Adsorption-Controlled Growth of Ga₃O₅ by Suboxide Molecular-Beam Epitaxy

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This paper introduces a growth method—suboxide molecular-beam epitaxy (S-MBE)—which enables the growth of Ga₃O₅ and related materials at growth rates exceeding 1 μm hr⁻¹ with excellent crystallinity in an adsorption-controlled regime. Using a Ga + Ga₃O₅ mixture with an oxygen mole fraction of x(O) = 0.4 as an MBE source, we overcome kinetic limits that had previously hampered the adsorption-controlled growth of Ga₃O₅ by MBE. We present growth rates up to 1.6 μm hr⁻¹ for Ga₃O₅/Al₂O₃ heterostructures with unprecedented crystalline quality and also at unparalleled low growth temperature for this level of perfection. We combine thermodynamic knowledge of how to create molecular-beams of targeted suboxides with a kinetic model developed for the S-MBE of III-VI compounds to identify appropriate growth conditions. Using S-MBE we demonstrate the growth of phase-pure, smooth, and high-purity homoepitaxial Ga₃O₅ films that are thicker than 4 μm. With the high growth rate of S-MBE we anticipate a significant improvement to vertical Ga₃O₅-based devices. We describe and demonstrate how this growth method can be applied to a wide-range of oxides. S-MBE rivals leading synthesis methods currently used for the production of Ga₃O₅-based devices.

I. INTRODUCTION

Molecular-beam epitaxy (MBE) involves the growth of epitaxial thin films from molecular-beams. In ‘conventional’ MBE the molecular-beams consist of elements. An example is the Ga (g) species that evaporate from a heated crucible containing Ga (l) or the As₄ (g) species that evaporate from a heated crucible containing As (s), where g, l, and s denote gaseous, liquid, and solid, respectively. In gas-source MBE the species in the molecular-beams originate from gases that are plumbed into the MBE from individual gas cylinders, for example, arsine or phosphine. In metal-organic MBE the species in the molecular-beams are metal-organic molecules like trimethylgallium or trimethylaluminum.¹ ‘Suboxide MBE’ refers to an MBE growth process utilizing molecular-beams of suboxides like Ga₂O (g) or In₂O (g). We have applied this method to the growth of Ga₃O₅ thin films and find that it can produce epitaxial Ga₃O₅ films with far greater perfection and at much higher growth rates than currently demonstrated by other MBE methods for the growth of this material.

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A. ‘Conventional’ MBE of Ga₂O₃ and related materials

Gallium-sesquioxide (Ga₂O₃) synthesized in its different polymorphs [i.e., α-Ga₂O₃ (rhombohedral), β-Ga₂O₃ (monoclinic), γ-Ga₂O₃ (cubic spinel), ε-Ga₂O₃ (hexagonal), and κ-Ga₂O₃ (orthorhombic)], is an emerging semiconductor possessing promising features for unprecedented high-power electronics. This is due to its large band gap (~ 5 eV)²,³ and very high breakdown field (up to 8 MV cm⁻¹).⁴ The band gap of Ga₂O₃ may be widened by alloying Ga₂O₃ with Al₂O₃ to form (AlₓGa₁₋ₓ)₂O₃.³ The synthesis of (AlₓGa₁₋ₓ)₂O₃/Ga₂O₃ heterostructures with high Al content x is desired for high-power transistors with large band gap offsets.⁵⁻⁶

It is known that the ‘conventional’ MBE of Ga₂O₃—i.e., when supplying monatomic Ga and active O species during growth—is strongly limited by the formation and subsequent desorption of its volatile suboxide Ga₂O.⁷⁻¹¹ In the adsorption-controlled regime (i.e., grown with an excess of Ga), its growth rate strongly decreases with increasing Ga flux, φGa, because not enough oxygen is available to oxidize the physisorbed Ga₂O to Ga₂O₃ (s) and the Ga₂O desorbs from the hot substrate. At sufficiently high φGa, film growth stops, and even goes negative (i.e., the Ga₂O₃ film is etched).⁸ This effect is enhanced as the growth temperature, Tₕ, increases due to the thermally activated desorption of Ga₂O from the growth surface. The enhanced, Tₕ-induced Ga₂O desorption leads to a decreasing growth rate even in the O-rich regime, resulting in a short growth rate plateau (the value of which is far below the available active O flux¹²), followed by an even further decreasing growth rate in the adsorption-controlled regime.⁹¹²¹³ These effects, i.e., the O-deficiency induced and thermally activated desorption of suboxides,⁹¹¹³¹³ are detrimental for the growth of III-VI (e.g., Ga₂O₃) and IV-VI materials in the adsorption-controlled regime.

Nevertheless, the MBE of thin films in the adsorption-controlled growth regime is often desired for high crystal perfection,¹⁴⁻¹⁶ smooth surface morphology,¹⁷ avoiding undesired oxidation states,¹⁸¹⁹ or suppressing the formation of electrically compensating defects.²⁰²¹

The decreasing growth rate of Ga₂O₃ is microscopically explained by a complex two-step reaction mechanism.¹¹,¹² In the first reaction step, all Ga oxidizes to Ga₂O via the reaction

$$2\text{Ga}(a) + \text{O}(a) \rightarrow \text{Ga}_2\text{O}(a, g),$$  \hspace{1cm} (1)

with adsorbate and gaseous phases denoted as a and g, respectively. The Ga₂O formed may either desorb from the growth surface (in the O-deficient regime or at elevated Tₕ) or be further oxidized to Ga₂O₃ via a second reaction step through the reaction

$$\text{Ga}_2\text{O}(a) + 2\text{O}(a) \rightarrow \text{Ga}_2\text{O}_3(s),$$  \hspace{1cm} (2)

with the solid phase denoted as s.

This two-step reaction mechanism and the resulting Ga₂O desorption defines the growth rate-limiting step for the ‘conventional’ MBE of Ga₂O₃ and related materials.¹¹,¹² This results in a rather narrow growth window associated with low growth rates in the adsorption-controlled regime.⁷⁻⁹,¹¹ A similar growth rate-limiting behavior, based on this two-step reaction mechanism, has also been reported for the growth of other III-VI (e.g., In₂O₃) and IV-VI (e.g., SnO₂) compounds by ‘conventional’ MBE.⁵,¹¹,¹³ This two-step growth process for the growth of III-VI and IV-VI oxides by ‘conventional’ MBE is fundamentally different from the single-step reaction mechanism of, for example, III-V²²⁻²⁴ and II-VI²⁵ compounds. It can be attributed to the different electronic configurations of the compound constituents, resulting in different compound stoichiometries between III-VI and IV-VI compared with III-V and II-VI materials, respectively.

