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Reaction kinetics and growth window for plasma-assisted molecular beam epitaxy of Ga$_2$O$_3$: Incorporation of Ga vs. Ga$_2$O desorption

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A detailed study of the reaction kinetics of the plasma-assisted molecular beam epitaxy (MBE) growth of the n-type semiconducting oxide Ga$_2$O$_3$ is presented. The growth rate as a function of gallium flux is measured in situ by laser reflectometry at different growth temperatures ($T_G$) and gallium-to-oxygen ratios ($r_{Ga}$). The flux of the suboxide Ga$_2$O desorbed off the growth surface is identified in situ by line-of-sight quadrupole mass spectrometry. The measurements reveal the influence of $T_G$ and $r_{Ga}$ on the competing formation of Ga$_2$O$_3$ and desorption of Ga$_2$O resulting in three different growth regimes: (i) Ga transport limited, (ii) Ga$_2$O desorption limited, and (iii) O transport limited. As a result, we present a growth diagram of gallium oxide. This diagram illustrates the regimes of complete, partial, and no Ga$_2$O and/or Ga desorption. The O-rich regime was identified by measuring the growth rate as described below. Growth rate with increasing Ga flux has also been observed previously by Tsai et al.\textsuperscript{13} In contrast, Oshima et al.\textsuperscript{11} and Okumura et al.\textsuperscript{10} have reported that the growth rate stays constant with increasing $\Phi_{Ga}$ in the Ga-rich regime. In addition to its dependence on $\Phi_{Ga}$, Sasaki et al.\textsuperscript{12} and Okumura et al.\textsuperscript{10} have shown the growth temperature ($T_G$) to influence the growth rate as well.

In this letter, we present a detailed, systematic study of the reaction kinetics involved in the MBE growth of Ga$_2$O$_3$. We show that the growth rate is governed by the competition between Ga$_2$O$_3$ accumulation and Ga$_2$O desorption as a function of $T_G$, $\Phi_{Ga}$, and $\Phi_O$. Based on this data, we develop a growth diagram that describes the growth window and different regimes of Ga incorporation as a function of both $T_G$ and the Ga-to-O ratio ($r_{Ga} = \Phi_{Ga}/\Phi_O$). This diagram may guide the optimization of MBE growth conditions for the further improvement of Ga$_2$O$_3$ structures.

Textured, nonpolycrystalline $\beta$-Ga$_2$O$_3$(201) with rotational domains was grown on c-plane sapphire ($\text{Al}_2\text{O}_3(0001)$) in a custom made MBE system. Quarters of 2-inch diameter, single-side polished, c-plane sapphire wafers were used as the substrates for this study. The rough backside of the substrate was sputter-coated with titanium to improve substrate heating. During growth, the substrate temperature was measured with a pyrometer. A standard shuttered hot-lip effusion cell was used to evaporate liquid Ga (7N purity). A radio frequency plasma source with a mass flow controller supplied activated oxygen from the research-grade O$_2$ gas (6N purity). The beam equivalent pressure (BEP)—which is proportional to the particle flux—was measured by a nude filament ion gauge positioned at the substrate location, and then removed prior to growth. The radio frequency power of the plasma source was maintained at 300 W throughout Ga$_2$O$_3$ growth.

The Ga flux was calibrated by measuring the growth rate of the Ga$_2$O$_3$ layer in the O-rich regime and low $T_G$ (i.e., no Ga$_2$O and/or Ga desorption). The O-rich regime was identified by measuring the growth rate as described below. With this calibration, we converted the measured BEPs into the equivalent Ga$_2$O$_3$ growth rates that are used throughout.

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this study. The Ga flux ranged from $\Phi_{\text{Ga}} = 1.5 \times 10^{-7}$ Torr $\approx 0.4$ A/s to $15 \times 10^{-7}$ Torr $\approx 4$ A/s. With O mass flows of 1 and 3, standard cubic centimeters per minute (SCCM), two different O fluxes of $\Phi_{\text{O}} = 1 \times 10^{-5}$ Torr $\approx 1.7$ A/s and $\Phi_{\text{O}} = 3 \times 10^{-5}$ Torr $\approx 5.1$ A/s, respectively, were used. Their calibration in A/s was made by the growth rates at stoichiometric flux conditions. With these calibrations, we define our Ga-to-O ratio as $r_{\text{Ga}} = \Phi_{\text{Ga}} / \Phi_{\text{O}}$. It is equal to 1 at the stoichiometric flux condition.

