



## Comparison of the growth kinetics of $\text{In}_2\text{O}_3$ and $\text{Ga}_2\text{O}_3$ and their suboxide desorption during plasma-assisted molecular beam epitaxy

Patrick Vogt and Oliver Bierwagen

Citation: [Applied Physics Letters](#) **109**, 062103 (2016); doi: 10.1063/1.4960633

View online: <http://dx.doi.org/10.1063/1.4960633>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/109/6?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Reaction kinetics and growth window for plasma-assisted molecular beam epitaxy of  \$\text{Ga}\_2\text{O}\_3\$ : Incorporation of Ga vs.  \$\text{Ga}\_2\text{O}\$  desorption](#)

[Appl. Phys. Lett.](#) **108**, 072101 (2016); 10.1063/1.4942002

[Growth model for plasma-assisted molecular beam epitaxy of N-polar and Ga-polar  \$\text{In}\_x\text{Ga}\_{1-x}\text{N}\$](#)

[J. Vac. Sci. Technol. B](#) **29**, 021206 (2011); 10.1116/1.3562277

[Rf-plasma-assisted molecular-beam epitaxy of  \$\beta\$ - \$\text{Ga}\_2\text{O}\_3\$](#)

[Appl. Phys. Lett.](#) **88**, 031105 (2006); 10.1063/1.2164407

[Growth kinetics of AlGaIn films by plasma-assisted molecular-beam epitaxy](#)

[Appl. Phys. Lett.](#) **81**, 295 (2002); 10.1063/1.1492853

[Kinetic modeling of N incorporation in GaInNAs growth by plasma-assisted molecular-beam epitaxy](#)

[Appl. Phys. Lett.](#) **77**, 214 (2000); 10.1063/1.126928

---

The advertisement features a blue background with a molecular structure graphic. On the left is a thumbnail of an 'Applied Physics Reviews' journal cover. The main text reads 'NEW Special Topic Sections' in large white letters. Below this, it says 'NOW ONLINE' in yellow, followed by 'Lithium Niobate Properties and Applications: Reviews of Emerging Trends' in white. The AIP Applied Physics Reviews logo is in the bottom right corner.

**NEW Special Topic Sections**

**NOW ONLINE**  
Lithium Niobate Properties and Applications:  
Reviews of Emerging Trends

**AIP** Applied Physics Reviews

# Comparison of the growth kinetics of $\text{In}_2\text{O}_3$ and $\text{Ga}_2\text{O}_3$ and their suboxide desorption during plasma-assisted molecular beam epitaxy

Patrick Vogt<sup>a)</sup> and Oliver Bierwagen<sup>b)</sup>

Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5–7, D-10117 Berlin, Germany

(Received 14 June 2016; accepted 25 July 2016; published online 8 August 2016)

We present a comprehensive study of the  $\text{In}_2\text{O}_3$  growth kinetics during plasma-assisted molecular beam epitaxy and compare it to that of the related oxide  $\text{Ga}_2\text{O}_3$  [P. Vogt and O. Bierwagen, Appl. Phys. Lett. **108**, 072101 (2016)]. The growth rate and desorbing fluxes were measured during growth *in-situ* by a laser reflectometry set-up and line-of-sight quadrupole mass spectrometer, respectively. We extracted the In incorporation as a function of the provided In flux, different growth temperatures  $T_G$ , and In-to-O flux ratios  $r$ . The data are discussed in terms of the competing formation of  $\text{In}_2\text{O}_3$  and desorption of the suboxide  $\text{In}_2\text{O}$  and O. The same three growth regimes as in the case of  $\text{Ga}_2\text{O}_3$  can be distinguished: (i) In-transport limited, O-rich (ii)  $\text{In}_2\text{O}$ -desorption limited, O-rich, and (iii) O-transport limited, In-rich. In regime (iii), In droplets are formed on the growth surface at low  $T_G$ . The growth kinetics follows qualitatively that of  $\text{Ga}_2\text{O}_3$  in agreement with their common oxide and suboxide stoichiometry. The quantitative differences are mainly rationalized by the difference in  $\text{In}_2\text{O}$  and  $\text{Ga}_2\text{O}$  desorption rates and vapor pressures. For the  $\text{In}_2\text{O}$ ,  $\text{Ga}_2\text{O}$ , and O desorption, we extracted the activation energies and frequency factors by means of Arrhenius-plots. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4960633>]

The transparent (semi)conducting oxide indium sesquioxide,  $\text{In}_2\text{O}_3$ , possesses a wide range of conventional device applications based on its conductivity and large band gap of  $E_g = (2.7 \pm 0.1)$  eV.<sup>1</sup> Undoped  $\text{In}_2\text{O}_3$  is used as an active gas-sensor material,<sup>2,3</sup> for instance.  $\text{In}_2\text{O}_3$  highly doped with tin, indium-tin oxide (ITO,  $\text{In}_2\text{O}_3:\text{Sn}$ ), is a transparent conducting oxide that is used as a transparent contact electrode for flat panel displays<sup>4</sup> or solar cells.<sup>5</sup>

