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Kinetic modeling of N incorporation in GaInNAs growth by plasma-assisted molecular-beam epitaxy
Comparison of the growth kinetics of In$_2$O$_3$ and Ga$_2$O$_3$ and their suboxide desorption during plasma-assisted molecular beam epitaxy

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We present a comprehensive study of the In$_2$O$_3$ growth kinetics during plasma-assisted molecular beam epitaxy and compare it to that of the related oxide Ga$_2$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 In$_2$O$_3$ and desorption of the suboxide In$_2$O and O. The same three growth regimes as in the case of Ga$_2$O$_3$ can be distinguished: (i) In-transport limited, O-rich (ii) In$_2$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 Ga$_2$O$_3$ in agreement with their common oxide and suboxide stoichiometry. The quantitative differences are mainly rationalized by the difference in In$_2$O and Ga$_2$O desorption rates and vapor pressures. For the In$_2$O, Ga$_2$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 sesquis-oxide, In$_2$O$_3$, possesses a wide range of conventional device applications based on its conductivity and large band gap of $E_g = (2.7 \pm 0.1) \text{ eV}$. Undoped In$_2$O$_3$ is used as an active gas-sensor material, for instance. In$_2$O$_3$ highly doped with tin, indium-tin oxide (ITO, In$_2$O$_3$:Sn), is a transparent conducting oxide that is used as a transparent contact electrode for flat panel displays or solar cells.

Beyond these conventional applications, In$_2$O$_3$ has the potential for novel applications that benefit from well-defined faceting and should also help to suppress the formation of compensating acceptor point defects (oxygen interstitials or metal vacancies).

The growth rate $\Gamma$ of In$_2$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 In$_2$O$_3$ formation. 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 In$_2$O, which desorbs off subsequently.

We have shown qualitatively the same behavior for the related oxide Ga$_2$O$_3$ which has the same oxide and suboxide stoichiometry. Furthermore, our comprehensive investigation of Ga$_2$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 Ga$_2$O.
However, due to the large mass of In2O of 246 atomic mass units, the signal-to-noise ratio was low, which prevented reliable quantification of $\Phi_{\text{In}}^{\text{des}}$ by our QMS data. Instead, $\Phi_{\text{In}}^{\text{des}}$ 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 Ga2O3. Mechanical pulling of these compounds.

Increasing $T_G > 700$ °C while keeping $\Phi_{\text{In}}$ and $\Phi_O$ identical leads to a different $\Gamma$-evolution. The maximum $\Gamma$ is decreased in comparison to the growth at $T_G = 700$ °C. In addition, a plateau of $\Gamma$ as for Ga2O3 growth19 in the O-rich regime is present. Comparing the $\Gamma$-evolution of In2O3 plotted in Fig. 1 with the one of Ga2O3 indicates that the loss of $\Gamma$ is caused by In2O and O desorption. This behavior is quantitatively described in Ref. 19 for Ga2O3 growth and can be readily transferred to the In2O3 growth in this letter.

Three growth regimes of In2O3 are the same as in the Ga2O3 growth19, (i) In-transport-limited O-rich growth regime with full In incorporation (the linear increase of the normalized $\Gamma$ by $\Phi (\rho = \Gamma/\Phi_O)$ with $\rho$), (ii) In2O-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 $\rho$).

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

$$r \text{In}_2\text{O}_3(g) + 3\text{O}_2(g) \rightarrow r\text{In}_2\text{O}_3(s) + (3 - r)\text{O}_3(g),$$

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

$$r \text{In}_2\text{O}_3(g) + 3\text{O}_2(g) \rightarrow r\text{In}_2\text{O}_3(s) + (3 - r + 2\beta)\text{O}_3(g).$$

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

$$r \text{In}_2\text{O}_3(g) + 3\text{O}_2(g) \rightarrow r\text{In}_2\text{O}_3(s) + (3 - r - z)\text{O}_3(g).$$

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

Now we discuss the quantitative differences in the $\Gamma$-evolutions of In2O3 and Ga2O3 regarding the flux range of...
The quantitative difference of the Ga$_2$O$_3$ becomes clear in Fig. 3. Here, for the sake of clarity, in Table I. In Fig. 4, the obtained functions for values are multiplied by to the data plotted in Fig. 2

\[
\frac{\phi_{\text{des}}^{\text{O/MezO}}(T_G)}{\phi_O} = 1 - \alpha(T_G),
\]

\[
\phi_{\text{MezO}}^{\text{des(O-rich)}}(T_G) = \lambda(T_G) = \beta(T_G) - \alpha(T_G),
\]

