as the red trace). The reflections of the films coincide with the $\alpha$-Ga$_2$O$_3$ 3030 peak. This, along with the absence of other diffraction peaks, indicates phase-pure $\alpha$-Ga$_2$O$_3$(10 1 0) with In incorporation of <1% in the $\alpha$-Ga$_2$O$_3$ layers, similar to what is observed for $\beta$-(Al,Ga)$_2$O$_3$ grown by MOCATAXY.\textsuperscript{18} Figures 2(b) and 2(c) plot transverse scans (rocking curves) for the conventional MBE and MOCATAXY grown $\alpha$-Ga$_2$O$_3$ samples as plotted in Fig. 2(a). The rocking curves are measured across the symmetric 3030 peak. The full width at half maxima (FWHM) of $\omega$ quantifies the out-of-plane mosaic spread of the $\alpha$-Ga$_2$O$_3$ film. For conventionally grown films the out-of-plane crystal distribution is $\Delta\omega \approx 0.55^\circ$ and for MOCATAXY grown films it is $\Delta\omega \approx 0.45^\circ$. The film thicknesses $d$ of the conventionally and MOCATAXY grown samples are $d = 73$ nm and $d = 127$ nm, respectively. Jinno et al. reported that $\alpha$-Ga$_2$O$_3$ films are fully relaxed for $d > 60$ nm.\textsuperscript{5} Since lattice mismatch and relaxation are not impacted by MOCATAXY, it is noteworthy that despite the MOCATAXY film being thicker, $\Delta\omega$ is substantially smaller compared to what is obtained by conventional growth. The same MOCATAXY grown sample shown here is studied by STEM in Fig. 4.

Surface morphologies and root mean square roughnesses ($R_q$) are measured by AFM and depicted in Figs. 2(d) and 2(e). The best surface roughness for conventionally grown $\alpha$-Ga$_2$O$_3$ with $d = 66$ nm is $R_q = 0.64$ nm, while the smoothest one for MOCATAXY grown samples with $d \sim 270$ nm has an $R_q = 0.94$ nm. The larger surface roughness for the MOCATAXY grown sample is likely due to faceting on the top surface of the $\alpha$-Ga$_2$O$_3$ thin film [see Fig. 4(a)]. We speculate that In does not only act as a catalyst but also acts as a surface active agent (surfactant) for the growth $\alpha$-Ga$_2$O$_3$ thin films. It is widely understood that In can act as a surfactant for the epitaxial growth of GaN-based films,\textsuperscript{20} and has also been observed during the growth of $\beta$-Ga$_2$O$_3$\textsuperscript{21} and $\beta$-(Al,Ga)$_2$O$_3$.\textsuperscript{18} Depending on the growth conditions and growth surface, which can affect the surface diffusion kinetics, surface chemical potentials, and the assessed growth mode, the suppression of faceting may be accomplished through the use of optimized conditions, while using In as a surfactant, enabling a modification in the surface free energies of the growing $\alpha$-Ga$_2$O$_3$ thin film and a change in its growth mode.\textsuperscript{18,21,30,31} However, surfactant-induced morphological phase-transitions from two-dimensional (2D) layer growth to three-dimensional (3D) island growth have also been observed during MBE growth.\textsuperscript{52} We believe that a similar effect occurs for the $\alpha$-Ga$_2$O$_3$ surfaces studied here when In may act as an (anti)surfactant during the growth of these films. Note, we have not fully explored all growth regimes made accessible through MOCATAXY in this study. Further studies may lead to additional improvements in the crystalline quality and surface morphologies of the $\alpha$-Ga$_2$O$_3$ thin films.

