Suboxide-related kinetics, etching, thermodynamics, and catalysis governing the MBE of Ga_2O_3, In_2O_3, SnO_2 and $(In,Ga)_2O_3$

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We have investigated the reaction kinetics and thermodynamics of Ga_2O_3, In_2O_3, and their alloy as a function of the MBE growth parameters [1–7], metal flux, oxygen flux, and substrate temperature. Measured quantities were the growth rate (rate of metal incorporation), the flux desorbing off the substrate, and the layer composition (in case of a simultaneous In and Ga flux). Based on the results we (i) identified layer etching by the corresponding metal, (ii) developed a generalized, quantitative reaction model that describes the binary growth rates, (iii) demonstrated the significant impact of the different strength of Ga-O and In-O bonds for the composition of the alloy $(In,Ga)_2O_3$, and (iv) discovered a catalytic effect that strongly widens the growth window of Ga_2O_3 towards higher growth temperatures and rates. While these studies were performed with heteroepitaxial Ga_2O_3 layers on c-plane sapphire, we also demonstrated the catalyzed growth for the case of homoepitaxy of $Ga_2O_3(010)$.[8] Moreover, from the fact that the suboxide SnO plays a role for layer etching and growth of SnO_2 we conclude on the generality of our findings for compounds that possess subcompounds that are volatile at growth temperature (i.e. not limited to the case of sesquioxides).[1,5] Refs. [1—4] resulted mainly from preparatory work for GraFOx (already performed before GraFOx was started in July 2016), whereas Refs. [5,6,8] originate completely from GraFOx work. Ref. [7] is a book chapter that summarizes all our findings and compares them to available literature.

Compared to other established semiconductors such as GaN, InN or their alloy, the metal (Me) incorporation evolution of our investigated oxides is different. This difference becomes apparent in the Me-rich growth regime where the growth rate of the binary oxides Ga_2O_3 and In_2O_3 decreases with increasing Me flux, as exemplarily shown in Fig. 1 for Ga_2O_3 growth. This behavior is related to the formation and desorption of the volatile suboxides Ga_2O for Ga_2O_3 and In_2O and In_2O_3 [1–3] as opposed to pure metal desorption resulting in a growth-rate plateau during the growth of GaN or InN. In addition, a higher growth temperature T_G further activates suboxide desorption, leading to a decreased growth rate even in the O-rich regime (discs and triangles in Fig. 1).[2] We have found qualitatively similar trends for the growth of SnO_2.[1,5] We consistently explain these results by a two-step reaction mechanism shown in Fig. 2.

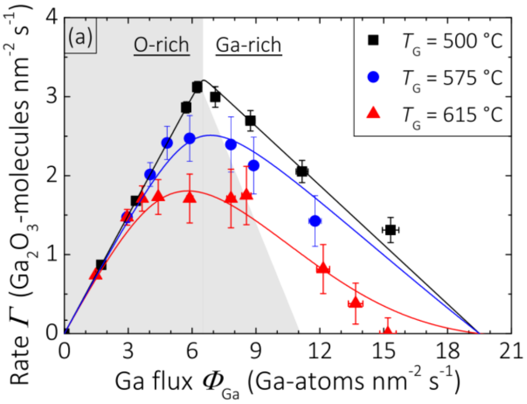

Fig. 1: The growth rate of Ga_2O_3 as function of the Ga flux for different growth temperatures. The O flux was kept constant.

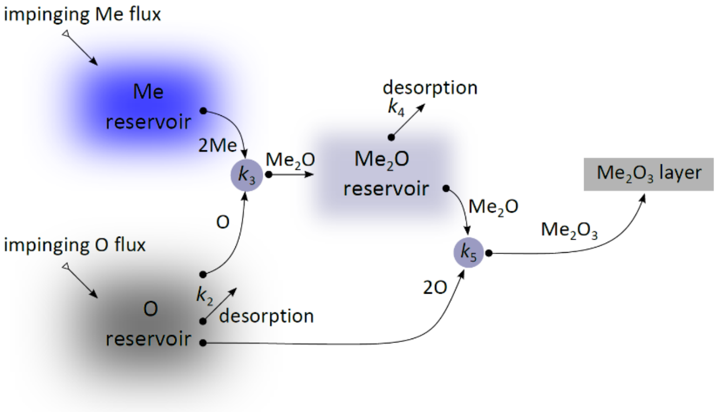

Fig. 2: Reaction scheme for Me_2O_3 MBE (Me=In, Ga), including all possible reactions occurring on the growth surface with reaction rate constants k_i.

