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ABSTRACT

This paper introduces a growth method—suboxide molecular-beam epitaxy (S-MBE)—which enables a drastic enhancement in the growth rates of Ga$_2$O$_3$ and related materials to over 1 μm h$^{-1}$ in an adsorption-controlled regime, combined with excellent crystallinity. Using a Ga + Ga$_2$O$_3$ 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 Ga$_2$O$_3$ by MBE. We present growth rates up to 1.6 μm h$^{-1}$ and 1.5 μm h$^{-1}$ for Ga$_2$O$_3$/Al$_2$O$_3$ and Ga$_2$O$_3$/Ga$_2$O$_3$ structures, respectively, with very high crystalline quality 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 Ga$_2$O$_3$ films that are thicker than 4.5 μm. With the high growth rate of S-MBE, we anticipate a significant improvement to vertical Ga$_2$O$_3$-based devices. We describe and demonstrate how this growth method can be applied to a wide range of oxides. With respect to growth rates and crystalline quality, S-MBE rivals leading synthesis methods currently used for the production of Ga$_2$O$_3$-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 As$_4$ (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 plasma-induced 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 such as trimethylgallium or trimethylaluminium. “Suboxide” MBE refers to an MBE growth process utilizing molecular beams of suboxides such as Ga$_2$O (g) or In$_2$O (g). We have applied this method to the growth of Ga$_2$O$_3$ thin films and find that it can produce epitaxial Ga$_2$O$_3$ films with greater crystalline perfection combined with much higher growth rates than currently demonstrated by any other MBE method for the growth of this material.

A. “Conventional” MBE of Ga$_2$O$_3$ and related materials

Gallium-sesquioxide (Ga$_2$O$_3$) synthesized in its different poly-morphs [i.e., α-Ga$_2$O$_3$ (rhombohedral), β-Ga$_2$O$_3$ (monoclinic), γ-Ga$_2$O$_3$ (cubic spinel), ε-Ga$_2$O$_3$ (hexagonal), and κ-Ga$_2$O$_3$ (orthorhombic)] is an emerging semiconductor possessing promising features for unprecedented high-power electronics. This is due to its large band gap (~5 eV) and very high breakdown field (up to 8 MV cm$^{-1}$). The band gap of Ga$_2$O$_3$ may be widened by alloying Ga$_2$O$_3$ with Al$_2$O$_3$ to form (Al$_x$Ga$_{1-x}$)$_2$O$_3$. The synthesis of (Al$_x$Ga$_{1-x}$)$_2$O$_3$/Ga$_2$O$_3$ heterostructures with high Al content x is desired for high-power transistors with large band gap offsets.

It is known that the “conventional” MBE of Ga$_2$O$_3$—i.e., when supplying elemental Ga and active O species during growth—is strongly limited by the formation and subsequent desorption of its volatile suboxide Ga$_2$O. In the adsorption-controlled regime (i.e., grown with an excess of Ga), the growth rate strongly decreases with increasing Ga flux, $\phi_{Ga}$, because not enough oxygen is available to oxidize the physisorbed Ga$_2$O to Ga$_2$O$_3$ (s) and the Ga$_2$O desorbs from the hot substrate. At sufficiently high $\phi_{Ga}$, film growth stops and even goes negative (i.e., the Ga$_2$O film is etched). This effect is enhanced as the growth temperature, $T_g$, increases due to the thermally activated desorption of Ga$_2$O from the growth surface. The enhanced, $T_g$-induced Ga$_2$O 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 flux $\phi_{O}$), followed by an even further decreasing growth rate in the adsorption-controlled regime. These effects, i.e., the O-deficiency induced and thermally activated desorption of suboxides, are detrimental for the growth of III–VI (e.g., Ga$_2$O$_3$ and IV–VI (e.g., SnO$_2$)) 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, smooth surface morphology, avoiding undesired oxidation states, or suppressing the formation of electrically compensating defects.

The growth rate evolution of Ga$_2$O$_3$ is microscopically explained by a complex two-step reaction mechanism. In the first reaction step, all Ga oxidizes to Ga$_2$O via the reaction

$$2Ga (a) + O (a) \rightarrow Ga_2O (a, g),$$

with adsorbate and gaseous phases denoted as a and g, respectively. The Ga$_2$O formed may either desorb from the growth surface (in the O-deficient regime or at elevated $T_g$) or be further oxidized to Ga$_2$O$_3$ via a second reaction step through the reaction

$$Ga_2O (a) + 2O (a) \rightarrow Ga_2O_3 (s),$$

with the solid phase denoted as s.