Beyond these conventional applications,  $\text{In}_2\text{O}_3$  has the potential for novel applications<sup>1</sup> that benefit from well defined doping, e.g., with the donor Sn or the (deep) acceptor Mg, controlling the  $n$ -type conductivity from the highly conductive<sup>6</sup> to the semi-insulating<sup>7</sup> regime. In combination with the related gallium sesquioxide,  $\text{Ga}_2\text{O}_3$ , with  $E_g = (4.7 \pm 0.2)$  eV,<sup>8</sup> band gap engineering and heterostructure oxide devices are foreseeable.<sup>9</sup> The realization of semiconductor devices typically requires the highest crystalline quality which is commonly achieved by epitaxial growth methods. During plasma-assisted molecular beam epitaxy (MBE), fluxes of atomic In  $\Phi_{\text{In}}$  and plasma “activated” oxygen  $\Phi_{\text{O}}$  form  $\text{In}_2\text{O}_3$  on a heated, single crystalline substrate in an ultra-high vacuum chamber. MBE-grown  $\text{In}_2\text{O}_3$  has been reported on  $\text{Al}_2\text{O}_3(0001)$ ,<sup>3,10,11</sup>  $(10\bar{1}2)^{12}$   $(11\bar{2}0)$ ,<sup>13</sup> and Y-stabilized  $\text{ZrO}_2(001)^{14}$  or  $(111)$ ,<sup>3</sup> for instance.

Oxides are typically grown under O-rich growth conditions, i.e., by providing excess O for the reaction with In. However, the In-rich growth conditions are known to improve the structural quality of  $\text{In}_2\text{O}_3(001)$ <sup>15,16</sup> by preventing faceting and should also help to suppress the formation of compensating acceptor point defects (oxygen interstitials or metal vacancies).<sup>17</sup>

The growth rate  $\Gamma$  of  $\text{In}_2\text{O}_3$  is limited by  $\Phi_{\text{In}}$  under O-rich growth conditions, and thus increases linearly with it

up to the stoichiometric flux  $\Phi_{\text{SF}}$  which consumes all available oxygen for the  $\text{In}_2\text{O}_3$  formation.<sup>18</sup> At  $\Phi_{\text{In}} > \Phi_{\text{SF}}$ , the In-rich growth regime is entered, where  $\Gamma$  decreases with increasing  $\Phi_{\text{In}}$  due to the oxygen-deficiency-induced formation of the volatile suboxide  $\text{In}_2\text{O}$ , which desorbs off subsequently.<sup>18</sup>

We have shown qualitatively the same behavior for the related oxide  $\text{Ga}_2\text{O}_3$  which has the same oxide and suboxide stoichiometry.<sup>18,19</sup> Furthermore, our comprehensive investigation of  $\text{Ga}_2\text{O}_3$  growth revealed a  $\Gamma$ -plateau in the O-rich regime at high growth temperatures  $T_G$ , which was also due to the suboxide desorption of  $\text{Ga}_2\text{O}$ .

In this letter, we show how  $\Gamma$  is governed by the competition between  $\text{In}_2\text{O}_3$  layer growth and desorption of  $\text{In}_2\text{O}$  and O as a function of  $T_G$ ,  $\Phi_{\text{In}}$ , and  $\Phi_{\text{O}}$ . We use the same methodology as for  $\text{Ga}_2\text{O}_3$ <sup>19</sup> and show that the reaction kinetics of  $\text{In}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  have qualitatively the same behaviour. The quantitative differences of the  $\Gamma$ -evolutions of  $\text{In}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  are analyzed by fitting the desorbing  $\text{In}_2\text{O}$ ,  $\text{Ga}_2\text{O}$ , and O fluxes as a function  $T_G$  on an Arrhenius-plot and extract the activation energies  $E_{\text{a,des}}^i$  as well as the frequency factors  $A_i$  of both materials. Finally, we rationalize these differences by the different  $\text{In}_2\text{O}$  and  $\text{Ga}_2\text{O}$  desorption activation energies and their vapor pressures.