In the growth method introduced in this work, which we call suboxide MBE (S-MBE), we avoid the first reaction step (1) by directly supplying a Ga₂O (g) molecular-beam to the growth front on the substrate surface. Using this approach, we bypass the growth rate-limiting step for ‘conventional’ Ga₂O₃ MBE by removing the O-consuming step to Ga₂O formation that occurs on the substrate in the ‘conventional’ MBE growth of Ga₂O₃.¹¹,¹² A related approach has been used by Ghose et al.²⁶,²⁷ with Ga₂O provided from Ga₂O₃ source material heated to temperatures well in excess of 1600 °C to produce a molecular beam of Ga₂O for the growth of Ga₂O₃ films by MBE.²⁸ Motivated by known vapor pressure data of oxides²⁹ and their mixtures with the respective metals, e.g., Ga + Ga₂O₃,³⁰ as well as the possibility of decomposing Ga₂O₃ by Ga and SnO₂ by Sn under MBE conditions,⁸ Hoffmann et al.³¹ have demonstrated how mixtures of Ga with Ga₂O₃ and Sn with SnO₂ provide MBE-relevant fluxes of Ga₂O and SnO, respectively, at source
temperatures below 1000 °C. This prior work has grown films using suboxide molecular beams by MBE at growth rates < 0.2 μm hr⁻¹.³¹,³²

As we demonstrate, S-MBE enables the synthesis of Ga₂O₃ in the highly adsorption-controlled regime, at growth rates > 1 μm hr⁻¹ with unparalleled crystalline quality for Ga₂O₃/Al₂O₃ heterostructures as well as homoepitaxial Ga₂O₃ at relatively low T_G. The growth rate of S-MBE is competitive with other established growth methods used in semiconductor industry—such as chemical vapor deposition (CVD)³³ or metal-organic CVD (MOCVD)³⁴—and moreover, leads to better structural perfection of the obtained thin films. With this improved perfection we expect an improvement of n-type donor mobilities in Ga₂O₃ thin films doped with Sn, Ge, or Si grown by S-MBE, as well. The relatively low T_G at which it becomes possible to grow high-quality films by S-MBE is a crucial enabler for materials integration where temperatures are limited, e.g., back end of line (BEOL) processes.

Figure 1 illustrates a schematic of how growth rate depends on cation flux during the MBE growth of different types of compounds, where both axes are normalized by the anion flux. Figure 1(a) depicts the observed behavior for III-V compounds, e.g., GaN.²⁴ Figure 1(b) shows the observed behavior for III-VI compounds, e.g., Ga₂O₃, when the group III cation is supplied by a molecular-beam of the group III element (e.g., Ga).⁸ In Fig. 1(c), the anticipated behavior for III-VI compounds is plotted, e.g., Ga₂O₃, when the group III element is supplied by a molecular-beam of a III₂VI₁ subcompound containing the group III constituent (e.g., Ga₂O).¹² The units of the horizontal and vertical axes are chosen to make the crossover occur at values of unity. For the sake of simplicity, henceforth, we only discuss the reaction behavior of GaN and Ga₂O₃ in detail. We emphasize, however, this discussion holds true for the MBE growth of AlN,²² InN,²³ In₂O₃ (Refs. 8,11,13) and other III-VI,¹¹,¹³ and II-VI compounds.²⁵

As drawn in Figs. 1(a)–1(c), the growth rate of GaN and Ga₂O₃ increases linearly with increasing φ_Ga in the N-rich [Fig. 1(a)] and O-rich regimes [Fig. 1(b) and 1(c)], respectively. Here, the incorporation of Ga is limited by the impinging φ_Ga or Ga₂O flux, φ_Ga₂O (i.e., Ga-transport and Ga₂O-transport limited growth regimes).

For GaN MBE [Fig. 1(a)], once the supplied φ_Ga exceeds the flux φ_N of active available N, the growth rate saturates, is independent of the φ_Ga/φ_N ratio, and is limited by φ_N and T_G. The measured plateau in growth rate for GaN MBE in the Ga-rich regime results from its single-step reaction kinetics. Here, Ga reacts directly with activated N via the reaction²⁴

$$\text{Ga (a) + N (a) } \rightarrow \text{GaN (s)}$$

and excess Ga either adsorbs onto or desorbs from the growth surface depending upon φ_N and T_G.
Figure 1(b) depicts the reaction kinetics of Ga$_2$O$_3$ in the Ga-rich regime (O-deficient growth regime) by supplying $\phi_{Ga}$. Here, the growth rate linearly decreases with increasing $\phi_{Ga}$, and the growth eventually stops at $\phi_{Ga} \geq 3\phi_{O}$ (in growth rate units). The fact that desorbing Ga$_2$O removes Ga and O from the growth surface—that cannot contribute to Ga$_2$O$_3$ formation—leads to the decreasing growth rate in the O-deficient growth regime. This behavior is microscopically governed by the two-step reaction process, Eqs. (1) and (2), and is fundamentally different from the single-step reaction kinetics, Eq. (3), governing the MBE of GaN [Fig. 1(a)].

In Fig. 1(c), the anticipated growth kinetics of Ga$_2$O$_3$ while using a Ga$_2$O$_3$ beam is depicted, showing a constant growth rate in the Ga$_2$O$_3$-rich regime (i.e., in an excess of Ga$_2$O). Excess Ga$_2$O (that cannot be oxidized to Ga$_2$O$_3$) either accumulates or desorbs off the growth surface without consuming or removing active O from its adsorbate reservoir—similar to the case presented for GaN in Fig. 1(a). Thus, with S-MBE, one may effectively achieve single-step reaction kinetics for Ga$_2$O$_3$ MBE [reaction (2)], as is the case for the growth of GaN by MBE [reaction (3)].

The synthesis of III-V and II-VI materials with cation flux-independent growth rates in adsorption-controlled growth regimes—originating from their simple single-step reaction kinetics [e.g., reaction (3)]—is beneficial for device-relevant growth rate control and the improvement of their crystal properties. Through the use of S-MBE, we convert the complex two-step reaction kinetics of III-VI [e.g., reactions (1) and (2)] and IV-VI compounds into simple single-step kinetics [e.g., (2)], the same as observed for III-V and II-VI materials. We therefore expect a similar growth behavior during S-MBE, i.e., constant growth rates in the adsorption-controlled regime, which are highly scalable by the provided active O flux. Such a regime should allow III-VI thin films (e.g., Ga$_2$O$_3$) and IV-VI films (e.g., SnO$_2$) to be grown much faster with excellent crystal quality at relatively low $T_G$.