All growth rates presented in this letter were measured by laser reflectometry. Here, a laser with a wavelength of 650 nm was used. With an incidence angle between the laser and the growth surface of 30°, one oscillation period corresponded to a change of layer thickness by 180 nm. The suboxide ($\text{Ga}_2\text{O}_3$) flux desorbing off the growth surface ($\Phi_{\text{Ga}_2\text{O}_3}$) was also measured by a line-of-sight quadrupole mass spectrometer (QMS), which allowed the mass of the desorbing species to be identified. The QMS signal was converted into an equivalent growth rate by scaling it to match the supplied Ga flux under conditions of complete suboxide formation (with an appropriate O flux). The crystallinity of the oxide films was verified by a spotty reflection high energy electron diffraction (RHEED) pattern during growth (corresponding to transmission diffraction of the electron beam through the apex of the faceted film surface) and by post-growth X-ray diffraction $0\ldots 20$ wide-range scans (not shown).

The growth rate ($\Gamma$) of $\text{Ga}_2\text{O}_3$ and $\Phi_{\text{Ga}_2\text{O}_3}$ as functions of $\Phi_{\text{Ga}}$ at substrate temperatures of $T_G = 500^\circ\text{C}$ and 660°C are depicted in Fig. 1. At the low growth temperature ($T_G = 500^\circ\text{C}$) in the O-rich regime, i.e., at $r_{\text{Ga}} \leq 1$, the growth rate increased linearly with $\Phi_{\text{Ga}}$. Since no desorbed signal could be detected by QMS, the entire Ga is fully incorporated into the film (unity sticking coefficient in this case). After reaching a maximum at $r_{\text{Ga}} = 1$, growth enters the Ga-rich regime and $\Gamma$ shows a linear decrease due to suboxide formation (as described in Ref. 14). The flux of desorbing suboxide could then be detected by QMS and is depicted as black circles in the plot in Fig. 1.

Identical fluxes result in a different evolution of the growth rate when a higher substrate temperature of 660°C as shown by the open, blue symbols in Fig. 1 is used. The maximum growth rate is decreased in comparison to growth at $T_G = 500^\circ\text{C}$. Additionally, $\Gamma$ forms a plateau in the O-rich regime, which resembles the $\Gamma$ evolution reported in Refs. 11 and 10 for the MBE growth of $\text{Ga}_2\text{O}_3$ on $\text{Al}_2\text{O}_3$(0001) and $\text{Ga}_2\text{O}_3$(010), respectively. QMS measurements reveal that this plateau arises due to $\text{Ga}_2\text{O}$ formation. The reactions for the layer growth and suboxide formation are

$$2\text{Ga}(g) + 3\text{O}(g) \rightarrow \text{Ga}_2\text{O}_3(s) ,$$

and

$$2\text{Ga}(g) + \text{O}(g) \rightarrow \text{Ga}_2\text{O}(g).$$

The labels $g$ and $s$ denote the gas and solid phase, respectively. The open and filled diamonds in Fig. 1 give the sum of $\Gamma + \Phi_{\text{Ga}_2\text{O}_3}$ for both growth temperatures. This sum is equal to $\Phi_{\text{Ga}}$, proving that the difference between Ga flux and $\text{Ga}_2\text{O}_3$ growth rate is solely due to suboxide desorption. Note that no Ga desorption was detected, indicating it is not responsible for the plateau in the growth rate. In a separate experiment, we observed Ga desorption instead of $\text{Ga}_2\text{O}_3$ desorption when Ga and O fluxes of 1.6 and 1.7 A/s, respectively, were supplied to a blank $\text{Al}_2\text{O}_3$(0001) surface at similarly high temperatures between 900 and 550°C. The different Ga species desorbing from the $\text{Al}_2\text{O}_3$ and $\text{Ga}_2\text{O}_3$ surfaces suggest that the $\text{Ga}_2\text{O}_3$ surface is required as a catalyst for $\text{Ga}_2\text{O}$ formation.

It is significant that a higher O flux resulted in a correspondingly higher maximum $\Gamma$, as shown by the red star in Fig. 1. This suggests that the growth rate may be normalized by the flux of active O, i.e., $r_T = \Gamma / \Phi_{\text{O}}$. In Fig. 2, the normalized growth rate ($r_T$) is plotted as a function of $r_{\text{Ga}}$ for four different growth temperatures. It shows the same evolution as in Fig. 1. For $T_G > 500^\circ\text{C}$, a plateau in the O-rich regime and a decrease of $r_T$ are presented. Additionally, we observe that in the O-rich regime, the maximum normalized growth rate $\beta$ (position of the plateau in Fig. 2) decreases with increasing $T_G$. The temperature dependence of $\beta$ is

![FIG. 1. $\text{Ga}_2\text{O}_3$ growth rate ($\Gamma$), $\text{Ga}_2\text{O}$ desorption rate ($\Phi_{\text{Ga}_2\text{O}_3}$), and their sum shown as a function of $\Phi_{\text{Ga}}$ at constant O flux of 1.7 A/s at two different growth temperatures ($T_G$). The lines are guides for the eye. The red star corresponds to the growth rate at a high temperature $T_G = 660^\circ\text{C}$ and a higher O flux of $\Phi_{\text{O}} = 5.1$ A/s.]