Textured, non-polycrystalline  $\text{In}_2\text{O}_3(111)$  with rotational domains<sup>3,11</sup> was grown on single-side polished 2 inch  $\text{Al}_2\text{O}_3(0001)$  substrates. The rough back side of the substrate was sputter-coated with titanium to improve substrate heating. During growth,  $T_G$  was measured with a pyrometer. A low  $T_G$  nucleation layer was used to ensure complete wetting<sup>14</sup> of the substrate and mimic homoepitaxy. Our custom made MBE system is equipped with a laser reflectometry set-up and line-of-sight quadrupole mass spectrometer (QMS) that allow to measure *in-situ*  $\Gamma$  and the desorbing  $\text{In}_2\text{O}$  from the  $\text{In}_2\text{O}_3$  growth surface  $\Phi_{\text{des}}^{\text{In}_2\text{O}}$ , respectively.<sup>18,19</sup>

<sup>a)</sup>Electronic mail: vogt@pdi-berlin.de

<sup>b)</sup>Electronic mail: bierwagen@pdi-berlin.de

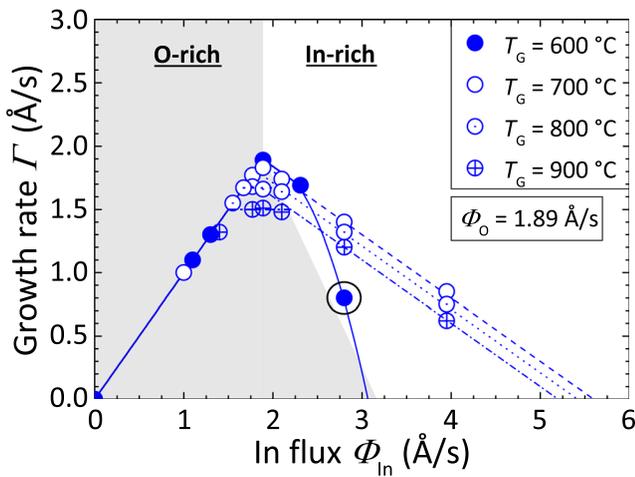


FIG. 1. The  $\text{In}_2\text{O}_3$  growth rate  $\Gamma$  as a function of the In flux  $\Phi_{\text{In}}$  at constant O flux  $\Phi_{\text{O}}$  of  $1.89 \text{ \AA/s}$  at four different growth temperatures  $T_G$ . For  $T_G > 700 \text{ }^\circ\text{C}$ ,  $\Gamma$  plateaus in the O-rich regime. The lines are guides to the eye.

However, due to the large mass of  $\text{In}_2\text{O}$  of 246 atomic mass units, the signal-to-noise ratio was low, which prevented reliable quantification of  $\Phi_{\text{des}}^{\text{In}_2\text{O}}$  by our QMS data. Instead,  $\Phi_{\text{des}}^{\text{In}_2\text{O}}$  was determined indirectly as the difference between the provided  $\Phi_{\text{In}}$  and  $\Gamma$  as described below and justified by the same Me-to-O stoichiometry like  $\text{Ga}_2\text{O}_3$ .<sup>19</sup> The crystallinity of the oxide films was verified *in-situ* by a spotty reflection high energy electron diffraction pattern during growth and *ex-situ* by X-ray diffraction  $\omega$ - $2\theta$  scans (not shown). A standard shuttered hot-lip effusion cell was used to evaporate liquid In (7N 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. Following the calibration reported in Refs. 18 and 19, the relation of  $\Phi_{\text{In}}$  between the measured BEP,  $\Gamma$ , and the In-particle flux is  $\Phi_{\text{In}} = 5.67 \times 10^{-7} \text{ Torr} \hat{=} 1.0 \text{ \AA/s} \hat{=} 3.1 \text{ In-atoms nm}^{-2} \text{ s}^{-1}$ , respectively. A radio frequency plasma source with a mass flow controller supplied  $\Phi_{\text{O}}$  from the research-grade  $\text{O}_2$  gas (6N purity). The radio frequency power was maintained at 200 W for the  $\text{In}_2\text{O}_3$  growth. The  $\text{O}_2$  mass flow was set to 0.5 standard cubic centimeters per minute (SCCM) resulting in  $\Phi_{\text{O}} = 5 \times 10^{-6} \text{ Torr} \hat{=} 1.89 \text{ \AA/s} \hat{=} 8.85 \text{ O-atoms nm}^{-2} \text{ s}^{-1}$ .

In order to investigate the origin of the In loss during growth and being able to compare it quantitatively with the Ga loss during  $\text{Ga}_2\text{O}_3$  growth, we conducted the same experiments as reported in Ref. 19.

The  $\Gamma$ -evolution of  $\text{In}_2\text{O}_3$  as a function of  $\Phi_{\text{In}}$  for different  $T_G$  is depicted in Fig. 1. In the O-rich regime and  $T_G = 700 \text{ }^\circ\text{C}$  (open discs), the In incorporation (i.e.,  $\Gamma$ ) increases linearly with  $\Phi_{\text{In}}$  until the stoichiometric flux ratio is reached at  $\Phi_{\text{In}} = \Phi_{\text{O}} = 1.89 \text{ \AA/s}$ . This ratio corresponds to  $r = \Phi_{\text{In}}/\Phi_{\text{O}} = 1$ . For a higher  $r > 1$ , the growth shifts into the In-rich regime and  $\Gamma$  decreases until the growth completely stops at  $\Phi_{\text{In}} \geq 3\Phi_{\text{O}}$ <sup>18</sup> showing the same trend in  $\Gamma$  as for  $\text{Ga}_2\text{O}_3$  growth which is due to the same Me-to-O stoichiometry of these compounds.