S-MBE utilizes molecular-beams of suboxides and builds upon prior thermodynamic work and thin film growth studies. For example, molecular-beams of the following suboxides have all been used in MBE: Ga$_2$O$_3$, GdO$_2$, LuO$_2$, La$_2$O$_3$, Nd$_2$O$_3$, PrO$_2$, Sc$_2$O$_3$, SnO$_2$, SiO$_2$, GeO$_2$ and YO$_2$. Even before these MBE studies, thin films of the suboxides SiO$_2$, SnO$_2$, and GeO$_2$ had been deposited by thermal evaporation, exploiting the same underlying vapor pressure characteristics that make S-MBE possible. In some of these cases the dominant species in the gas phase were not identified, but subsequent vapor pressure studies and thermodynamic calculations establish that they were suboxides.

What is new about S-MBE is the use of suboxide molecular-beams in a targeted way to achieve epitaxial growth of desired oxides (e.g., Ga$_2$O$_3$) at high growth rates in an adsorption-controlled regime. This enables the benefits of the far simpler (from a growth kinetics, growth control, and growth standpoint) plateau growth regime shown in Fig. 1(c) to be harnessed rather than the growth regime shown in Fig. 1(b) that has posed limits to the growth of Ga$_2$O$_3$ films by ‘conventional’ MBE up to now.

II. DETAILED DESCRIPTION OF S-MBE

The use of a Ga$_2$O$_3$ molecular-beam to grow Ga$_2$O$_3$ (s) thin films by MBE in the O-rich regime (i.e., in an excess of active O) has been demonstrated by placing the stoichiometric solid of the compound Ga$_2$O$_3$ into a crucible and using it as an MBE source. Possible reactions that produce a Ga$_2$O$_3$ molecular-beam by the thermal decomposition of Ga$_2$O$_3$ are:

\[ \text{Ga}_2\text{O}_3 (s) \rightarrow \text{Ga}_2\text{O}(a, g) + \text{O}_2 (a, g) \] (4)

\[ \text{Ga}_2\text{O}_3 (s) \rightarrow \text{Ga}_2\text{O}(a, g) + 2\text{O}(a, g) . \] (5)

One disadvantage of using Ga$_2$O$_3$ (s) as the MBE source is that Ga$_2$O$_3$ does not evaporate congruently. Our thermodynamic calculations indicate that when Ga$_2$O$_3$ (s) is heated to a temperature where the Ga$_2$O$_3$ (g) that it evolves has a vapor pressure of 0.1 Pa (a vapor pressure typical for MBE growth), the Ga$_2$O$_3$ molecular-beam is only 98.0% Ga$_2$O$_3$ molecules. The other 2% of the beam is Ga, O$_2$, and O species.

The other disadvantage of using Ga$_2$O$_3$ (s) as the MBE source is that quite high effusion cell temperatures are required to evolve appreciable $\phi_{\text{Ga}_{2}\text{O}_3}$; temperatures in excess of \( \sim 1600 \) °C, \( \sim 1700 \) °C, or \( \sim 1800 \) °C have been used. At such high effusion cell temperatures, crucible choices become limited and prior researchers have used iridium crucibles. Ga$_2$O$_3$ thin films synthesized utilizing an iridium crucible at an effusion cell temperature of \( \sim 1700 \) °C were limited to growth rates < 0.14 \( \mu \text{m/hr} \), with \( \sim 5 \times 10^{18} \text{ cm}^{-3} \) iridium contamination in the
grown Ga$_2$O$_3$ films. These aspects of Ga$_2$O$_3$ compound sources hamper the synthesis of semiconducting Ga$_2$O$_3$ layers at growth rates exceeding 1 μm hr$^{-1}$ with device-relevant material properties. For comparison, the Ga + Ga$_2$O$_3$ mixture that we describe next and have used to grow Ga$_2$O$_3$ films at growth rates exceeding 1 μm hr$^{-1}$ provides a Ga$_2$O molecular-beam that is 99.98% pure according to our thermodynamic calculations. This is for the same Ga$_2$O vapor pressure of 0.1 Pa, which happens at a source temperature about 600 °C lower for this Ga + Ga$_2$O$_3$ mixture than for pure Ga$_2$O$_3$, enabling us to use crucibles that do not result in iridium-contaminated films.

Years ago as well as more recently, Ga + Ga$_2$O$_3$ mixed sources producing a Ga$_2$O molecular-beam have been studied and suggested as efficient suboxide sources for oxide MBE. Using this mixed source, a Ga$_2$O (g) molecular-beam is produced by the chemical reaction

$$4\text{Ga}(l) + \text{Ga}_2\text{O}_3(s) \rightarrow 3\text{Ga}_2\text{O}(s, g),$$

with the liquid phase denoted as $l$. S-MBE uses the thermodynamic and kinetic properties of Ga+Ga$_2$O$_3$ mixtures favoring reaction (6) under MBE conditions.

For the S-MBE of Ga$_2$O$_3$, we explored Ga-rich and Ga$_2$O$_3$-rich mixtures of Ga + Ga$_2$O$_3$ with stoichiometries

$$5\text{Ga}(l) + \text{Ga}_2\text{O}_3(s) \rightarrow 3\text{Ga}_2\text{O}(g) + \text{Ga}(l),$$

and

$$\frac{5}{2}\text{Ga}(l) + \text{Ga}_2\text{O}_3(s) \rightarrow \frac{15}{8}\text{Ga}_2\text{O}(g) + \frac{3}{8}\text{Ga}_2\text{O}_3(s),$$

respectively. The latter mixture has an oxygen mole fraction of $x(O) = 0.4$ and the properties of this Ga$_2$O$_3$-rich mixture are described below. The corresponding reaction rate constants $\kappa_{\text{Ga-rich}}$ and $\kappa_{\text{Ga}_2\text{O}_3\text{-rich}}$ define the production rate of Ga$_2$O (g) at a given temperature $T_{\text{mix}}$ of the Ga + Ga$_2$O$_3$ mixture.

The flux of Ga$_2$O (g) in the molecular-beam emanating from the mixed Ga + Ga$_2$O$_3$ sources is significantly larger than that of Ga (g) emanating from the same source. This is also true under MBE conditions. The resulting high ratio of Ga$_2$O/Ga $\gg 1$ provides a more controllable and cleaner growth environment than accessible by decomposing a stoichiometric Ga$_2$O$_3$ source, which produces molecular-beam ratios of Ga$_2$O/Ga, Ga$_2$O/O$_2$, and Ga$_2$O/O. Hence, the growth surface of the substrate during film growth using S-MBE is exposed to controllable and independently supplied molecular-beams of Ga$_2$O and reactive O adsorbates.

We have experienced that a Ga$_2$O$_3$-rich mixture enables higher $T_{\text{mix}}$ and higher, stable Ga$_2$O (g) molecular-beams than a Ga-rich mixture. This enables S-MBE to achieve higher growth rates. This experimental observation is confirmed by our thermodynamic calculations of the phase diagram of Ga (l) + Ga$_2$O$_3$ (s) mixtures, which we describe next.