![FIG. 2. Growth rates normalized by the O flux ($r_T = \Gamma / \Phi_{\text{O}}$) as a function of the Ga-to-O ratio ($r_{\text{Ga}}$) for four different growth temperatures. The supplied active O flux was 1.7 A/s for $T_G = 500, 600, 660^\circ\text{C}$ and 5.1 A/s for 700°C. The growth rate evolution is parametrized by the maximum growth rate ($\beta$) and the O flux ($\alpha$) that may react with Ga (to form $\text{Ga}_2\text{O}_3$ or $\text{Ga}_2\text{O}$), normalized by the active O flux. Inset: the influence of $T_G$ on $\alpha$ and $\beta$. The lines are guides for the eye.]
depicted in the inset of Fig. 2. Furthermore, the inset shows the fraction of the maximum O flux that is available to react with Ga (to Ga$_2$O$_3$ or Ga$_2$O), denoted by $x$. The value of $x$ is calculated by extending the growth rate evolution from the Ga-rich regime until it intersects the curve in the O-rich regime (see the dotted gray line for $T_G = 600$ °C, for example).

The width of the plateau is determined by the remaining active O atoms that are not incorporated into the Ga$_2$O$_3$ layer, but instead react to form Ga$_2$O. Since only one O atom is needed to form Ga$_2$O—instead of the three needed for Ga$_2$O$_3$—the width of the plateau in $\Gamma$ is $\lambda = 3(\alpha - \beta)$. The plateau at a given $T_G$ covers the range of $r_{Ga}$ from $\beta$ to $\beta + \lambda$. Once all active O atoms are consumed by reactions (1) and (2), growth shifts into the Ga-rich regime. Here, the growth rate decreases due to insufficient O atoms to oxidize the Ga to Ga$_2$O$_3$. Finally, the growth stops at a Ga flux three times the stoichiometric flux, as all available Ga and O are consumed by the formation of Ga$_2$O (i.e., at a Ga-to-O ratio of $r_{Ga} = 3\lambda$).

Now, we give the reactions for three growth regimes, which we define as follows: (i) Ga transport limited O-rich growth with full Ga incorporation (the linear increase of $r_G$ with $r_{Ga}$), (ii) Ga$_2$O desorption limited O-rich growth with partial Ga incorporation (the plateau of $r_G$), (iii) O transport limited Ga-rich growth with partial Ga incorporation (the decrease of $r_G$ with $r_{Ga}$).

For regime (i) (i.e., for $0 \leq r_{Ga} < \beta \leq 1$), the reaction is
\[
r_{Ga} 2Ga(g) + 3O(g) \rightarrow r_{Ga}Ga_2O_3(s) + (3 - r_{Ga})O(g). \tag{3}
\]

The plateau of regime (ii) ($0 < \beta \leq r_{Ga} \leq \beta + \lambda = 3\lambda - 2\beta$) is described by the reaction
\[
r_{Ga} 2Ga(g) + 3O(g) \rightarrow r_{Ga}Ga_2O_3(s) + (r_{Ga} - \beta)Ga_2O(s) + (3 - r_{Ga} + 2\beta)O(g). \tag{4}
\]

The end of the plateau ($r_{Ga} = \beta + \lambda$) corresponds to the stoichiometric growth conditions. For Ga-rich growth in regime (iii) ($\beta + \lambda < r_{Ga} \leq 3\lambda$), the growth rate decreases and
\[
r_{Ga} 2Ga(g) + 3O(g) \rightarrow r_{Ga}Ga_2O_3(s) + (r_{Ga} - \beta)Ga_2O(s) + (r_{Ga} - \beta)Ga_2O(g) + 3(1 - x)O(g). \tag{5}
\]

The coefficient $\gamma$ decreases linearly with increasing $r_{Ga}$, from unity at $r_{Ga} = \beta + \lambda = 3\lambda - 2\beta$ to zero at $r_{Ga} = 3\lambda$, i.e., $\gamma = -(2\beta)^{-1}(r_{Ga} - 3\lambda)$.

Practical information for the MBE growth of Ga$_2$O$_3$ is included in Fig. 3, which depicts the growth rate normalized by the maximum growth rate, $\rho = \Gamma/\Gamma_{max}$, as a function of $T_G$. Here, the temperature evolution of $\rho$ for five different Ga-to-O ratios ranging from 0.18 (O-rich) to 1.65 (Ga-rich) is plotted. For all five data sets, the growth rate decreases with increasing growth temperature. The constant growth rate at low $T_G$ is reflected by reaction (3) for $r_{Ga} \leq 1$ (regime (i)) and reaction (5) for $r_{Ga} > 1$ with $x = \beta = 1$ (regime (iii)). The decreasing growth rate at higher $T_G$ for $r_{Ga} \leq 1$ and $\beta < 1$ is described by the plateau (reaction (4), regime (ii)) and reaction (5) for $r_{Ga} > 1$ and $x < 1$ (regime (iii)). No layer growth occurs at growth temperatures when $\beta = 0$ for $r_{Ga} \leq 1$, and/or $x = 0$ for $r_{Ga} > 1$, and additionally, for $r_{Ga} > 3\lambda$.