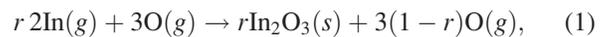
In the In-rich regime at lower  $T_G = 600 \text{ }^\circ\text{C}$  (filled discs), In forms droplets on the growth surface as observed by scanning electron microscopy (not shown), which strongly reduces  $\Gamma$  as exemplarily indicated by the black circle in Fig. 1.

Increasing  $T_G > 700 \text{ }^\circ\text{C}$  while keeping  $\Phi_{\text{In}}$  and  $\Phi_{\text{O}}$  identical leads to a different  $\Gamma$ -evolution. The maximum  $\Gamma$  is decreased in comparison to the growth at  $T_G = 700 \text{ }^\circ\text{C}$ . In addition, a plateau of  $\Gamma$  as for the  $\text{Ga}_2\text{O}_3$  growth<sup>19</sup> in the O-rich regime is present. Comparing the  $\Gamma$ -evolution of  $\text{In}_2\text{O}_3$  plotted in Fig. 1 with the one of  $\text{Ga}_2\text{O}_3$  indicates that the loss of  $\Gamma$  is caused by  $\text{In}_2\text{O}$  and O desorption. This behavior is quantitatively described in Ref. 19 for  $\text{Ga}_2\text{O}_3$  growth and can be readily transferred to the  $\text{In}_2\text{O}_3$  growth in this letter. The length of the plateau  $\lambda$  is parameterized and defined in Ref. 19 by the fraction of the maximum O flux that is available to oxidize In to  $\text{In}_2\text{O}_3$  or  $\text{In}_2\text{O}$ , named as  $\alpha$ , and the maximum  $\Gamma$  normalized by  $\Phi_{\text{O}}$  in the O-rich regime, named as  $\beta$ . Note, that the normalization by  $\Phi_{\text{O}}$  is reasonable since the surface reaction kinetics is determined by the Me-to-O flux ratio as reported in Ref. 19 for  $\text{Ga}_2\text{O}_3$  and exemplarily shown for  $\text{In}_2\text{O}_3$  in Fig. 3 different  $\Phi_{\text{In}}$  and  $\Phi_{\text{O}}$  but same  $r$  (filled and crossed discs).

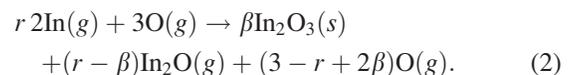
A qualitative explanation that  $\text{In}_2\text{O}$  and not In desorption is responsible for the plateau of  $\Gamma$  in the O-rich regime is the following: the decreasing  $\Gamma$  with increasing  $r$  in the In-rich regime for all investigated  $T_G > 700 \text{ }^\circ\text{C}$  is due to the oxygen-deficiency-induced  $\text{In}_2\text{O}$  formation and *not* because of In desorption.<sup>18</sup> For this reason, In desorption instead of  $\text{In}_2\text{O}$  formation and its desorption at even lower  $r$  in the O-rich regime (i.e., in the excess of O) is unphysical. Indium desorption, in turn, would lead to a plateau in the In-rich regime (i.e., O-limited growth regime) and not to a decrease of  $\Gamma$  as plotted in Fig. 1.

Three growth regimes of  $\text{In}_2\text{O}_3$  are the same as in the  $\text{Ga}_2\text{O}_3$  growth:<sup>19</sup> (i) In-transport-limited O-rich growth regime with full In incorporation (the linear increase of the normalized  $\Gamma$  by  $\Phi_{\text{O}}$  ( $\rho = \Gamma/\Phi_{\text{O}}$ ) with  $r$ ), (ii)  $\text{In}_2\text{O}$ -desorption-limited O-rich growth regime with partial In incorporation (the plateau of  $\rho = \beta$ ), and (iii) O-transport-limited In-rich growth regime with partial In incorporation (the decrease of  $\rho$  with  $r$ ).

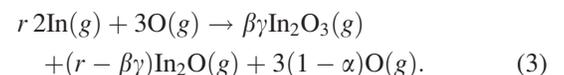
For regime (i), i.e., for  $0 \leq r < \beta \leq 1$ , the reaction is



with  $g$  and  $s$  indicating the gaseous and solid phases, respectively. The plateau in regime (ii) for  $0 < \beta \leq r \leq \beta + \lambda = 3\alpha - 2\beta$  is described by the reaction



The end of the plateau  $r = \beta + \lambda$  corresponds to stoichiometric growth conditions. For In-rich growth in regime (iii),  $\beta + \lambda < r \leq 3\alpha$ , the growth rate decreases and



The coefficient  $\gamma = -(r - 3\alpha/2\beta)$  decreases linearly with increasing  $r$  from unity at  $r = \beta + \lambda = 3\alpha - 2\beta$  to zero at  $r = 3\alpha$ .