This two-step reaction mechanism and the resulting Ga$_2$O desorption define the growth-rate-limiting step for the “conventional” MBE of Ga$_2$O$_3$ and related materials. This results in a rather narrow growth window associated with low growth rates in the adsorption-controlled regime.

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 Ga$_2$O (g) molecular beam to the growth front of the substrate surface. Using this approach, we bypass the growth-rate-limiting step of Ga$_2$O$_3$ by removing the O-consuming step to Ga$_2$O$_3$ formation that occurs on the substrate in the “conventional” MBE growth of Ga$_2$O$_3$. A related approach has been used by Ghose et al. when Ga$_2$O$_3$ provided from Ga$_2$O$_3$ source material heated to temperatures well in excess of 1600°C to produce a molecular beam of Ga$_2$O$_3$ for the growth of Ga$_2$O$_3$ films by MBE. Motivated by known vapor pressure data of oxides and their mixtures with the respective metals, e.g., Ga + Ga$_2$O$_3$, as well as the possibility of decomposing Ga$_2$O$_3$ by Ga and SnO$_2$ by Sn under MBE conditions, Hoffmann et al. demonstrated how mixtures of Ga with Ga$_2$O$_3$ and Sn with SnO$_2$ provide MBE-relevant fluxes of Ga$_2$O$_3$ and SnO$_2$, respectively, at source temperatures below 1000°C. This prior work has shown films using suboxide molecular beams by MBE at growth rates $\leq 0.2 \mu$m h$^{-1}$. As we demonstrate, S-MBE enables the synthesis of Ga$_2$O$_3$ in the highly adsorption-controlled regime, at growth rates $>1 \mu$m h$^{-1}$ with unparalleled crystalline quality for Ga$_2$O$_3$/Al$_2$O$_3$ heterostructures as well as homoepitaxial Ga$_2$O$_3$ 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) or metal–organic CVD (MOCVD) —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 Ga$_2$O$_3$ 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 material integration where temperatures are limited, e.g., back end of line (BEOL) processes.

Figure 1 illustrates a schematic of how the growth rates of III–V and III–VI compounds depend on cation fluxes during their MBE growth. In this figure, all growth rate axes are normalized by III–V and III–VI compound stoichiometries between III–V and IV–VI compared with III–V and II–VI materials, respectively.
cation is supplied by a molecular beam of the group III element (e.g., Ga). In Fig. 1(c), the anticipated behavior for III–VI compounds is plotted, e.g., Ga$_3$O$_5$, when the group III element is supplied by a molecular beam of a III–VI subcompound containing the group III constituent (e.g., Ga$_2$O$_3$). The units of the horizontal and vertical axes are chosen to make the crossover between the anion-rich [gray areas in panels (a)–(c)] and cation-rich flux regimes [white areas in panels (a)–(c)] to occur at values of unity. For the sake of simplicity, henceforth, we only discuss the reaction behavior of GaN and Ga$_3$O$_5$ in detail. We emphasize, however, that this discussion holds true for the MBE growth of AlN, InN, In$_2$O$_5$ (Refs. 8, 11, and 13), and other III–VI and II–VI compounds.

As drawn in Figs. 1(a)–1(c), the growth rate of GaN and Ga$_3$O$_5$ increases linearly with increasing $\phi_{Ga}$ in the N-rich [Fig. 1(a)] and O-rich regimes [Figs. 1(b) and 1(c)], respectively. Here, the incorporation of Ga is limited by the impinging $\phi_{Ga}$ or Ga$_2$O$_5$ flux, $\phi_{Ga_3O_5}$ (i.e., Ga-transport and Ga$_2$O$_5$-transport limited growth regimes).

For GaN MBE [Fig. 1(a)], once the supplied $\phi_{Ga}$ exceeds the flux $\phi_{N}$ of active available N, the growth rate saturates, is independent of the $\phi_{Ga}/\phi_{N}$ ratio, and is limited by $\phi_{N}$ and $T_G$. The measured plateau in the 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 reaction:

$$\text{Ga} (a) + \text{N} (a) \rightarrow \text{GaN} (s), \tag{3}$$

and excess Ga either adsors onto or desorbs from the growth surface depending upon $\phi_{N}$ and $T_G$. Note that Eq. (3) and its discussion given in the text are identical for II–VI compounds (e.g., ZnO).

