

(Fundamentals of the) Molecular Beam Epitaxy of Sesquioxides: The example of Ga₂O₃, In₂O₃, and their alloy

O. Bierwagen^{1,*}, P. Vogt¹, P. Mazzolini¹

¹ Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany

*Corresponding author: bierwagen@pdi-berlin.de

Abstract

This talk will quantitatively discuss and model the two-step growth kinetics identified for the MBE of In₂O₃ and Ga₂O₃. The oxides grow via intermediate formation and competing desorption of the volatile suboxide In₂O and Ga₂O. The thermodynamic advantage for the Ga₂O₃ formation that counteracts the kinetic advantage for the In₂O₃ formation leads to preferred Ga-incorporation during the growth of their alloy and even an enhancement of the Ga₂O₃ growth rate without any In-incorporation by metal-exchange catalysis. For the device-application relevant homoepitaxy of Ga₂O₃(010) under Ga₂O-desorption limited growth conditions the formation of {110} facets and a strongly enhanced growth rate by metal-exchange catalysis under an additional In-flux are demonstrated. The kinetic and thermodynamic concepts can be generalized to further oxides possessing volatile suboxides and physical vapor deposition methods.

1. Introduction

In₂O₃ and Ga₂O₃ are well-known semiconducting oxides with band gaps of 2.7 and ≈ 4.8 eV, respectively, that are conventionally used in gas sensing applications. Recently, Ga₂O₃ has been recognized as a promising wide band-gap semiconductor for novel applications, such as, power electronics and UV sensing. Band-gap engineering by alloying In₂O₃ and Ga₂O₃ can tune the detection wavelength of UV sensors and enable heterostructure devices. These novel applications require doped, single crystalline material that can be grown by molecular beam epitaxy (MBE). Understanding the fundamentals that control the growth of oxide films by MBE significantly enhances our control over the growth.

2. Experimental

For the present MBE study the In and Ga metal fluxes were provided from conventional effusion cells whereas molecular oxygen passed through an RF plasma source provided the activated oxygen flux. We measured the desorption and growth rate in-situ during heteroepitaxy on c-Al₂O₃ substrates by line-of-sight quadrupole mass spectrometry and laser reflectivity, respectively. The films composition of the alloy was measured after growth by scanning electron microscopy-based energy dispersive X-ray spectroscopy. For the homoepitaxial films on Ga₂O₃(010) substrates the surface morphology was measured in-situ by reflection high-energy electron diffraction as well as ex-situ atomic force microscopy (AFM) and the layer thickness was determined from the Pendellösung fringes of ex-situ X-ray diffraction (XRD). The growth kinetics and thermodynamics governing the metal incorporation was derived from growth series at constant oxygen flux with varying metal fluxes (from highly oxygen-rich to highly metal-rich) and varying growth temperatures.

3. Results and Discussion

The two-step growth via the intermediate formation and potential desorption of the volatile suboxide and comparison is schematically illustrated in Fig.1. Based on this schematics the growth rate of Ga₂O₃ was quantitatively modeled by rate-equations and is compared to experimental data [1, 2] in Fig.2.[4] The kinetically preferred oxidation of In over that of Ga is illustrated in Fig.3 by a higher peak growth rate.[1, 3]. Fig.4 shows a stronger decrease of the In- than the Ga-incorporation at increasing growth temperature during growth of InGaO₃, illustrating the thermodynamically preferred incorporation of Ga over In.[5] Formation of a regular surface with {110} facets under Ga-rich growth conditions is indicated in Fig.5.[7] The strongly enhance growth rate due to metal exchange catalysis [6] is demonstrated in Fig.5 for homoepitaxy of Ga₂O₃(010).[7]

4. Conclusion

A detailed understanding of the growth kinetics and thermodynamics allows the model-based prediction of the growth window and regions therein that lead to improved material quality. The In-based metal exchange catalysis strongly widens this growth window enabling high growth rates at high growth temperatures required for a high material quality. The above findings likely apply to further oxides with similar kinetic and thermodynamic properties. The {110} facets found during homoepitaxy on Ga₂O₃(010) suggest the (110) surface to be a potentially more stable substrate orientation for Ga₂O₃ homoepitaxy under Ga-rich conditions.

Acknowledgements

This work was performed in the framework of GraFOx, a Leibniz-ScienceCampus partially funded by the Leibniz association.

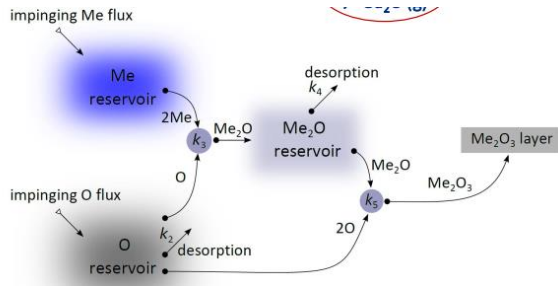


Fig.1: Schematics of the 2-step growth model involving suboxide (Me_2O) formation in a first step (rate constant k_3), further oxidation to the Me_2O_3 layer (rate constant k_5) and competing suboxide desorption ((rate constant k_4).