The calculated Ga–O phase diagram in Fig. 2 shows that at $T_{\text{mix}}$ below the three-phase equilibrium of gas + Ga(l) + Ga$_2$O$_3$(s) around 907 K, a two-phase region of Ga(l) + Ga$_2$O$_3$(s) forms, which does not change with respect to temperature or oxygen mole fraction between 0 and 0.6. Note that all thermodynamic calculations in the present work were performed using the Scientific Group Thermodata Europe (SGTE) substance database (SSUB5) within the Thermo-Calc software. For $T_{\text{mix}} > 907$ K, the two-phase regions are gas + Ga (l) when the mole fraction of oxygen is below 1/3, corresponding to what we refer to as Ga-rich mixtures, and gas + Ga$_2$O$_3$(s) when the mole fraction of oxygen is between 1/3 and 0.6, which we refer to as Ga$_2$O$_3$-rich mixtures. These two-phase regions become a single gas-phase region at $T_{\text{mix}}$ of (907 − 1189) K for Ga-rich mixtures and at (907 − 1594) K for Ga$_2$O$_3$-rich mixtures, respectively. All of these phase transition temperatures decrease with decreasing pressure as shown on the pressure versus temperature ($P − T$) phase diagrams in Fig. 3.
FIG. 3. Ga–O pressure versus temperature ($P - T$) phase diagrams at fixed mole fractions of oxygen of $x(O) = 0.2$ [panel (a)] and $x(O) = 0.4$ [panel (b)]. These oxygen mole fractions are chosen to illustrate the difference between (a) Ga-rich mixtures and (b) Ga$_2$O$_3$-rich mixtures.

FIG. 4. Gibbs energies of the gas, Ga($l$), Ga$_2$O$_3$(s) phases at temperature $T = 1100$ K and total pressure $P = 0.1$ Pa. The brown dotted line shows the activity (or partial pressure) of oxygen when $0 < x(O) < 0.33$. In this range the gas phase is in equilibrium with Ga($l$) and the activity of oxygen is $6.4 \times 10^{-24}$ Pa. The green dashed line corresponds to the case where $0.33 < x(O) < 0.6$. In this range the gas phase is in equilibrium with Ga$_2$O$_3$(s) and the activity of oxygen is $P_{O_2} = 1.8 \times 10^{-16}$ Pa. This difference in the partial pressure of O$_2$ between the two regimes is huge and shows the advantage of growing Ga$_2$O$_3$ films from Ga$_2$O$_3$-rich (Ga + Ga$_2$O$_3$) mixtures.

To contrast the difference between Ga-rich versus Ga$_2$O$_3$-rich mixtures we have performed additional thermodynamic calculations at oxygen mole fractions of $x(O) = 0.2$ and $x(O) = 0.4$. These two chosen oxygen mole fractions correspond to Ga-rich and Ga$_2$O$_3$-rich mixtures, respectively. In Figs. 3(a) and 3(b) the solid (red) lines denote the three-phase equilibrium between gas + Ga ($l$) + Ga$_2$O$_3$ (s); these are identical at $x(O) = 0.2$ and $x(O) = 0.4$. The dotted (black) lines denote the equilibrium between the gas and gas + Ga ($l$) phase regions for $x(O) = 0.2$ and the gas and gas + Ga$_2$O$_3$ (s) phase regions for $x(O) = 0.4$, i.e., their respective boiling temperature/pressure.

Figure 4 shows Gibbs energies of the gas, Ga($l$), Ga$_2$O$_3$(s) phases at temperature $T = 1100$ K and total pressure $P = 0.1$ Pa. There are seven distinct atomic and molecular species in the gas phase: Ga, Ga$_2$, GaO, Ga$_2$O, O, O$_2$, and O$_3$. The kink in the Gibbs energy of the gas phase at $x(O) = 0.33$ corresponds to the composition of the Ga$_2$O species because it is the major species in the gas phase. It can be seen that the values of the oxygen activity in the gas+Ga ($l$)
vs. in the gas + Ga$_2$O$_3$ (s) regions differ by more than seven orders of magnitude, i.e., $6.4 \times 10^{-24}$ Pa vs. $1.8 \times 10^{-16}$ Pa as indicated by the brown and green common tangent lines in Fig. 4.

In Fig. 5(a) the partial pressure of oxygen in the gas phase is plotted as a function of temperature (for a total pressure of 0.1 Pa) for a Ga-rich mixture at $x(O) = 0.2$ and a Ga$_2$O$_3$-rich mixture at $x(O) = 0.4$. It can be seen that the oxygen partial pressure in the Ga$_2$O$_3$-rich mixture at $x(O) = 0.4$ is orders of magnitude higher than that at $x(O) = 0.2$ at relevant MBE growth temperatures. For example, the value of the partial pressures of oxygen at $T_{\text{mix}} = 1000$ K at $x(O) = 0.2$ is $5.6 \times 10^{-25}$ Pa and at $x(O) = 0.4$ is $4.5 \times 10^{-21}$ Pa. The higher oxygen activity of Ga$_2$O$_3$-rich mixtures compared with Ga-rich mixtures makes it easier to form fully oxidized Ga$_2$O$_3$ thin films. At lower total pressure, all lines shift to lower temperatures.

Further, our thermodynamic calculations plotted in Fig. 5(b) show the ratio of the partial pressures of Ga$_2$O to Ga in the gas phase as a function of the temperature of a Ga-rich mixture [$x(O) = 0.2$] and of a Ga$_2$O$_3$-rich mixture [$x(O) = 0.4$], where the total pressure is fixed at 0.1 Pa. The ratio of the partial pressures of Ga$_2$O to Ga in a Ga-rich mixture with $x(O) = 0.2$ is much lower than this ratio in a Ga$_2$O$_3$-rich mixture with $x(O) = 0.4$. For example, the $P_{\text{Ga}_2\text{O}_3}/P_{\text{Ga}}$ ratio is 158 in a Ga-rich mixture [$x(O) = 0.2$] and 1496 in a Ga$_2$O$_3$-rich mixture [$x(O) = 0.4$] at $T_{\text{mix}} = 1000$ K. The higher Ga$_2$O/Ga ratios at higher $T_{\text{mix}}$ are another reason why Ga$_2$O$_3$-rich mixtures are preferred. Higher Ga$_2$O/Ga ratios and the higher purity of the Ga$_2$O molecular-beam [99.98% Ga$_2$O according to our calculations at $x(O) = 0.4$] mean that the Ga$_2$O$_3$ films are formed by a single-step reaction [reaction (2)] and that reaction (1) is bypassed.