Figure 1(b) depicts the reaction kinetics of Ga$_3$O$_5$ in the Ga-rich regime (O-deficient growth regime) by supplying $\phi_{Ga_3}$. Here, the growth rate linearly decreases with increasing $\phi_{Ga_3}$, and the growth eventually stops at $\phi_{Ga_3} \geq 3\phi_{O}$ (in growth rate units). The fact that desorbing Ga$_2$O removes Ga and O from the growth surface—leading to the decreasing growth rate in the O-deficient growth regime—governs 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$_3$O$_5$ while using a Ga$_2$O$_5$ beam is depicted, showing a constant growth rate in the Ga$_2$O$_5$-rich regime (i.e., in an excess of Ga$_2$O$_5$). Excess Ga$_2$O (that cannot be oxidized to Ga$_3$O$_5$) 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$_3$O$_5$ MBE [reaction (2)], as is the case for the growth of GaN by “conventional” 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 In$_2$O$_3$) and IV–VI films (e.g., SnO$_2$) to be grown much faster with excellent crystalline 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$_3$, Lu$_2$O$_3$, LaO$_3$, NdO$_3$, PrO$_3$, ScO$_3$, SnO$_2$, TiO$_2$, YO. Even before these MBE studies, thin films of the suboxides SiO$_2$, SnO, and GeO 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 recognition that the use of suboxide molecular beams reduces the complexity of the reaction kinetics of III–O and IV–O compounds from a complex two-step reaction mechanism to a simple single-step reaction process. The growth kinetics during the S-MBE of III–O and IV–O compounds are equal to those of III–V and II–VI materials when they are grown by “conventional” MBE. Using this knowledge, S-MBE is applied in a targeted way to achieve epitaxial growth of desired oxides (e.g., Ga$_2$O$_3$) at very high growth rates in an adsorption-controlled regime. This leads to the benefits of the far simpler (from a growth kinetics, growth control, and growth standpoint) growth rate-plateau regime shown in Fig. 1(c) to be harnessed rather than the growth rate-decrease regime shown in Fig. 1(b) that has posed limits to the growth of Ga$_2$O$_3$ films and related materials by “conventional” MBE up to now.

II. DETAILED DESCRIPTION OF S-MBE

The use of a Ga$_2$O$_3$ (g) 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 a 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

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

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

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) has a vapor pressure of 0.1 Pa (a vapor pressure typical for MBE growth), the Ga$_2$O$_3$ molecular beam contains only 98.0% Ga$_2$O$_3$ molecules. The remaining 2% of the beam consists of 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 \( \sim 1600 \text{ } ^\circ\text{C} \) to \( \sim 1700 \text{ } ^\circ\text{C} \) or \( \sim 1800 \text{ } ^\circ\text{C} \). 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 \( \sim 1700 \text{ } ^\circ\text{C} \) were limited to growth rates \( \sim 0.14 \text{ } \mu\text{m} \text{ h}^{-1} \) (Ref. 32) with \( \sim 5 \times 10^{18} \text{ cm}^{-2} \) 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 \( \mu\text{m} \text{ h}^{-1} \) 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 \( \mu\text{m} \text{ h}^{-1} \) provides a Ga$_2$O$_3$ molecular beam that is 99.98% pure according to our thermodynamic calculations. This is for the same Ga$_2$O$_3$ vapor pressure of 0.1 Pa, which happens at a source temperature about 600 \( \text{ } ^\circ\text{C} \) 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$_3$ molecular beam have been studied and suggested as efficient suboxide sources for oxide MBE. Using this mixed source, a Ga$_2$O$_3$ (g) molecular beam is produced by the chemical reaction

\[ 4\text{Ga} (\ell) + \text{Ga}_2\text{O}_3 (s) \rightarrow 3\text{Ga}_2\text{O} (s,g) , \tag{6} \]

with the liquid phase denoted as \( \ell \). 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

\[ 5\text{Ga} (\ell) + \text{Ga}_2\text{O}_3 (s) \xrightarrow{k_{\text{Ga} + \text{Ga}_2\text{O}_3}} 3\text{Ga}_2\text{O} (g) + \text{Ga} (\ell) \tag{7} \]

and

\[ \frac{5}{2} \text{Ga} (\ell) + \text{Ga}_2\text{O}_3 (s) \xrightarrow{k_{\text{Ga} + \text{Ga}_2\text{O}_3} \text{Ga-rich}} \frac{15}{8} \text{Ga}_2\text{O} (g) + \frac{3}{8} \text{Ga}_2\text{O}_3 (s) , \tag{8} \]