In Figs. 3(a) and 3(b), the impact of $\phi_{\text{Ga}}$ and $T_G$, respectively, on $\Delta\omega$ for samples grown by conventional MBE in the O-rich regime (blue squares) and in the $\Gamma$-plateau regime (green circles), as well as for samples grown by
(Color online) HAADF-STEM images show an overview of an α-Ga₂O₃/(0110) film grown on α-Al₂O₃/(0110). (a) The epitaxial film shows increased contrast due to misfit dislocations at the film/substrate interface. Threading dislocation propagate through the film and terminating at the intersection of its surface periodic faceting. (b) Enlarged image of the film/substrate interface (i.e. the α-Al₂O₃–α-Ga₂O₃ interface) is shown. Burger circuits are drawn around the edge dislocations. (c) Fast Fourier transform (FFT) of the interface region is shown. Diffraction peak separation at (2024) and (0110) indicate strain relaxation of the α-Ga₂O₃/(0110) on α-Al₂O₃/(0110).
function fitted to the Al intensity line scan profile (see S-Fig. 2 Ref. 27).

A fast Fourier transform (FFT), of the interface region shown in Fig. 4(b), is displayed in Fig. 4(c). A thin film completely strained to the substrate will show a singular diffraction peak. However, when the film relaxes its interplanar spacing $d_{\text{inl}}$ changes, resulting in an additional peak, shifted from the substrate peak. However, shifted peaks in the in-plane direction are not visible because the $\alpha$-Ga$_2$O$_3$ (0006) reflection peak is approximately 10x weaker than in $\alpha$-Al$_2$O$_3$. The strain relaxation is observed in the 202 and 1011 diffraction peaks of $\alpha$-Ga$_2$O$_3$. The strain relaxation is accomplished by the formation of edge dislocations at the interface, where the 2024 peak is correlated to the yellow Burgers circuit and the 1011 peak to the cyan Burgers circuit. In addition, no phase separation or secondary phases were observed by STEM within the $\alpha$-Ga$_2$O$_3$ film grown by MOCATAXY. However, a bi-layer structure from overlapping $\alpha$-Ga$_2$O$_3$ grains when viewed in projection is observed with a slip along the [1022] direction (see S-Fig. 3 Ref. 27). The presence of this bi-layer structure indicates that the film is not single-crystalline. The bi-layer structure was confirmed using an ab initio TEM (abTEM) simulation (3) which produced a matching HAADF image from the crystallographic information framework.

This TEM investigation of MOCATAXY grown $\alpha$-Ga$_2$O$_3$ shows comparable crystal quality to what is measured for conventional MBE (29) with regards to edge dislocation density and phase purity. We note that the difference in projection direction may have prevented imaging of the bi-layer structure in this previous report. No faceting of $\alpha$-Ga$_2$O$_3$ was observed by conventional MBE when grown on $m$-plane $\alpha$-Al$_2$O$_3$.  

4. Conclusion

Phase-pure $\alpha$-Ga$_2$O$_3$(1010) on $\alpha$-Al$_2$O$_3$(1010) was grown using conventional MBE and MOCATAXY with thickness up to $d = 262$ nm. We mapped out the $\Gamma$-dependence on $\phi_{\text{Ga}}$ and $T_G$ and its impact on the crystalline quality and surface morphologies. We identified and explored previously inaccessible growth regimes by MOCATAXY, and showed that it vastly extends the growth regime and improves the out-of-plane mosaic spread of the grown $\alpha$-Ga$_2$O$_3$ films. Using In-mediated catalysis, we observe faceting on top of the $\alpha$-Ga$_2$O$_3$(1010) layers. This study confirms that this new MBE growth mode can be applied to the growth of $\alpha$-Ga$_2$O$_3$ and is not limited to the growth of the $\beta$-Ga$_2$O$_3$ and $\beta$-(Al,Ga)$_2$O$_3$ polymorphs. We emphasize more studies are needed to determine the kinetic parameters that form $\alpha$-Ga$_2$O$_3$ during conventional MBE and MOCATAXY growth, as well as to further improve the quality of the grown $\alpha$-Ga$_2$O$_3/\alpha$-Al$_2$O$_3$ heterostructures, and to understand the mechanisms leading to the surface faceting of $\alpha$-Ga$_2$O$_3$.

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27) See Supplemental Material for a model of Γ as a function of f₀ at T₀ = 680 °C (S-Fig. 1) as well as images obtained by STEM (S-Figs. 2 and 3) and an included crystallographic model.