Now we discuss the quantitative differences in the  $\Gamma$ -evolutions of  $\text{In}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  regarding the flux range of

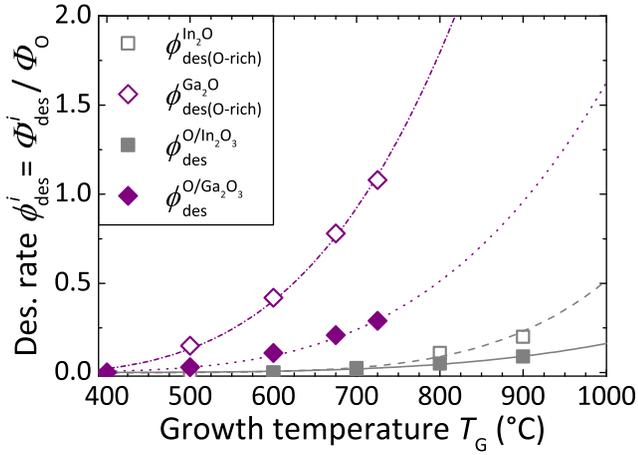


FIG. 2. Maximum desorption rates from the respective growth surface normalized by  $\Phi_O$  of the suboxides ( $\phi_{\text{des(O-rich)}}^{\text{Me}_2\text{O}}$ ) and O ( $\phi_{\text{des}}^{\text{O/Me}_2\text{O}_3}$ ) as a function of  $T_G$ . The lines are Arrhenius-plots according to Eq. (6).

the plateau, the metal adsorption, and suboxide desorption temperature. Figure 2 plots the normalized  $\text{In}_2\text{O}$  (open squares),  $\text{Ga}_2\text{O}$  (open diamonds), and O (filled squares and diamonds) desorption rates from respective  $\text{In}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  surfaces  $\phi_{\text{des(O-rich)}}^{\text{Me}_2\text{O}}$  and  $\phi_{\text{des}}^{\text{O/Me}_2\text{O}_3}$  with  $\text{Me} = \text{In, Ga}$  as a function of  $T_G$ . The index (O-rich) refers to the maximum suboxide desorption in the O-rich regime at the end of the plateau where all O is either consumed for layer growth or suboxide formation. The desorption rates are described as

$$\phi_{\text{des}}^{\text{O/Me}_2\text{O}_3}(T_G) = 1 - \alpha(T_G), \quad (4)$$

$$\phi_{\text{des(O-rich)}}^{\text{Me}_2\text{O}}(T_G) = \lambda(T_G) = 3(\alpha(T_G) - \beta(T_G)). \quad (5)$$

In order to obtain the desorption rates in  $\text{\AA}/\text{s}$ , these values are multiplied by  $\Phi_O$ . It can be seen that  $\phi_{\text{des(O-rich)}}^{\text{Ga}_2\text{O}} > \phi_{\text{des(O-rich)}}^{\text{In}_2\text{O}}$  and  $\phi_{\text{des}}^{\text{O/Ga}_2\text{O}_3} > \phi_{\text{des}}^{\text{O/In}_2\text{O}_3}$  for all measured  $T_G$ . The quantitative difference of the  $\Gamma$ -evolutions of  $\text{In}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  becomes clear in Fig. 3. Here, for the sake of clarity,  $\Gamma$  is normalized by its maximum value ( $\mathcal{R} = \Gamma/\Gamma_{\text{max}}$ ) and plotted as a function of  $T_G$  for both materials at different  $r$ . For  $\text{In}_2\text{O}_3$ , in the highly O-rich regime (filled and crossed discs)  $\mathcal{R}$  is constant over the entire range of  $T_G$ . At higher  $\Phi_{\text{In}}$ , for example, at  $r = 1$  (stoichiometric growth, open discs) and  $r = 1.5$  (In-rich growth, dotted discs)  $\mathcal{R}$  decreases slightly due to  $\text{In}_2\text{O}$  and O desorption in both regimes (as also plotted in Figs. 1 and 2). For  $\text{Ga}_2\text{O}_3$  (triangles), in contrast, the decrease of  $\mathcal{R}$  is much stronger due to stronger  $\text{Ga}_2\text{O}$  and O desorption as can be seen by different  $\phi_{\text{des}}^i$  with  $i = \text{Me}_2\text{O}, \text{O/Me}_2\text{O}_3$  for both materials (Fig. 2) that cause the decrease of  $\Gamma$  at the same  $T_G$ .