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

The flux of Ga$_2$O$_3$ (g) in the molecular beam emanating from the mixed Ga + Ga$_2$O$_3$ sources is significantly larger than that of Ga (g)\textsuperscript{26,27} emanating from the same source. This is also true under MBE conditions\textsuperscript{31,35}. The resulting high ratio of Ga$_2$O$_3$/Ga > 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$_3$/Ga, Ga$_2$O$_3$/O, 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$_3$ 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$_3$ (g) molecular beams than a Ga-rich mixture. Thus, Ga$_2$O$_3$-rich mixtures enable higher growth rates by S-MBE than Ga-rich mixtures. This experimental observation is confirmed by our thermodynamic calculations of the phase diagram of Ga (\( \ell \)) + 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 (\( \ell \)) + Ga$_2$O$_3$ (s) around 907 K, a two-phase region of Ga (\( \ell \)) + 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 Thermoeatape Data (SGTE) substance database (SSUBS\textsuperscript{36}) within the Thermo-Calc software.\textsuperscript{4} For \( T_{\text{mix}} > 907 \text{ } K \), the two-phase regions are gas + Ga (\( \ell \)) 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 a \(T_{\text{mix}}\) of (907–1189) K for Ga-rich mixtures and at (907–1594) K for \(\text{Ga}_2\text{O}_3\)-rich mixtures, respectively. All of these phase transition temperatures decrease with decreasing pressure, as shown in the pressure vs temperature \((P − T)\) phase diagrams in Fig. 3.

To contrast the difference between Ga-rich vs \(\text{Ga}_2\text{O}_3\)-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 \(\text{Ga}_2\text{O}_3\)-rich mixtures, respectively. In Figs. 3(a) and 3(b), the solid (red) lines denote the three-phase equilibrium between gas + Ga(\(ℓ\)) + \(\text{Ga}_2\text{O}_3\); 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 \(x(O) = 0.2\) as well as the gas and gas + \(\text{Ga}_2\text{O}_3\) (s) phase regions for \(x(O) = 0.4\), i.e., their respective boiling temperature/pressure.

Figure 4 shows Gibbs energies of the gas, Ga(\(ℓ\)), \(\text{Ga}_2\text{O}_3\)(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, \(\text{Ga}_2\), \(\text{GaO}\), \(\text{Ga}_2\text{O}_3\), O, \(\text{O}_2\), and \(\text{O}_3\). The kink in the Gibbs energy of the gas phase at \(x(O) = 0.33\) corresponds to the composition of the \(\text{Ga}_2\text{O}\) species because it is the major species in the gas phase.
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., $6.4 \times 10^{-25}$ Pa vs $1.8 \times 10^{-18}$ 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 $T_{\text{max}}=1000$ 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.

Furthermore, our thermodynamic calculations plotted in Fig. 5(b) show the ratio of the partial pressures of Ga$_2$O$_3$ 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$_3$ 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 $T_{\text{max}}=1000$ K. The higher Ga$_2$O$_3$/Ga ratios at higher $T_{\text{max}}$ are another reason why Ga$_2$O$_3$-rich mixtures are preferred. Higher Ga$_2$O$_3$/Ga ratios and the higher purity of the Ga$_2$O$_3$ 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, outgassed the mixture, and set our desired Ga$_2$O$_3$ flux for the growth of Ga$_2$O$_3$. We measured the flux of the Ga$_2$O$_3$ (g) molecular beam reaching the growth surface prior to and after growth using a quartz crystal microbalance. The $10 \times 10$ mm$^2$ substrates were back-side coated with a 10 nm thick Ti adhesion layer followed by 200 nm of Pt, enabling the otherwise transparent substrates to be radiatively heated during MBE growth. For S-MBE growth the substrate was held within a substrate holder made of Haynes® 214® alloy, and loaded into the growth chamber. The growth temperature $T_G$ was measured by an optical pyrometer operating at a wavelength of 1550 nm. To determine the surface crystal phases during growth, in situ high-energy electron diffraction (RHEED) using 13 keV electrons was utilized. After growth x-ray reflectivity (XRR), optical reflectivity in a microscope (ORM),$^{42}$ 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, and STEM) and heteroepitaxial (XRR, ORM, SEM, STEM, and 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 Ka$_1$ radiation.