We used Ga metal (7N purity) and Ga$_2$O$_3$ powder (5N purity) for the Ga + Ga$_2$O$_3$ mixtures, loaded them into a 40 cm$^3$ Al$_2$O$_3$ crucible and inserted it into a commercial dual-filament, medium temperature MBE effusion cell. After mounting the effusion cell to our Veeco GEN10 MBE system and evacuating the source, we heated it up, outgased the mixture, and set our desired Ga$_2$O flux for the growth of Ga$_2$O$_3$. We measured the flux of the Ga$_2$O (g) molecular-beam reaching the growth surface prior to and after growth using a quartz crystal microbalance. The film surface was monitored during growth by reflection high-energy electron diffraction (RHEED) using 13 keV electrons. After growth x-ray reflectivity (XRR), optical reflectivity in a microscope (ORM),$^{62}$ scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), and secondary-ion mass spectrometry (SIMS) were used to accurately measure the thicknesses of homoepitaxial (ORM, SEM, SIMS, SEM) and heteroepitaxial (XRR, ORM, SEM, STEM, SIMS) grown Ga$_2$O$_3$ films to determine the growth rate. X-ray diffraction was performed using a four-circle x-ray diffractometer with Cu K$\alpha_1$ radiation.
III. RESULTS FOR Ga2O3 USING S-MBE

A. Growth rates and growth model

Figure 6 plots the growth rate of Ga2O3 as a function of \( \phi_{Ga2O} \) at different \( T_G \) and constant \( \phi_O \). The growth rates obtained follow the anticipated growth kinetics depicted in Fig. 1(c). In the adsorption-controlled regime, an increase in \( \phi_{Ga2O} \) (at otherwise constant growth parameters) does not lead to a decrease in the growth rate as observed for ‘conventional’ Ga2O3 MBE [Fig. 1(b)], but instead results in a constant growth rate: a growth rate-plateau. The data clearly show that we have overcome the growth rate-limiting step by using a Ga2O (g) suboxide molecular-beam while reducing the complexity of the Ga2O3 reaction kinetics from a two-step [Eqs. (1) and (2)] to a single-step [Eq. (2)] reaction mechanism.

The reaction kinetics of S-MBE for the growth of Ga2O3 can be described in a similar way as ‘conventional’ III-V [e.g., reaction (3)] and II-VI MBE. We therefore set up a simple reaction-rate model describing the growth of Ga2O3 (s) by S-MBE (this same model applies to other III-VI and IV-VI compounds, as well):

\[
\frac{dn_{Ga2O}}{dt} = \phi_{Ga2O} - \kappa_{Ga2O} n_{Ga2O} n_O^2 - \gamma_{Ga2O} n_{Ga2O} , \quad (9)
\]

\[
\frac{dn_O}{dt} = \sigma \phi_O - 2 \kappa_{Ga2O} n_{Ga2O} n_O^2 - \gamma_O n_O , \quad (10)
\]

\[
\frac{dn_{Ga2O}:O}{dt} = \Gamma = \kappa_{Ga2O} n_{Ga2O} n_O^2 . \quad (11)
\]

The Ga2O3, Ga2O, and O adsorbate densities are denoted as \( n_{Ga2O} \), \( n_{Ga2O:O} \), and \( n_O \), respectively. Their time derivative is described by the operator \( d/dt \). The reaction rate constant \( \kappa_{Ga2O} \) kinetically describes the growth rate \( \Gamma \) of Ga2O3 (s) on the growth surface. The desorption rate constants of Ga2O and O adsorbates are denoted as \( \gamma_{Ga2O} \) and \( \gamma_O \), respectively.

The flux of available O adsorbates, for Ga2O to Ga2O3 oxidation at a given \( T_G \), is determined by its sticking coefficient \( \sigma \) on the Ga2O3 growth surface and is described by a sigmoid function

\[
\sigma(T_G) = \left[ \sigma_0 \exp\left(-\frac{\Delta \sigma}{k_B(T_G - dT_G)}\right) + 1 \right]^{-1} , \quad (12)
\]

with dimensionless pre-factor \( \sigma_0 \), energy \( \Delta \sigma \), and temperature off-set \( dT_G \). Equation (12) reflects the decreasing probability of O species to adsorb as \( T_G \) is increased. This leads to an effectively lower surface density of active O for Ga2O3 oxidation and thus to lower growth rates.

![FIG. 6. Measured growth rate of Ga2O3(201)/Al2O3(0001) as a function of \( \phi_{Ga2O} \) at different \( T_G \) (as indicated in the figure). Solid lines are fits of our model, Eqs. (9)–(11), to the data. A flux of \( \phi_O \) was provided by an oxidant—a mixture of O2 and approximately 80% O2—supplied continuously during growth at a background pressure of \( 1 \times 10^{-6} \) Torr. The dashed line reveals the transition between O-rich and Ga2O-rich growth regimes and indicates the maximum available O flux (which equals the growth rate value of the plateau) for Ga2O to Ga2O3 conversion at a given \( T_G \).](image)
at \( T_G = 500^\circ\text{C} \). For comparison, the data point plotted as an open-dotted hexagon (see also Fig. 6) shows the highest possible growth rate at a five times lower active \( \phi_0 \) and the same \( T_G \). This result shows quite clearly the accuracy of our model and demonstrates the S-MBE of Ga\(_2\)O\(_3\) thin films at growth rates exceeding 1 \( \mu\text{m hr}^{-1} \). In addition, the growth rate values plotted in Fig. 7(b) were obtained by homoepitaxial growth of \( \beta\)-Ga\(_2\)O\(_3\)(010) on \( \beta\)-Ga\(_2\)O\(_3\)(010). The growth rate of Ga\(_2\)O\(_3\) on Ga\(_2\)O\(_3\)(010) is 2.1 times larger than the growth rate on Al\(_2\)O\(_3\)(0001) at similar growth conditions—e.g., as plotted in Figs. 7(a) [open hexagon] and 7(b) [solid diamond], respectively. This result suggests that the growth rate of S-MBE grown Ga\(_2\)O\(_3\)(010) and other surfaces of Ga\(_2\)O\(_3\) may vastly exceed 1 \( \mu\text{m hr}^{-1} \) in the adsorption-controlled regime. The higher growth rate is likely due to the surface-dependent adhesion energies between of Ga\(_2\)O adsorbates and substrate\(^{11,12,65} \), similar to what has been observed for Ga adsorbates during the ‘conventional’ MBE of Ga\(_2\)O\(_3\).\(^{45} \) Fluctuations in \( T_G \) and \( \phi_\text{Ga}_2\text{O}_3 \) for different samples and during the long duration growth of the ‘thick’ sample (> 3 hours) are considered by the standard deviations of the measured values of \( T_G \) and \( \phi_\text{Ga}_2\text{O}_3 \) as given in Fig. 7.