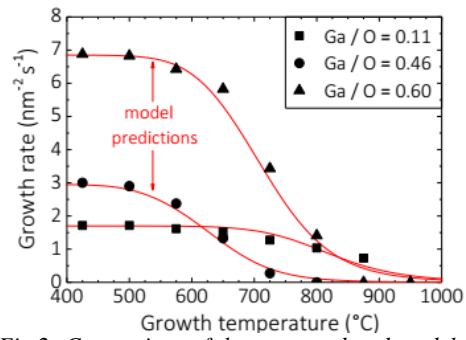


Fig.2: Comparison of the measured and modeled Ga_2O_3 growth rate under different Ga/O flux ratios as a function of growth temperature.

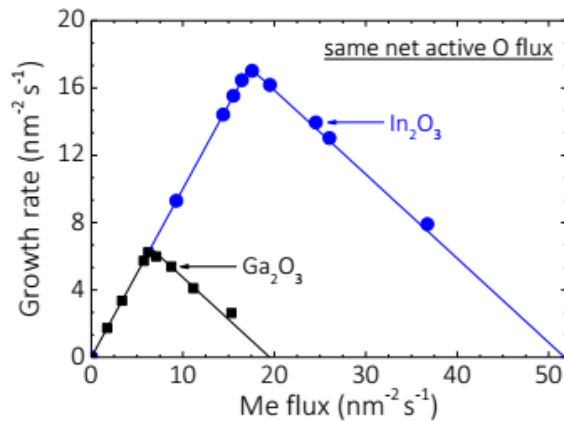


Fig.3: Comparison of the Ga_2O_3 and In_2O_3 growth kinetics at low growth temperature indicating the kinetic advantage for In_2O_3 formation due to larger oxidation efficiency.

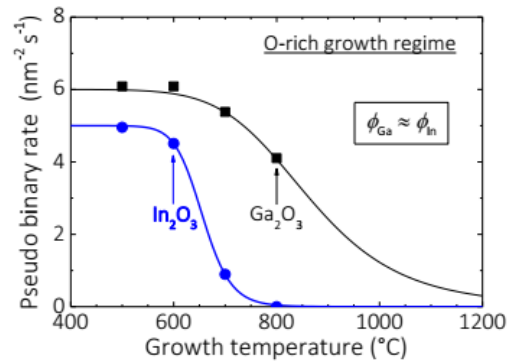


Fig.4: Comparison of In- and Ga-incorporation during nominal InGaO_3 growth under slightly O-rich conditions. At elevated temperatures the thermodynamically preferred Ga-incorporation becomes apparent.

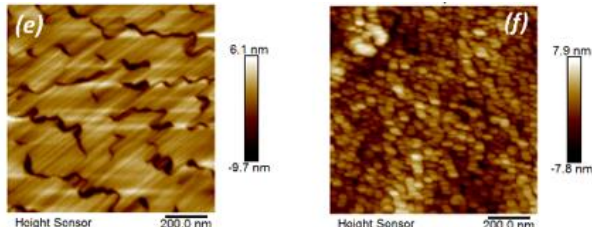


Fig.5: AFM images of homoepitaxial $\text{Ga}_2\text{O}_3(010)$ films grown under (e) slightly Ga-rich and (f) O-rich conditions indicating a regular, faceted (e) and rough (f) surface.

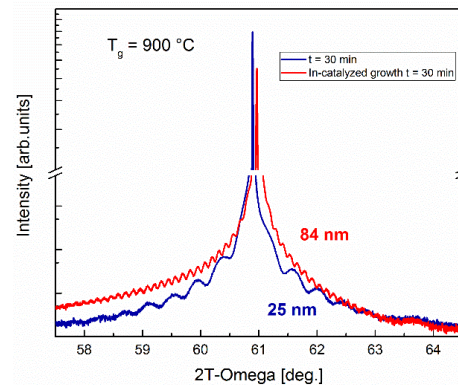


Fig.6: XRD symmetric out-of-plane 2-Theta-omega scans of homoepitaxial $\text{Ga}_2\text{O}_3(010)$ films grown under slightly Ga-rich conditions with (red) and without (blue) additional In-flux. The film thickness derived from the Pendellösung fringes indicates a significantly increased growth rate due to the metal-exchange catalysis.

References

- [1] P. Vogt et al., Appl. Phys. Lett. 106 (2015) 081910
- [2] P. Vogt et al., Appl. Phys. Lett. 108 (2016) 072101
- [3] P. Vogt et al., Appl. Phys. Lett. 109 (2016) 062103
- [4] P. Vogt et al., (submitted) (2018)
- [5] P. Vogt et al., APL Materials 4 (2016) 086112
- [6] P. Vogt et al., Phys. Rev. Lett. 119 (2017) 196001
- [7] P. Mazolini et al., in preparation (2018)