III. RESULTS FOR Ga$_2$O$_3$ USING S-MBE

A. Growth rates and growth model

Figure 6 plots the growth rate of Ga$_2$O$_3$ as a function of $\phi_{\text{Ga}_2\text{O}_3}$ at different $T_G$ and constant $\phi_G$. The growth rates obtained follow the anticipated growth kinetics depicted in Fig. 1(c). In the desorption-controlled regime, an increase in $\phi_{\text{Ga}_2\text{O}_3}$ (at otherwise constant growth parameters) does not lead to a decrease in the growth rate as observed for “conventional” Ga$_2$O$_3$ MBE [Fig. 1(b)]$^{15}$ 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 Ga$_2$O$_3$ (g) suboxide molecular beam while reducing the complexity of the Ga$_2$O$_3$ 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 Ga$_2$O$_3$ (s) 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
Changing the partial pressure of O\(_3\) in the chamber. Note that O\(_3\) supplies O to the surface of the growing film when it decomposes by the reaction: O\(_3\) (g) → O\(_2\) (g) + O (g). A similar behavior of an increasing desorption or recombination rate of active O species with increasing T\(_G\), has also been observed during O plasma-assisted MBE using elemental Ga and O molecular beams.

Based on this model, we scaled up \(\phi_0\) in order to achieve Ga\(_2\)O\(_3\) (s) growth rates that exceed 1 \(\mu\)m h\(^{-1}\). Figure 7(a) demonstrates our fastest (to date) growth rate of 1.6 \(\mu\)m h\(^{-1}\) of a β-Ga\(_2\)O\(_3\) thin film grown on Al\(_2\)O\(_3\)(0001), at T\(_G\) = 500 °C. For comparison, the data point plotted as a hollow hexagon (see also Fig. 6) shows the highest possible growth rate at a five times lower active \(\phi_0\) and similar T\(_G\). This result demonstrates, scaling up the active O enables S-MBE to scale up the growth rates of Ga\(_2\)O\(_3\) thin film exceeding 1 \(\mu\)m h\(^{-1}\).

The Ga\(_2\)O\(_3\), Ga\(_3\)O, and O adsorbate densities are denoted as \(n_{Ga_2O_3}, n_{Ga_3O},\) and \(n_O\), respectively. Their time derivative is described by the operator d/dt. The reaction rate constant \(k_{Ga_2O_3}\) kinetically describes the growth rate \(\Gamma\) of Ga\(_2\)O\(_3\) (s) on the growth surface. The desorption rate constants of Ga\(_2\)O and O adsorbates are denoted as \(y_{Ga_2O}\) and \(y_O\), respectively.

The flux of available O adsorbates, for Ga\(_2\)O to Ga\(_2\)O\(_3\) oxidation at a given T\(_G\), is determined by its sticking coefficient \(\sigma\) on the Ga\(_2\)O\(_3\) growth surface and is described by a sigmoid function

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

with dimensionless pre-factor \(\sigma_0\) and energy \(\Delta\sigma\). 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 Ga\(_2\)O oxidation and thus to lower growth rates.

We find that \(\sigma\) does not depend on the concentration of active O and only weakly on the partial pressure of active O (values not shown in this work). Thus, the active O may be scaled up or down by either changing the concentration of O\(_3\) in the O\(_3\) beam or by changing the partial pressure of O\(_3\) in the chamber. Note that O\(_3\) supplies O to the surface of the growing film when it decomposes by the reaction: O\(_3\) (g) → O\(_2\) (g) + O (g). A similar behavior of an increasing desorption or recombination rate of active O species with increasing T\(_G\), has also been observed during O plasma-assisted MBE using elemental Ga and O molecular beams.

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in the adsorption-controlled regime. In addition, the growth rate values plotted in Fig. 7(b) were obtained by homoepitaxial growth of $\beta$-Ga$_2$O$_3$(010) on 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 Fig. 7(a) (hollow diamond) and Fig. 7(b) (solid diamond), respectively. This result suggests that the growth rate of S-MBE grown on Ga$_2$O$_3$(010) and other surfaces of Ga$_2$O$_3$ may vastly exceed 1 $\mu$m$^{-1}$ in the adsorption-controlled regime. The higher growth rate of Ga$_2$O$_3$(010) compared with Ga$_2$O$_3$(201) is similar to what has been observed during the “conventional” MBE of Ga$_2$O$_3$.\cite{Sugiyama1987, Sugiyama1988} Fluctuations in $T_G$ and $\phi_{Ga_2O_3}$ for different samples and, e.g., during the long duration growth of the “thick” sample (>3 h), are considered by the standard deviations of the measured values of $T_G$ and $\phi_{Ga_2O_3}$, as given in Fig. 7.