To quantitatively evaluate  $\phi_{\text{des}}^i$ , we use exponential fits to the data plotted in Fig. 2

$$\phi_{\text{des}}^i(T_G) = A_i \exp\left(-\frac{E_{\text{a,des}}^i}{k_B T_G}\right), \quad (6)$$

with  $k_B$  the Boltzmann constant. The activation energy of desorption  $E_{\text{a,des}}^i$  and frequency factor  $A_i$  obtained by fitting the data plotted in Fig. 2 by Eq. (6) (Arrhenius-plot) is given in Table I. In Fig. 4, the obtained functions for  $\phi_{\text{des}}^{\text{Me}_2\text{O}}$  and

TABLE I. Obtained activation energies for desorption  $E_{\text{a,des}}^i$  and frequency factors  $A_i$  by fitting the data plotted in Fig. 2 by Eq. (6) (Arrhenius-plot).

	$\text{In}_2\text{O}$	$\text{Ga}_2\text{O}$	$\text{O/In}_2\text{O}_3$	$\text{O/Ga}_2\text{O}_3$
$E_{\text{a,des}}^i$ (eV)	$1.03 \pm 0.19$	$0.59 \pm 0.01$	$0.74 \pm 0.05$	$0.68 \pm 0.03$
$A_i \times 10^3$	6.19	1.04	0.14	0.79

(for comparison to them) the equilibrium vapor pressures  $p_j$  with  $j = \text{In, Ga, In}_2\text{O, and Ga}_2\text{O}$  as a function of  $T_G$  are depicted. We converted the fluxes into units of standard atmospheres (atm) by kinetic theory of gases ( $p_k = \Phi_{\text{des}}^k \sqrt{2\pi m_k k_B T_G}$  with mass of the suboxide  $m_k$  and  $k = \text{Ga}_2\text{O, In}_2\text{O}$ ). It can be seen that the desorbing rates of  $\text{Ga}_2\text{O}$  and  $\text{In}_2\text{O}$  and corresponding vapor pressures show the same trend, i.e.,  $\phi_{\text{des}}^{\text{Ga}_2\text{O}}$  is larger than  $\phi_{\text{des}}^{\text{In}_2\text{O}}$  by roughly one order of magnitude. We conclude that the higher vapor pressure of  $\text{Ga}_2\text{O}$  compared to that of  $\text{In}_2\text{O}$  causes the higher sensitivity of  $\Gamma$  to  $T_G$  for  $\text{Ga}_2\text{O}_3$  growth.

In the In-rich regime (iii) at  $T_G \leq 600^\circ\text{C}$ , In forms droplets, whereas no Ga droplet formation was observed under similar growth conditions for  $\text{Ga}_2\text{O}_3$  growth down to  $T_G = 500^\circ\text{C}$ .<sup>19</sup> In order to understand this difference, we quantitatively compare the vapor pressures of the suboxides with the loss of  $\Gamma$  in the Me-rich regime. Exemplarily, we obtain  $\phi_{\text{des}}^{\text{In}_2\text{O}} = 4.0 \times 10^{-9}$  atm (star in Fig. 4 and circle in Fig. 1 at  $\Phi_{\text{In}} = 2.8 \text{ \AA}/\text{s}$ ) and  $\phi_{\text{des}}^{\text{Ga}_2\text{O}} = 6.4 \times 10^{-10}$  atm (filled square in Fig. 4 in this letter and Fig. 1 in Ref. 19 at  $\Phi_{\text{Ga}} = 4 \text{ \AA}/\text{s}$ ) for the loss in  $\Gamma$  of  $\text{In}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$ , respectively. In both cases,  $p_{\text{In}_2\text{O}}$  and  $p_{\text{Ga}_2\text{O}}$  are well in excess of the loss of  $\Gamma$ , which means that In droplet formation is not caused by limited  $\text{In}_2\text{O}$  desorption. As an alternative explanation, we suggest the oxidation velocity of In to  $\text{In}_2\text{O}_3$  to be slower than that of Ga to  $\text{Ga}_2\text{O}_3$ , since here, all Ga could be oxidized at even lower  $T_G$  and  $p_{\text{Ga}_2\text{O}}$ . Comparing  $p_{\text{In}}$  and  $p_{\text{Ga}}$  shows that Me desorption for both materials is not the reason for the decreasing  $\Gamma$  in the Me-rich regime.