The rapid formation of the suboxide occurs in the first oxidation step of the Me (characterized by a high rate constant k_3). The formed suboxide can be further oxidized to the solid oxide Me_2O_3 through a second oxidation step (characterized by rate constant k_5) if sufficient oxygen is available. Otherwise, the suboxide may concurrently desorb (characterized by rate constant k_4) due to a lack of oxygen or driven by a high substrate temperature. The growth-temperature dependence enters the model by an activated behavior of all rate constants. A quantitative description of the associated growth kinetics by a simple rate-equation based model largely explains the observed dependence of the growth rate on the growth parameters (c.f. lines in Fig.1 for the case of Ga_2O_3). We believe this model to be generally valid for the MBE of compounds that possess volatile subcompounds and have demonstrated its validity for Ga_2O_3, In_2O_2, and SnO_2.[5]

When exposing the oxide film to its respective metal at elevated temperature in the absence of oxygen (in the MBE growth chamber) we were able to etch the oxide (film or substrate) by suboxide formation and desorption according to:

$$4Me + Me_2O_3 \rightarrow 3Me_2O \text{ and}$$

$$Sn + SnO_2 \rightarrow 2SnO$$

for the case of sesquioxides Me=Ga, In and for SnO_2 with its respective suboxide SnO, respectively.[1] Besides the technological significance of etching substrate surfaces prior to growth to remove unintentional surface impurities, demonstrated by Ahmadi et al. at UCSB [9], these reactions can be also utilized in suboxide effusion cells that require significantly lower cell temperatures than necessary for the suboxide formation and sublimation by decomposition of the oxide material itself. We have demonstrated this approach in project C3.10 with the example of a SnO and a Ga_2O source.

While the growth kinetics are qualitatively the same for Ga_2O_3 and In_2O_3, a weaker dependence on T_G and generally higher achievable growth rates at fixed O-flux were found for In_2O_3. This quantitative difference originates from: (i) the lower vapor pressure of In_2O compared to that of Ga_2O, and (ii) the higher oxidation efficiency of In compared to the one of Ga.[1,3]

Despite the strong kinetic advantage for the oxidation of In, we found Ga atoms to be thermodynamically favorably incorporated into $In_xGa_{1-x}O_3$.[4] This behavior is shown in Fig. 3 (filled and crossed symbols). In reference experiments, we observed the decomposition of In_2O_3 by a supply of Ga adatoms but no decomposition of Ga_2O_3 by In adatoms. These results reveal that the Ga–O bonds are stronger than the In–O bonds in $In_xGa_{1-x}O_3$, in agreement with thermochemical calculations.[4] However, the thermodynamic suppression of In by Ga can be kinetically controlled by the supplied O flux. For example, a strong excess of O (inset of Fig. 3) enables full In incorporation whereas no In is incorporated under metal-rich growth conditions. These thermodynamic findings are not limited to MBE but also apply, for example, to pulsed laser deposition (PLD) of $(In_xGa_{1-x})_2O_3$ layers with decreased and full In-incorporation at a low and high O_2-pressure, respectively. This was demonstrated by our associated partner Leipzig University.[see Fig. 1 of Ref. 10]

Conversely, at ternary growth conditions with suppressed In-incorporation we found a significantly higher Ga_2O_3 growth rate compared to the growth of Ga_2O_3 in the absence of In. This systematic behavior, shown in Fig. 4 (top) can be understood by the kinetically favored oxidation of In (due to higher oxidation efficiency) and subsequent exchange of In by the thermodynamically favored Ga by the (net) reactions:

$$2In + 3O \rightarrow In_2O_3 \qquad \text{and} \qquad 2Ga + In_2O_3 \rightarrow Ga_2O_3 + 2In.$$

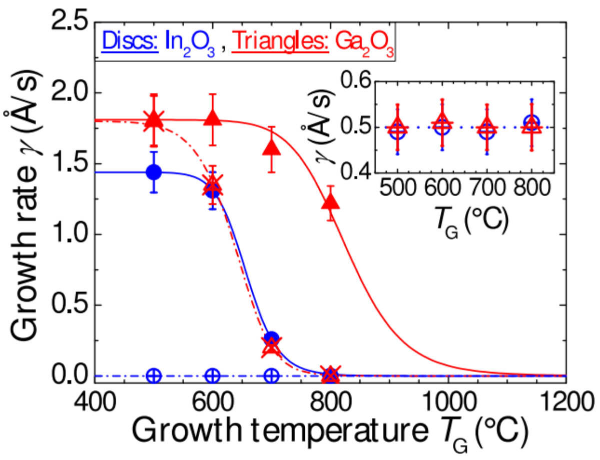

Fig. 3: Pseudo-binary growth rates of In_2O_3 (discs) and Ga_2O_3 (triangles) from the ternary compound $(In_xGa_{1-x})_2O_3$ as a function of growth temperature. The In-to-(In+Ga) flux ratio was set to 0.5. The impact of the (In+Ga)-to-O flux ratio r_{Me} is demonstrated by different symbols: filled (O-rich, $r_{Me}=0.5$), crossed (Me-rich, $r_{Me}=2.0$), and inset: highly O-rich, $r_{Me}=0.1$).