B. Structural properties

We investigated the impact of variable growth conditions (i.e., $\phi_{Ga_2O_3}$, $\phi_O$, 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 hollow 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 is a measure of the out-of-plane mosaic spread of the Ga$_2$O$_3$ layer. The obtained $\Delta\omega = 0.11\times 400''$ (arc sec) does not change with the growth rate and is particularly remarkable since $\beta$-Ga$_2$O$_3$(201) films grown on Al$_2$O$_3$(0001), using elemental Ga$^{54+}$ or compound Ga$_2$O$_3$ sources, usually show much broader line profiles in their out-of-plane crystal distributions (from $\Delta\omega \approx 0.23''$ to $\Delta\omega \approx 1.00''$). 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$_3$ adsorbrates (crystallites) on the growth surface may occur, similar to the formation of Ga droplets during GaN growth.\cite{Wakino2013} 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 Ga$_2$O$_3$(201) films on Al$_2$O$_3$(0001) with thicknesses $>1$ $\mu$m and have not mapped all growth regimes (e.g., Ga$_2$O$_3$ “droplet” formation at very high $\phi_{Ga_2O_3}$). Further investigations of the structural perfection and electrical properties of Ga$_2$O$_3$ grown by S-MBE need to be performed. This could be particularly interesting for the growth of Ga$_2$O$_3$(s) at even higher Ga$_2$O$_3$ ($g$) fluxes, which push even further into the adsorption-controlled regime.

We used S-MBE to grow homoepitaxial $\beta$-Ga$_2$O$_3$(010) films on Ga$_2$O$_3$(010) substrates. Figure 9 shows the $\theta$–$2\theta$ XRD scans of two selected Ga$_2$O$_3$(010) films grown under the same growth conditions. The $\theta$–$2\theta$ XRD profiles of the Ga$_2$O$_3$(010) film with thickness $d = 0.74$ $\mu$m (plotted in blue) and the one of the substrate (data not shown) coincide. The Ga$_2$O$_3$(010) layer with $d = 4.55$ $\mu$m (depicted in gray) also shows small contributions of the meta stable $\gamma$-Ga$_2$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 and $d = 4.55$ $\mu$m is comparable and narrower than the one obtained for the bare Ga$_2$O$_3$(010) substrate (depicted as a black line). [Note that the measured XRD spectra were obtained on different 10 x 10 mm$^2$ substrates, which were all cut from the same 1 in. diameter Ga$_2$O$_3$(010) wafer from Synoptics.] We attribute the different rocking curve widths measured to the non-uniformity in the crystalline perfection across the 1 in. diameter Ga$_2$O$_3$ substrate on which these measurements were made.

STEM of the “thick” film with $d = 4.55$ $\mu$m [the same sample as plotted as a gray line in Fig. 9 and solid square in Fig. 7(b)] are shown in Figs. 10(a)–10(e). The epilayer shows a clear, uniform, and single-crystalline $\beta$-Ga$_2$O$_3$(010) film. Defects such as dislocations or strain fields are not observed throughout this sample, indicating the very high crystal quality of this film. Only a thin $\gamma$-Ga$_2$O$_3$(110) layer at the top of the surface of the Ga$_2$O$_3$(010)/Ga$_2$O$_3$(010) homoepitaxial film can be seen, as marked by white circles in Figs. 10(b), 10(d), and 10(e). The 440 $\gamma$-Ga$_2$O$_3$ peak measured by XRD is attributed to this thin surface phase, which may increase with increasing film thickness and $T_G$. The formation of a $\gamma$-Ga$_2$O$_3$ surface phase has also been
observed during the growth of $\beta$-$\text{Ga}_2\text{O}_3$ by “conventional” MBE and might be an intrinsic issue for the homoepitaxy of $\text{Ga}_2\text{O}_3(010)$.

The surface morphology of $\text{Ga}_2\text{O}_3(010)$ films grown by S-MBE at growth rates $>1$ $\mu$m h$^{-1}$ was investigated by atomic force microscopy (AFM) and is plotted in Figs. 11(a)–11(c). The root mean square (rms) roughness of the “thin” film with $d = 0.74$ $\mu$m is lower than the one measured for the “thick” film with $d = 4.1$ $\mu$m grown at similar conditions. The thick film with $d = 4.55$ $\mu$m grown at $T_G = 575$ °C shows a smoother surface, indicating that the thickness of the film does not influence the surface morphology detrimentally. This evolution in the rms roughness follows the same trend as observed by XRD scans of the same layers (blue and gray lines in the inset of Fig. 9), i.e., no decrease in crystalline quality with increasing film thickness of the $\text{Ga}_2\text{O}_3(010)/\text{Ga}_2\text{O}_3(010)$ structures was observed. We note that the difference in surface morphology seen in Figs. 11(a) and 11(b) may be caused by the slightly different off-cuts and crystal qualities among the bare $\beta$-$\text{Ga}_2\text{O}_3(010)$ substrates used, similar to the observed spread in rocking curves widths, as shown in Fig. 9.