The inset in Fig. 3 exemplarily shows the temperature dependence of $\rho$ for $r_{Ga} = 0.90$ at temperatures below 750 °C. Furthermore, the normalized desorption rate $\Phi_{Ga_2O}/\Gamma_{max}$ is plotted in the same temperature range. Their sum equals unity for all growth temperatures, again confirming a reduced growth rate at higher $T_G$ due to volatile Ga$_2$O formation catalyzed by the Ga$_2$O$_3$ layer.

By combining the results in Figs. 1–3, we conclude that a higher $r_{Ga}$ and $T_G$ promote the formation and desorption of Ga$_2$O, but that they can also result in a stabilized Ga$_2$O$_3$ growth rate at sufficiently high $T_G$. The detailed regimes (i)–(iii) can describe all growth rate scenarios in this study (Figs. 1–3) and those reported in the literature for homo- and heteroepitaxial growth.$^{10,14,24}$

By merging all data shown in Figs. 1–3, we derive a Ga$_2$O$_3$ growth diagram (GD) using controllable experimental parameters $\Phi_{Ga_2O}$, $\Phi_O$, and $T_G$, as shown in Fig. 4. It depicts the three growth regimes (i)–(iii) as explained above. The growth window is formed by the union of these three regimes.
Note that in Fig. 4, in addition to regime (iii) where \( x = 1 \), in the regime (iii), the oxygen desorption \( x < 1 \) is taken into account. Here, the oxygen density on the growth surface is lower than in (iii) \( (x < 1) \), and therefore, the maximum growth rate at a given \( r_{Ga} \) in the Ga-rich regime is decreased. Both scenarios are described by reaction (5). In addition, this diagram shows the no growth regime (iv), which includes all possible no growth scenarios: full Ga adsorption, full Ga desorption, and layer decomposition by etching as described in Ref. 14.

This GD may be qualitatively applied for other Ga\(_2\)O\(_3\) surfaces. The difference in adhesion energies of the Ga adatoms at the various Ga\(_2\)O\(_3\) surfaces would result in a growth temperature shift in the GD. The shape of the growth diagram remains the same due to the preserving stoichiometry (i.e., two Ga atoms and three O atoms).

In summary, we have studied the growth rate evolution of the heteroepitaxial growth of Ga\(_2\)O\(_3\)(101) on Al\(_2\)O\(_3\)(0001) by plasma-assisted molecular beam epitaxy, and the competing desorption of Ga\(_2\)O. The growth rate and desorbed flux were measured in situ by laser reflectometry and line-of-sight quadrupole mass spectroscopy, respectively. The Ga flux, Ga-to-O ratio, and growth temperature were systematically varied in order to understand the reaction kinetics of the Ga\(_2\)O\(_3\) growth. By combining our results, we developed a growth diagram with three distinctive growth regimes: (i) complete Ga incorporation (i.e., Ga transport limited growth regime (O-rich)), (ii) plateau of growth rate at increasing Ga flux (i.e., Ga\(_2\)O desorption limited growth regime (O-rich)), (iii) a decreasing growth rate at increasing Ga flux (i.e., O-transport-limited growth regime (Ga-rich)). In all the cases, the difference between the provided Ga flux and the growth rate is related to the formation and desorption of the volatile Ga\(_2\)O, which is catalyzed by the Ga\(_2\)O\(_3\) surface. No Ga desorption was observed at the investigated growth temperatures. Growth rates lower than the Ga flux were either caused by the growth in the Ga-rich regime or by a higher growth temperature. These findings are likely applicable to ozone MBE. In addition, we speculate that Ga\(_2\)O desorption may also play a role in the growth of Ga\(_2\)O\(_3\) by metal-organic chemical vapor deposition.

Our results give guidance for the improvement of growth rates, crystal quality, and electronic structure during Ga\(_2\)O\(_3\) growth. For example, higher growth rates on the Ga\(_2\)O\(_3\)(100) surface may be realized by lower growth temperatures that suppress Ga\(_2\)O desorption. In order to improve crystal quality, high-temperature growth is needed, and our results reveal that an increased O flux helps maintain reasonable growth rates in this case. In the plateau regime, the growth rate is Ga flux-independent when the growth temperature is stable. Finally, growth in this regime and more in the Ga-rich regime may suppress the formation of Ga vacancies, which are responsible for the compensation of electrical donors.

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