### B. Structural properties

We investigated the impact of variable growth conditions (i.e., \( \phi_\text{Ga}_2\text{O}_3 \), \( \phi_0 \), and \( T_G \)) on the structural perfection of epitaxial Ga\(_2\)O\(_3\) (s) films grown on Al\(_2\)O\(_3\)(0001) and Ga\(_2\)O\(_3\)(010) substrates. Figure 8 shows \( \theta\)-2\( \theta \) x-ray diffraction (XRD) scans of selected Ga\(_2\)O\(_3\) films—the same samples depicted in Fig. 7(a) [solid blue hexagon and open-dotted hexagon]. The reflections of the films coincide with the \( \beta\)-Ga\(_2\)O\(_3\) phase grown with their (201) plane parallel to the (0001) plane of the Al\(_2\)O\(_3\) substrate. The inset shows transverse scans (rocking curves) across the symmetric 402 reflection of the same layers. The full width at half maxima (FWHM) in \( \omega \) of the profiles are a measure of the out-of-plane mosaic spread of the Ga\(_2\)O\(_3\) layer. The obtained \( \Delta\omega = 0.11^\circ \approx 400'' \) (arcseconds) does not change with growth rate and is particularly remarkable since \( \beta\)-Ga\(_2\)O\(_3\)(201) films grown on Al\(_2\)O\(_3\)(0001), using elemental Ga\(^{67} \) or compound Ga\(_2\)O\(_3\) sources\(^{27} \), usually show much broader line profiles in their out-of-plane crystal distributions (from \( \Delta\omega \approx 0.23^\circ^{27} \) to \( \Delta\omega \sim 1.00^\circ^{7} \)). Thus, the profiles in Fig. 8 reveal a well-oriented and high quality epitaxial Ga\(_2\)O\(_3\)(201) thin film. Furthermore, reflection high-energy electron diffraction (RHEED) and XRR measurements reveal a sharp and well-defined interface between Ga\(_2\)O\(_3\)(201) and Al\(_2\)O\(_3\) as well as a relatively smooth surface morphology obtained by S-MBE. We note that in the highly adsorption-controlled regime at lower \( T_G \) the accumulation of Ga\(_2\)O

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**FIG. 7.** (a) Examples of measured growth rates of 1.6 \( \mu\text{m hr}^{-1} \) (solid hexagon), 0.7 \( \mu\text{m hr}^{-1} \) (open hexagon), and 0.2 \( \mu\text{m hr}^{-1} \) (open-dotted hexagon; the same data point is shown in Fig. 6) of Ga\(_2\)O\(_3\)(201) grown on Al\(_2\)O\(_3\)(0001) at \( \phi_\text{Ga}_2\text{O}_3 \) of 11.4, 9.5, and 3.0 \( \times 10^{14} \) Ga\(_2\)O molecules cm\(^{-2}\) s\(^{-1}\), respectively. The oxygen flux was provided by an oxidant (\( O_2 + 80\%\) O\(_3\)) background pressure of 5 \( \times 10^{-6} \) Torr (solid hexagon and open hexagon) as well as 1 \( \times 10^{-6} \) Torr (open-dotted hexagon). (b) Examples of measured growth rates of 1.5 \( \mu\text{m hr}^{-1} \) (solid diamond), 1.17 \( \mu\text{m hr}^{-1} \) (open diamond), and 1.05 \( \mu\text{m hr}^{-1} \) (solid square) of Ga\(_2\)O\(_3\)(010) grown on Ga\(_2\)O\(_3\)(010) at \( \phi_\text{Ga}_2\text{O}_3 \) of 8.4, 7.6, and 9.5 \( \times 10^{14} \) Ga\(_2\)O molecules cm\(^{-2}\) s\(^{-1}\), respectively. The oxygen flux was provided by an oxidant (\( O_2 + 80\%\) O\(_3\)) background pressure of 5 \( \times 10^{-6} \) Torr. Growth temperatures, \( T_G \), are indicated in the figure. Lines are estimations from our model, Eqs. (9)-(11), including all kinetic parameters\(^{64} \). The dashed line shows the estimated intersection between the O-rich to the Ga\(_2\)O-rich growth regime\(^{64} \). The blue shaded area indicates the adsorption-controlled growth rate-regime only accessible by S-MBE with growth rates \( \geq 1 \mu\text{m hr}^{-1} \).
shows the respective rocking curves across the symmetric regime. The blue line corresponds to a film with thickness of \( d = 0.15 \mu m \) grown at \( \phi_{Ga_2O} = 11.4 \times 10^{14} \text{Ga}_2\text{O molecules cm}^{-2} \text{s}^{-1} \) where \( \phi_{O} \) was provided by an oxidant \((O_2 + 80 \%) \text{O}_3 \) background pressure of \( 5 \times 10^{-6} \text{Torr} \) [see also solid blue hexagon in Fig. (7)(a)]. The gray line corresponds to a \( \text{Ga}_2\text{O}_3 \) film with thickness \( d = 0.05 \mu m \) grown at \( \phi_{Ga_2O} = 3.0 \times 10^{14} \text{Ga}_2\text{O molecules cm}^{-2} \text{s}^{-1} \) where \( \phi_{O} \) was provided by an oxidant \((O_2 + 80 \%) \text{O}_3 \) background pressure of \( 1 \times 10^{-6} \text{Torr} \) [see also gray open-dotted hexagon in Fig. (7)(a)].

For both samples \( T_G \) was 500°C. The reflections from the \( \text{Ga}_2\text{O}_3 \) film are identified to originate from the monoclinic \( \beta \)-phase, \(^{66}\) as indicated in the figure. (Inset) Transverse XRD scans across the \( 402 \) peak with their FWHM indicated in the figure (same value for both films). The 0006 peaks of the \( \text{Al}_2\text{O}_3 \) substrates are marked by an asterisk. RHEED images taken at the end of the growth along the [010] azimuth of the \( \text{Ga}_2\text{O}_3 \) films grown at growth rates of 1.6 \( \mu m \text{ hr}^{-1} \) and 0.2 \( \mu m \text{ hr}^{-1} \) are outlined by the blue and gray boxes, respectively.

adsorbates (crystallites) on the growth surface may occur, similar to the formation of Ga droplets during GaN growth. \(^{36}\) This effect is indicated by the slightly spotty RHEED image (outlined by the blue square) in Fig. 8. We have not yet optimized the growth for \( \text{Ga}_2\text{O}_3(201) \) films on \( \text{Al}_2\text{O}_3(0001) \) with thicknesses \( \geq 1 \mu m \) and mapped all growth regimes (e.g., \( \text{Ga}_2\text{O} \) 'droplet' formation at very high \( \phi_{Ga_2O} \) ). Further investigations of the structural perfection and electrical properties of \( \text{Ga}_2\text{O}_3 \) grown by \( S\)-MBE need to be performed. This could be particularly interesting for the growth of \( \text{Ga}_2\text{O}_3 \) (s) at even higher \( \text{Ga}_2\text{O} \) (g) fluxes, which push even further into the adsorption-controlled regime.