In summary, we studied the plasma-assisted oxide molecular beam epitaxy of  $\text{In}_2\text{O}_3$ . The In flux, In-to-O flux ratio, and growth temperature were systematically changed

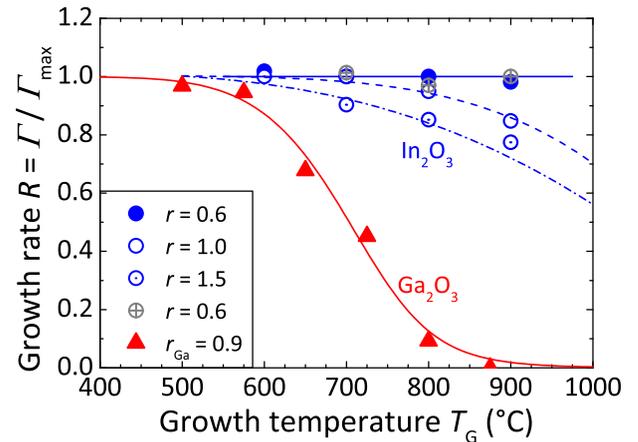


FIG. 3. Growth rate normalized by its maximum value  $\mathcal{R} = \Gamma/\Gamma_{\text{max}}$  as a function of growth temperature  $T_G$  for different In fluxes  $\Phi_{\text{In}}$ . The O flux  $\Phi_O$  was  $1.89 \text{ \AA}/\text{s}$  (filled, open, and dotted discs) and  $3.78 \text{ \AA}/\text{s}$  (crossed discs). The triangles show  $\mathcal{R}$  for  $\text{Ga}_2\text{O}_3$  at  $r_{\text{Ga}} = \Phi_{\text{Ga}}/\Phi_O = 0.9$  with  $\Phi_O = 1.7 \text{ \AA}/\text{s}$ . The lines are guides to the eye.

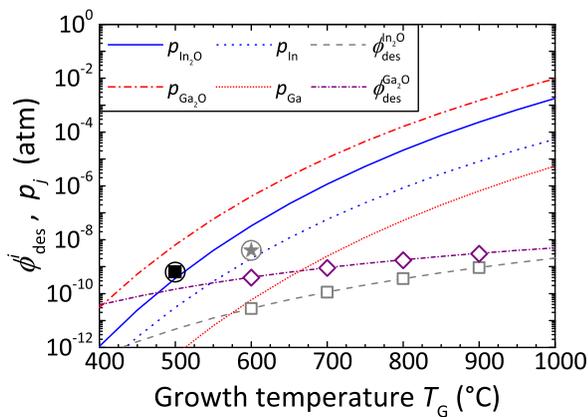


FIG. 4. The normalized desorption rates by  $\Phi_O$  ( $\phi_{des(O-rich)}^{Me_2O}$ ) and the vapor pressure curves of the suboxides and metals  $p_j$  ( $j = \text{In}_2\text{O}$  (solid line<sup>20</sup>),  $\text{Ga}_2\text{O}$  (dashed-dotted line<sup>21</sup>),  $\text{In}$  (dotted line<sup>22</sup>),  $\text{Ga}$  (short-dotted red line<sup>22</sup>)) as a function of growth temperature  $T_G$  are plotted. The lines are functions according to Eq. (6). The filled square and star are quantitative examples of  $\phi_{des(O-rich)}^{Ga_2O}$  and  $\phi_{des(O-rich)}^{In_2O}$ , respectively (values given in the text).

in order to understand the surface reaction kinetics of the  $\text{In}_2\text{O}_3$  growth and compared it to that of  $\text{Ga}_2\text{O}_3$  discussed in Ref. 19. In qualitative agreement with  $\text{Ga}_2\text{O}_3$  growth, our results indicate three distinctive growth regimes: (i) complete  $\text{In}$  incorporation, i.e.,  $\text{In}$ -transport-limited growth regime (O-rich), (ii) plateau of the growth rate at increasing  $\text{In}$  flux ( $\text{In}_2\text{O}$ -desorption-limited growth regime, O-rich), and (iii) a decreasing growth rate at increasing  $\text{In}$  flux, i.e., O-transport-limited growth regime ( $\text{In}$ -rich). In all cases, the difference between provided fluxes and growth rate is related to the desorption of  $\text{In}_2\text{O}$  and  $\text{O}$ . No  $\text{In}$  desorption was observed at all investigated growth temperatures. At lower growth temperatures, in the metal-rich regime,  $\text{In}$  droplet formation was detected for  $\text{In}_2\text{O}_3$  whereas for  $\text{Ga}_2\text{O}_3$  no  $\text{Ga}$  accumulation was observed under similar growth conditions. As the suboxide vapor pressures cannot explain this qualitative difference, we propose slower oxidation of  $\text{In}$  than  $\text{Ga}$  to be the cause. Growth rates lower than the  $\text{In}$  flux were either caused by the growth in the  $\text{In}$  rich regime, a higher growth temperature, or  $\text{In}$  accumulation. The suboxide desorption was fitted by an Arrhenius-plot, yielding activation energies and frequency factors that can be used with Eqs. (4)–(6) to calculate the  $\text{In}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  MBE growth rates for all growth temperatures above the metal adsorption

temperature. The strong (weak) decrease of the  $\text{Ga}_2\text{O}_3$  ( $\text{In}_2\text{O}_3$ ) growth rate with increasing growth temperature is related to the higher vapor pressure of  $\text{Ga}_2\text{O}$  than that of  $\text{In}_2\text{O}$ .