### C. Impurities

We investigated the incorporation of impurities into the $\text{Ga}_2\text{O}_3(010)$ thin films grown with growth rates $>1$ $\mu$m h$^{-1}$ by SIMS. Figure 12 shows the SIMS profile of the same film as plotted in Fig. 7 (solid square) and Figs. 10 and 11(c). This profile reveals that the $\text{Ga}_2\text{O}_3$-rich ($\text{Ga} + \text{Ga}_2\text{O}_3$) mixtures employed lead to $\text{Ga}_2\text{O}_3(010)$ thin films with very low impurity incorporation. Only a slight increase of B $\sim 10^{16}$ cm$^{-3}$ is detected. This impurity likely originates from our use of an Al$_2$O$_3$ crucible for the $\text{Ga}_2\text{O}_3$-rich ($\text{Ga} + \text{Ga}_2\text{O}_3$) mixture. We note that we have also used pyrolytic boron nitride (pBN) crucibles for the $\text{Ga} + \text{Ga}_2\text{O}_3$ mixture but find high concentrations of B in the grown films by SIMS ($\sim 10^{20}$ B cm$^{-3}$) when the background pressure of a mixture of $\text{O}_2 + 80\%\text{O}_3$ is $P_0 = 5 \times 10^{-6}$ 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 $T_{\text{mix}} = 1020\,$°C used for growth, the vapor pressure of B$_2$O$_3$ is significant. The small Si and Al peaks measured at the film–substrate interface originate from unintentionally incorporated Si and Al at the substrate surface. Note that 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. All other detected impurities in the epitaxial layer, i.e., Si (SIMS detection limit signal, $S_{\text{Si}} = 5 \times 10^{15}$ cm$^{-3}$), Fe ($S_{\text{Fe}} = 1 \times 10^{15}$ cm$^{-3}$), Sn ($S_{\text{Sn}} = 5 \times 10^{14}$ cm$^{-3}$), Al ($S_{\text{Al}} = 2 \times 10^{16}$ cm$^{-3}$), In ($S_{\text{In}} = 2 \times 10^{15}$ cm$^{-3}$) (not shown), and C ($S_{\text{C}} = 5 \times 10^{16}$ cm$^{-3}$) (not shown) in the film are below the detection limit of the cation standards used.
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 the high Ga$_2$O fluxes used to grow Ga$_2$O$_3$ with growth rates exceeding $>$1 $\mu$m h$^{-1}$—do not lead to significant impurity incorporation into the grown Ga$_2$O$_3$(010) films. This is an advantage of S-MBE compared with the growth Ga$_2$O$_3$ from a crucible containing pure Ga$_2$O$_3$. Using a Ga$_2$O$_3$ compound source at extremely high effusion cell temperatures ($\sim$1700 °C) not only produces a flux containing a relatively low Ga$_2$O molecular beam resulting in low Ga$_2$O$_3$ film growth rates but also results in films contaminated with iridium. Nonetheless, electrical transport properties are extremely sensitive to impurities, and measurements of mobility in doped Ga$_2$O$_3$ films grown by S-MBE remain to be performed. It could turn out that a higher purity Ga$_2$O$_3$ powder will be needed than the 5N Ga$_2$O$_3$ powder we have used in this study.

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.

The quality of the homoepitaxial $\beta$-Ga$_2$O$_3$(010) films (with thicknesses $>$ 4.5 $\mu$m) assessed by XRD (Fig. 9), STEM (Fig. 10), AFM (Fig. 11), and SIMS (Fig. 12) reveal that S-MBE with growth rates $>$ 1 $\mu$m h$^{-1}$ 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 $\mu$m-range.

Based on our model and experimental results, we anticipate growth rates up to 5 $\mu$m h$^{-1}$ on Ga$_2$O$_3$(010) and other growth surfaces to be possible by S-MBE. This estimation is based on the physical MBE limit: the mean free path $\lambda$ of the species (e.g., Ga$_2$O and O$_3$) emanating from their sources to the target. In our estimate, we have used an upper limit for the O partial pressure of $P_O \sim 2 \times 10^{-4}$ Torr (resulting in $\lambda \sim 0.1$ m) and a lower $T_G$ limit of $T_G \geq 725$ °C [required for the adsorbed species (e.g., Ga$_2$O and O) to crystallize into a homoepitaxial film of Ga$_2$O$_3$ grown at a high growth rate].