We performed \( S\)-MBE for homoepitaxial \( \beta\)-\( \text{Ga}_2\text{O}_3(010) \) films grown on \( \beta\)-\( \text{Ga}_2\text{O}_3(010) \) substrates. Figure 9 shows the \( \theta-2\theta \) XRD scans of two selected \( \text{Ga}_2\text{O}_3(010) \) films grown under the same growth conditions. The \( \theta-2\theta \) XRD profiles of the \( \text{Ga}_2\text{O}_3(010) \) film with thickness \( d = 0.74 \mu m \) (plotted in dark blue) and the one of the substrate (data not shown) coincide. The \( \text{Ga}_2\text{O}_3(010) \) layer with \( d = 4.1 \mu m \) (depicted as pale blue) shows small contributions of the metastable \( \gamma\)-\( \text{Ga}_2\text{O}_3 \) phase. The inset of Fig. 9 shows the respective rocking curves across the symmetric 020 reflections of the same films as plotted in the main graph of Fig. 9. The obtained FWHM of the rocking curve of the film with \( d = 0.74 \mu m \) is comparable to the one obtained for the bare \( \text{Ga}_2\text{O}_3(010) \) substrate (depicted as a black line). [Note that the measured XRD spectra were obtained on different \( 10 \times 10 \text{mm}^2 \) substrates which were all cut from the same 1" diameter \( \text{Ga}_2\text{O}_3(010) \) wafer from Synoptics.] The rocking curve of the ‘thick’ film with \( d = 4.1 \mu m \) is considerably broader than the rocking curve detected for the ‘thin’
The small Si peak measured at the top of the surfaces of their Ga$_2$O$_3$(010)/Ga$_2$O$_3$(010) structures can be seen, as marked by white circles in Figs. 10(b) and 10(e).

The surface morphology of Ga$_2$O$_3$(010) films grown by S-MBE at growth rates $>$ 1 µm hr$^{-1}$ were investigated by atomic force microscopy (AFM) and are plotted in Figs. 11(a)–11(c). The root mean square (rms) roughness of the ‘thin’ film with $d = 0.74$ µm is lower than the one measured for the ‘thick’ film with $d = 4.1$ µm. This evolution in rms roughness follows the same trend as observed by XRD scans of the same layers (dark blue and pale blue lines in the inset of Fig. 9), i.e., a slight decrease in crystal quality with increasing film thickness of the Ga$_2$O$_3$(010)/Ga$_2$O$_3$(010) structures.

C. Impurities

We investigated the incorporation of impurities into the Ga$_2$O$_3$(010) thin films grown with growth rates $>$ 1 µm hr$^{-1}$ by SIMS. Figure 12 shows the SIMS profile of the same film as plotted in Figs. 7 (solid square), Fig. 10, and Fig. 11(c). This profile reveals that the Ga$_2$O$_3$-rich (Ga + Ga$_2$O$_3$) mixtures employed lead to Ga$_2$O$_3$(010) thin films with low impurity incorporation. Only a slight increase of Al impurities with increasing film thickness and a slight incorporation of B are detected. These impurities likely originate from our use of an Al$_2$O$_3$ crucible for the Ga$_2$O$_3$-rich (Ga + Ga$_2$O$_3$) mixture. We note that we have also used pyrolytic boron nitride (pBN) crucibles for the Ga+Ga$_2$O$_3$ mixture, but find high concentrations of B in the grown films by SIMS (~ $10^{20}$ B cm$^{-3}$) when the background pressure of a mixture of O$_2 + 80$%O$_3$ is $P_O = 5 \times 10^{-6}$ Torr.

We attribute this to the oxidation of the surface of the pBN crucible to B$_2$O$_3$ at the high oxidant pressures used. At the $T_{mix} = 1020^\circ$C used for growth, the vapor pressure of B$_2$O$_3$ is significant. The small Si peak measured at the film-substrate interface originates from unintentional incorporated Si at the substrate surface. Note, we have tried Ga$_2$O-polishing (for the first time) to remove the Si from the surface prior to growth. Our observation is that Ga$_2$O-polishing does not provide the same reduction in Si contamination at the sample surface as can be accomplished by Ga-polishing.

Our SIMS results show that the low effusion cell temperatures and Ga$_2$O$_3$-rich (Ga + Ga$_2$O$_3$) mixtures employed for S-MBE—in order to produce such high Ga$_2$O fluxes to
Nonetheless, electri-
as solid diamond, open diamond, and solid
as dark blue and pale blue
of the corresponding Ga
pared to the growth Ga
not lead to significant impurity incorporation into the grow
[this is the same sample depicted by the solid square in Fig.
shown in Figs.
show the SIMS profile of the Ga
impurity incorporation could be detected. Gray and white ar-
as indicated on the figures. The XRD patterns of the same lay-
lines, respectively. The growth rates of the films shown in (a), (b) and (c), are depicted in Fig.
images of the corresponding Ga
square, respectively. The thicknesses of the films in (a) and (c) are \(d = 0.74\) µm and the thickness of the film with the morphology shown in (b) is \(d = 4.1\) µm. \(T_E\) was set to 550°C for the films shown in (a) and (b) and to \(T_E = 575\) °C for the film plotted in (c). RHEED images
3- or 5N Ga
powder will be needed than the 5N Ga
films contaminated with iridium. \(^{32,56,57}\) Nonetheless, electrical transport properties are extremely sensitive to impurities
and measurements of mobility in doped Ga
films grown by S-MBE remain to be performed. It could turn out that a higher purity Ga
powder we have used in this study.\(^{32}\)

\[ \text{D. Summary} \]

The growth rates we have achieved by S-MBE are more than one order of magnitude faster than what has been reported for the growth of Ga\(_2\)O\(_3\) films from pure Ga\(_2\)O\(_3\) sources.\(^{32}\)

The quality of the homoepitaxial \(\beta\)-Ga\(_2\)O\(_3\)(010) films (with thickness > 4 µm) assessed by XRD (Fig. 9), STEM (Fig. 10), AFM (Fig. 11) and SIMS (Fig. 12), reveal that S-MBE with growth rates > 1 µm hr\(^{-1}\) is competitive to other industrial relevant synthesis methods [such as (MO)CVD] for the growth of vertical Ga\(_2\)O\(_3\)-based structures with thicknesses in the µm-range.