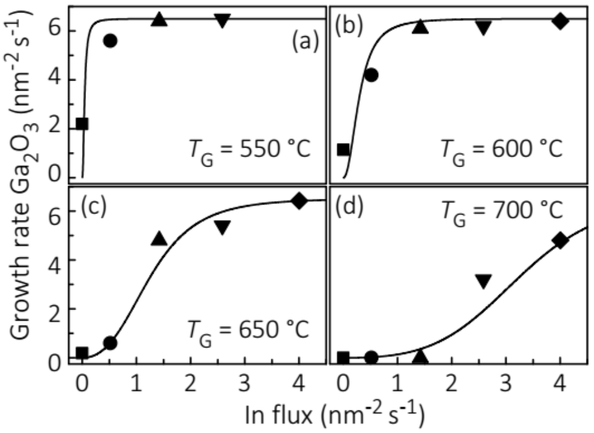

Fig. 4: (a)–(d) Dependence of the growth rate of Ga_2O_3 on the In flux for different growth temperatures as indicated in the figures. Symbols represent experimental data and solid lines are model predictions.[6]

The In adatoms which result from the In–Ga exchange in In_2O_3 can be re-oxidized before desorbing, and thus catalyzes Ga_2O_3 growth. This metal-exchange catalysis strongly extends the Ga_2O_3 growth domain towards higher T_G because the rate-limiting step for Ga_2O_3 formation in the absence of In – i.e. the formation and desorption of the volatile suboxide Ga_2O [5] – is bypassed.[6] Kracht et al. at Giessen University demonstrated that metal-exchange catalysis is not limited to In as catalyst. Instead of In, they used Sn,[11] which also has a significantly higher oxidation efficiency than Ga.[1]

Our first studies of growing the application-relevant β-Ga_2O_3(010) confirmed our previous results from heteroepitaxy. Also for the case of homoepitaxy, substrate etching by a Ga-flux as well as a significant growth rate enhancement by metal-exchange catalysis is observed. [8] Fig. 5 shows the strongly enhanced growth rate of β-Ga_2O_3(010) at high growth temperature by metal-exchange catalysis using an additional In-flux.

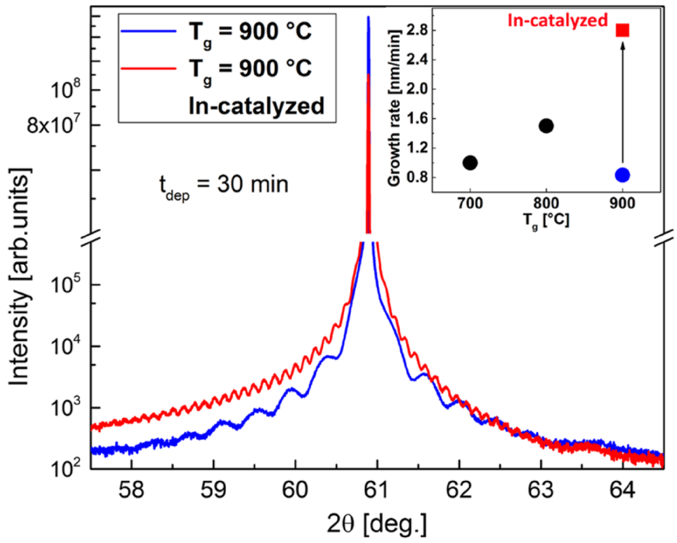

Fig. 5: XRD 2theta-omega scan of the (020) reflection of the same homoepitaxially grown layers with (red curve) and without (blue) an additional In-flux of 1/3 the Ga-flux during the deposition process at a growth temperature of 900°C, a Ga flux of 2.2 $nm^{-2}s^{-1}$ (corresponding to a growth rate of 3.5 nm/min at full incorporation), and slightly Ga-rich growth conditions. The inset shows the corresponding growth rates extracted from the thickness fringes as well as those of lower growth temperatures without additional In-flux.

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GraFox publications are highlighted by an “*”.