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

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

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

In the In-rich regime (iii) at $T_G \leq 600{\degree}\text{C}$, In droplets, whereas no Ga droplet formation was observed under similar growth conditions for Ga$_2$O$_3$ growth down to $T_G = 500{\degree}\text{C}$. 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 $\phi_{\text{In$_2$O$_3$}}^\text{des} = 4.0 \times 10^{-9}$ atm (star in Fig. 4 and circle in Fig. 1 at $\Phi_{\text{In}} = 2.8$ Å/s and $\phi_{\text{Ga$_2$O$_3$}}^\text{des} = 6.4 \times 10^{-10}$ atm (filled square in Fig. 4 in this letter and Fig. 1 in Ref. 19 at $\Phi_{\text{Ga$_2$O$_3$}} = 4$ Å/s) for the loss in $\Gamma$ of In$_2$O$_3$ and Ga$_2$O$_3$, respectively. In both cases, $p_{\text{In$_2$O$_3$}}$ and $p_{\text{Ga$_2$O$_3$}}$ are well in excess of the loss of $\Gamma$, which means that In droplet formation is not caused by limited In$_2$O desorption. As an alternative explanation, we suggest the oxidation velocity of In to In$_2$O$_3$ to be slower than that of Ga to Ga$_2$O$_3$, since here, all Ga could be oxidized at even lower $T_G$ and $p_{\text{Ga$_2$O$_3$}}$. Comparing $p_{\text{In$_2$O$_3$}}$ and $p_{\text{Ga$_2$O$_3$}}$ 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 In$_2$O$_3$. The In flux, In-to-O flux ratio, and growth temperature were systematically changed.

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

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_{a,\text{des}}^i$ (eV)</th>
<th>$A_i \times 10^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$O</td>
<td>1.03 ± 0.19</td>
<td>6.19</td>
</tr>
<tr>
<td>Ga$_2$O</td>
<td>0.59 ± 0.01</td>
<td>1.04</td>
</tr>
<tr>
<td>O/In$_2$O$_3$</td>
<td>0.74 ± 0.05</td>
<td>0.14</td>
</tr>
<tr>
<td>O/Ga$_2$O$_3$</td>
<td>0.68 ± 0.03</td>
<td>0.79</td>
</tr>
</tbody>
</table>

**FIG. 2.** Maximum desorption rates from the respective growth surface normalized by $\Phi_O$ of the suboxides ($\phi_{\text{des(O-rich)}}^{\text{MezO}}$) and O ($\phi_{\text{des}}^{\text{O/MezO}}$) as a function of $T_G$. The lines are Arrhenius-plots according to Eq. (6). **FIG. 3.** Growth rate normalized by its maximum value $R = \Gamma / \Gamma_{\text{max}}$ as a function of growth temperature $T_G$ for different In fluxes $\Phi_{\text{In}}$. The O flux $\Phi_O$ was 1.89 Å/s (filled, open, and dotted discs) and 3.78 Å/s (crossed discs). The triangles show $R$ for Ga$_2$O$_3$ at $r_{\text{Ga}} = \Phi_{\text{Ga$_2$O$_3$}} / \Phi_O = 0.9$ with $\Phi_O = 1.7$ Å/s. The lines are guides to the eye.
in order to understand the surface reaction kinetics of the In$_2$O$_3$ growth and compared it to that of Ga$_2$O$_3$ discussed in Ref. 19. In qualitative agreement with Ga$_2$O$_3$ growth, our results indicate three distinctive growth regimes: (i) complete In incorporation, i.e., In-transport-limited growth regime (O-rich), (ii) plateau of the growth rate at increasing In flux (In$_2$O-desorption-limited growth regime, O-rich), and (iii) a decreasing growth rate at increasing In flux, i.e., O-transport-limited growth regime (In-rich). In all cases, the difference between provided fluxes and growth rate is related to the desorption of In$_2$O and O. No In desorption was observed at all investigated growth temperatures. At lower growth temperatures, in the metal-rich regime, In droplet formation was detected for In$_2$O whereas for Ga$_2$O$_3$ no Ga accumulation was observed under similar growth conditions. As the suboxide vapor pressures cannot explain this qualitative difference, we propose slower oxidation of In than Ga to be the cause. Growth rates lower than the In flux were either caused by the growth in the In rich regime, a higher growth temperature, or 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 In$_2$O$_3$ and Ga$_2$O$_3$ MBE growth rates for all growth temperatures above the metal adsorption temperature. The strong (weak) decrease of the Ga$_2$O$_3$ (In$_2$O$_3$) growth rate with increasing growth temperature is related to the higher vapor pressure of Ga$_2$O than that of In$_2$O.

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

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

FIG. 4. The normalized desorption rates by $\Phi_0$ ($\Phi_{\text{des}}(\text{In}_{\text{rich}})$) and the vapor pressure curves of the suboxides and metals $p_j$ (In$_2$O (solid line$^{20}$), Ga$_2$O (dashed-dotted line$^{21}$), In (dotted line$^{22}$), Ga (short-dotted red line$^{22}$)) 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 $\Phi_{\text{des}}(\text{Ga}_{\text{rich}})$ and $\Phi_{\text{des}}(\text{In}_{\text{rich}})$, respectively (values given in the text).