Based on our model and experimental results, we anticipate growth rates up to 5 µm hr\(^{-1}\) on Ga\(_2\)O\(_3\)(010) and other growth surfaces to be possible by S-MBE. This estima-
IV. OUTLOOK AND ALTERNATIVES OF S-MBE

We have demonstrated the growth of high quality \( \text{Ga}_2\text{O}_3 \) (s) thin films by S-MBE in the adsorption-controlled regime using \( \text{Ga}(l) + \text{Ga}_2\text{O}_3 \) (s) mixtures. The high growth rate \( > 1 \mu \text{m hr}^{-1} \), and unparalleled crystal quality of the homoepitaxial and heteroepitaxial structures obtained (with \( d \gg 1 \mu \text{m} \)) suggest the possibility of unprecedented mobilities of \( \text{Ga}_2\text{O}_3 \) thin films containing n-type donors (Sn, Ge, Si) grown by S-MBE.

We have also developed Sn + SnO\(_2\) and Ge + GeO\(_2\) mixtures in order to produce SnO\(_2\) (g) and GeO\(_2\) (g) beams for use as n-type donors in \( \text{Ga}_2\text{O}_3 \)-based heterostructures. Furthermore, we have grown SnO\(_2\) using a Sn + SnO\(_2\) mixture.\(^{31}\) Moreover, we have grown \( \text{Ga}_2\text{O}_3 \) doped with SnO using \( \text{Ga}_2\text{O}_3 \) and SnO beams and achieved controllable Sn-doping levels in these \( \text{Ga}_2\text{O}_3 \) films.\(^{70}\) Nevertheless, the improvement of the n-type mobilities obtained during S-MBE, at growth rates \( > 1 \mu \text{m hr}^{-1} \), still needs to be demonstrated and shown to exceed the state-of-the-art mobilities in \( \text{Ga}_2\text{O}_3 \) films grown by ‘conventional’ MBE.\(^{71}\)

Our comprehensive thermodynamic analysis of the volatility of 128 binary oxides plus additional two-phase mixtures of metals with their binary oxides,\(^ {55}\) e.g., Ga + \( \text{Ga}_2\text{O}_3 \), have led us to recognize additional systems appropriate for growth by S-MBE. This thermodynamic knowledge coupled with our understanding of the S-MBE growth of \( \text{Ga}_2\text{O}_3 \) enabled us to develop In + In\(_2\text{O}_3\) and Ta + Ta\(_2\text{O}_5\) mixtures from which we have grown high-quality bixbyite In\(_2\text{O}_3\)\(^{64,72}\) and In\(_2\text{O}_3\)-SnO\(_2\) (ITO, with up to 30% Sn)\(^ {64,72}\) as well as rutile TaO\(_2\)\(^ {73}\) by S-MBE, respectively.

Growing thin films with very high crystalline qualities at growth rates \( > 1 \mu \text{m hr}^{-1} \) by using suboxide molecular-beams—with up to \( 5 \mu \text{m hr}^{-1} \) anticipated growth rates by our model—will make MBE competitive to other established synthesis methods, such as CVD\(^ {33}\) or MOVPE.\(^ {34}\) The \( T_G \) that we have demonstrated for high quality \( \text{Ga}_2\text{O}_3 \) layers grown by S-MBE is significantly lower than what has been demonstrated for the growth of high quality \( \text{Ga}_2\text{O}_3 \) films by CVD or MOVPE. This makes S-MBE advantageous for BEOL processing. Additionally, \( \text{Ga}_2\text{O}_3 \) grown with a vast excess of \( \text{Ga}_2\text{O}_3 \) (g) and high oxygen activity in \( \text{Ga}_2\text{O}_3\)-rich mixtures may suppress Ga vacancies in the \( \text{Ga}_2\text{O}_3 \) layers formed, which are believed to act as compensating acceptors\(^ {20,74}\) potentially improving the electrical performance of n-type \( \text{Ga}_2\text{O}_3 \)-based devices significantly.

The development of Al + Al\(_2\text{O}_3\) mixtures for the growth of epitaxial \( \text{Al}_2\text{O}_3 \) and (Al, Ga\(_{1-x}\))\(_2\text{O}_3\) at comparably high growth rates by S-MBE is foreseeable. In order to fabricate vertical high-power devices, thin film thicknesses in the micrometer range are desired. S-MBE allows the epitaxy of such devices in relatively short growth times (i.e., within a few hours as demonstrated for \( \text{Ga}_2\text{O}_3\) (010) in this work) while maintaining nanometer scale smoothness. In addition, the use of a Al\(_2\text{O}_3 \) (g) and \( \text{Ga}_2\text{O}_3 \) (g) molecular-beams during (Al, Ga\(_{1-x}\))\(_2\text{O}_3 \) S-MBE may also extend its growth domain towards higher adsorption-controlled regimes—being beneficial for the performance of (Al, Ga\(_{1-x}\))\(_2\text{O}_3\)-based heterostructure devices.

Our demonstration of high quality films of \( \text{Ga}_2\text{O}_3 \), \( \text{Ga}_2\text{O}_3 \) doped with SnO\(_2\),\(^ {70}\) In\(_2\text{O}_3\),\(^ {64,72}\) ITO,\(^ {64,72}\) TaO\(_2\),\(^ {73}\) LaInO\(_3\),\(^ {75}\) and LaAlO\(_3\),\(^ {76}\) suggests that this synthesis-science approach—utilizing a combination of thermodynamics to identify which suboxides can be produced in molecular-beams in combination with a kinetic model of the growth process—can be applied to a wide-range of oxide compounds.\(^ {55}\) We anticipate S-MBE to be applicable to all materials that form via intermediate reaction products (a subcompound). Examples following this reasoning include ZrO\(_2\), Pb(Zr,Ti)O\(_3\), and (Hf,Zr)O\(_2\) all via the supply of a molecular-beam of ZrO (predicted by our thermodynamic calculations\(^ {55}\)) \( \text{Ga}_2\text{Se}_3 \) via \( \text{Ga}_2\text{Se}_5 \),\(^ {11,77,78}\) In\(_2\text{Se}_3\) through In\(_2\text{Se}_5\),\(^ {11,79,80}\) In\(_2\text{Te}_3\) by In\(_2\text{Te}_5\),\(^ {11,81}\) or Sn\(_2\)Se via SnSe.\(^ {11,82}\)

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Competing interests: The authors P. V., D. G. S., F. V. E. H., K. A., Z.-K. L., B. J. B., S.-L. S., Cornell University (D-9573) and the Pennsylvania State University (2020-5155) have filed a patent entitled: Adsorption-Controlled Growth of Ga$\text{S}_2\text{O}_3$ by Suboxide Molecular-Beam Epitaxy.

VI. DATA AVAILABILITY

No data that support the findings in this study are required and provided.

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