IV. OUTLOOK AND ALTERNATIVES OF S-MBE

We have demonstrated the growth of high quality Ga$_2$O$_3$ (s) thin films by S-MBE in the adsorption-controlled regime using Ga (ℓ) + Ga$_2$O$_3$ (s) mixtures. The high growth rate $>$ 1 $\mu$m h$^{-1}$ and unparalled crystalline quality of the homoepitaxial and heteroepitaxial structures obtained (with $d \gg 1$ $\mu$m) suggest the possibility of unprecedented mobilities of Ga$_2$O$_3$ thin films containing n-type donors (Sn, Ge, Si) grown by S-MBE.
We have also developed Sn + SnO₂ and Ge + GeO₂ mixtures in order to produce SnO (g) and GeO (g) beams for use as n-type donors in Ga₂O₃-based heterostructures. Furthermore, we have grown SnO₂ using a Sn + SnO₂ mixture. Moreover, we have grown Ga₂O₃ doped with SnO using Ga₂O and SnO beams and achieved controllable Sn-doping levels in these Ga₂O₃ films. Nevertheless, the improvement of the n-type mobilities obtained during S-MBE, at growth rates >1 μm h⁻¹, still need to be demonstrated and shown to exceed the state-of-the-art mobilities in Ga₂O₃ films grown by “conventional” MBE.²⁹

Our comprehensive thermodynamic analysis of the volatility of 128 binary oxides plus additional two-phase mixtures of metals with their binary oxides, e.g., Ga + Ga₂O₃, 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 Ga₂O₃ enabled us to develop In + In₂O₃ and Ta + Ta₂O₅ mixtures from which we have grown high-quality bixbyte In₂O₃ and In₂O₃:SnO₂ (ITO) as well as rutile Ta₂O₅ by S-MBE, respectively.

Growing thin films with very high crystalline qualities at growth rates >1 μm h⁻¹ by using suboxide molecular beams—with up to 5 μm h⁻¹ anticipated growth rates by our model—will make MBE competitive with other established synthesis methods, such as CVD or MOVPE. The Tc₂ that we have demonstrated for high-quality Ga₂O₃ layers grown by S-MBE is significantly lower than what has been demonstrated for the growth of high-quality Ga₂O₃ films by CVD or MOVPE. This makes S-MBE advantageous for BEOL processing. Additionally, Ga₂O₃ grown with a vast excess of Ga₂O₃ (g) and high oxygen activity in Ga₂O₃-rich mixtures may suppress Ga vacancies in the Ga₂O₃ layers formed, which are believed to act as compensating acceptors—potentially improving the electrical performance of n-type Ga₂O₃-based devices significantly.

The development of Al + Al₂O₃ mixtures for the growth of epitaxial Al₂O₃ and (Al₉Ga₄)₂O₃ 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 required. However, sufficient nanometer scale smoothness. In addition, the use of an Al₂O₃ (g) and Ga₂O₃ (g) molecular beams during (Al₉Ga₄)₂O₃ S-MBE may also extend its growth domain toward higher adsorption-controlled regimes—being beneficial for the performance of (Al₉Ga₄)₂O₃-based heterostructure devices.

Our demonstration (not shown in this work) of high-quality films of Ga₂O₃, Ga₂O₃ doped with SnO, In₂O₃, ITO, Ta₂O₅, LanthO₃ and LaAlO₃ 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.³⁵ We anticipate S-MBE to be applicable to all materials that form via intermediate reaction products (a subcompound). Examples following this reasoning include ZrO₂, Pb₂(Zr, Ti)O₃, and (H₂ZrO) all via the supply of a molecular beam of ZrO₂ (predicted by our thermodynamic calculations)³⁶ Ga₂Se₅ via Ga₂Se₅, In₃Se₅ through In₃Se₅, In₃Te₅ by In₃Te₅, or Sn₃Se₅ via Sn₃Se₅.

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DATA AVAILABILITY

The data supporting the findings of this study are available within the paper. Additional data related to the growth and structural characterization are available at https://doi.org/10.34863/a2lw-kh18. Any additional data connected to the study are available from the corresponding author upon reasonable request.

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