These findings can be likely transferred to ozone MBE and may also be a qualitative guidance for the  $\text{In}_2\text{O}_3$  growth by metal-organic chemical vapor deposition. In addition, the overall reaction kinetics might be generalized to all oxides that possess suboxides when knowing their vapor pressures.

We would like to thank Vladimir Kaganer for critically reading the manuscript, Hans-Peter Schönherr for technical MBE support, and Anne-Kathrin Bluhm for SEM imaging.

<sup>1</sup>O. Bierwagen, *Semicond. Sci. Technol.* **30**, 024001 (2015).

<sup>2</sup>C. Y. Wang, V. Cimalla, T. Kups, C.-C. Röhlig, T. Stauden, O. Ambacher, M. Kunzer, T. Passow, W. Schirmacher, W. Pletschen *et al.*, *Appl. Phys. Lett.* **91**, 103509 (2007).

<sup>3</sup>J. Rombach, A. Papadogianni, M. Mischo, V. Cimalla, L. Kirste, O. Ambacher, T. Berthold, S. Krischok, M. Himmerlich, S. Selve *et al.*, “The role of surface electron accumulation and bulk doping for gas-sensing explored with single-crystalline  $\text{In}_2\text{O}_3$  thin films,” *Sens. Actuators, B* (published online).

<sup>4</sup>G. S. Chae, *Jpn. J. Appl. Phys., Part 1* **40**, 1282 (2001).

<sup>5</sup>A. N. Tiwari, G. Khrypunov, F. Kurdzesau, D. L. Bätzner, A. Romeo, and H. Zogg, *Prog. Photovoltaics: Res. Appl.* **12**, 33 (2004).

<sup>6</sup>O. Bierwagen and J. S. Speck, *Phys. Status Solidi A* **211**, 48 (2014).

<sup>7</sup>O. Bierwagen and J. S. Speck, *Appl. Phys. Lett.* **101**, 102107 (2012).

<sup>8</sup>M. Higashiwaki, K. Sasaki, H. Murakami, Y. Kumagai, A. Koukitu, A. Kuramata, T. Masui, and S. Yamakoshi, *Semicond. Sci. Technol.* **31**, 034001 (2016).

<sup>9</sup>S. Fujita and K. Kaneko, *J. Cryst. Growth* **401**, 588 (2014).

<sup>10</sup>Z. Mei, Y. Wang, X. Du, Z. Zeng, M. Ying, H. Zheng, J. Jia, Q. Xue, and Z. Zhang, *J. Cryst. Growth* **289**, 686 (2006).

<sup>11</sup>K. H. L. Zhang, V. K. Lazarov, P. L. Galindo, F. E. Oropeza, D. J. Payne, and R. G. Egdell, *Cryst. Growth Des.* **12**, 1000 (2012).

<sup>12</sup>P. Vogt, A. Trampert, M. Ramsteiner, and O. Bierwagen, *Phys. Status Solidi A* **212**, 1433 (2015).

<sup>13</sup>M. Y. Chern, Y. C. Huang, and W. L. Xu, *Thin Solid Films* **515**, 7866 (2007).

<sup>14</sup>O. Bierwagen and J. S. Speck, *J. Appl. Phys.* **107**, 113519 (2010).

<sup>15</sup>O. Bierwagen, M. E. White, M.-Y. Tsai, and J. S. Speck, *Appl. Phys. Lett.* **95**, 262105 (2009).

<sup>16</sup>O. Bierwagen, J. Rombach, and J. S. Speck, *J. Phys.: Condens. Matter* **28**, 224006 (2016).

<sup>17</sup>S. Lany and A. Zunger, *Phys. Rev. Lett.* **98**, 045501 (2007).

<sup>18</sup>P. Vogt and O. Bierwagen, *Appl. Phys. Lett.* **106**, 081910 (2015).

<sup>19</sup>P. Vogt and O. Bierwagen, *Appl. Phys. Lett.* **108**, 072101 (2016).

<sup>20</sup>J. Valderrama-N and K. T. Jacob, *Thermochim. Acta* **21**, 215 (1977).

<sup>21</sup>C.-J. Frosch and C.-D. Thurmond, *J. Phys. Chem.* **66**, 877 (1962).

<sup>22</sup>C. B. Alcock, V. P. Itkin, and M. K. Horrigan, *Can. Metall. Q.* **23**, 309 (1984).