Substrate-orientation dependence of $\beta$-Ga$_2$O$_3$ (100), (010), (001), and ($\overline{2}01$) homoepitaxy by indium-mediated metal-exchange catalyzed molecular beam epitaxy (MEXCAT-MBE)
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ABSTRACT

We experimentally demonstrate how In-mediated metal-exchange catalysis (MEXCAT) allows us to widen the deposition window for $\beta$-$\text{Ga}_2\text{O}_3$ homoepitaxy to conditions otherwise prohibitive for its growth via molecular beam epitaxy (e.g., substrate temperatures $\geq 800^\circ\text{C}$) on the major substrate orientations, i.e., (010), (001), (\bar{2}01), and (100) $6^\circ$-offcut. The obtained crystalline qualities, surface roughnesses, growth rates, and In-incorporation profiles are shown and compared with different experimental techniques. The growth rates, $\Gamma$, for fixed growth conditions are monotonously increasing with the surface free energy of the different orientations with the following order: $\Gamma(010) > \Gamma(001) > \Gamma(\bar{2}01) > \Gamma(100)$. Ga$_2$O$_3$ surfaces with higher surface free energy provide stronger bonds to the surface ad-atoms or ad-molecules, resulting in decreasing desorption, i.e., a higher incorporation/growth rate. The structural quality in the case of (\bar{2}01), however, is compromised by twin domains due to the crystallography of this orientation. Notably, our study highlights $\beta$-$\text{Ga}_2\text{O}_3$ layers with high structural quality grown by MEXCAT-MBE not only in the most investigated (010) orientation but also in the (100) and (001) ones. In particular, MEXCAT on the (001) orientation results in both growth rate and structural quality comparable to the ones achievable with (010), and the limited incorporation of In associated with the MEXCAT deposition process does not change the insulating characteristics of unintentionally doped layers. The (001) surface is therefore suggested as a valuable alternative orientation for devices.

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electrical properties of the deposited layers\(^9\) but can be prevented by an appropriate offcut of the substrate as recently demonstrated by MOVPE (100)-homoepitaxy.\(^7\) On (010)-oriented substrates, the symmetry of the growth surface prevents double positioning and thus twin formation. For the other available Ga\(_3\)O\(_5\) orientations—\(\theta\), (001) and (201)—systematic experimental work on the structural quality of the deposited layers is lacking so far. The second challenge is the limited growth rate during MBE of Ga\(_2\)O\(_3\),\(^8,11,15\) which is related to the peculiar two-step growth kinetics via the intermediate formation of the suboxide Ga\(_2\)O\(_3\) in the first step and its further oxidation to Ga\(_2\)O\(_3\) in the second step.\(^9\) As Ga\(_2\)O\(_3\) has a significantly higher vapor pressure than Ga,\(^9\) its desorption limits the growth rate due to the following three factors: (1) metal-rich conditions, providing insufficient O-flux \(\Phi_0\) to oxidize all formed suboxide,\(^9\) (2) high substrate temperatures (\(T_g\)) at which the thermally activated desorption of Ga\(_2\)O\(_3\) outperforms its oxidation even under O-rich growth conditions,\(^9\) and (3) \(\bar{\beta}\)-Ga\(_2\)O\(_3\) substrate orientations that provide only weak bonds to the adsorbed Ga\(_2\)O\(_3\), resulting in a low activation energy for its desorption. In fact, surfaces with higher stability (i.e., cleavage planes) such as (100) and (001) have been found to suffer from very limited growth rates with respect to noncleavage planes such as (010) during MBE,\(^9,10,15\) while MOVPE evidences almost identical growth rates for \(\bar{\beta}\)-Ga\(_2\)O\(_3\) homoepitaxy on different substrate orientations.

For these reasons, the homoepitaxy of \(\bar{\beta}\)-Ga\(_2\)O\(_3\) by MBE has so far been mostly restricted to the (010) orientation and growth conditions that are not limiting its growth rate (e.g., O-rich, \(T_g < 800^\circ\mathrm{C}\))\(^10,15,23\). In contrast, metal-rich deposition conditions are predicted to avoid the formation of gallium vacancies (acting as compensating deep acceptors)\(^10,15\) and higher \(T_g\) generally result in higher crystalline quality and allows us to increase the stability range of \(\bar{\beta}\)-(Al\(_x\)Ga\(_{1-x}\))\(_2\)O\(_3\) alloys.\(^9\) Moreover, substrate orientations other than (010) are desirable to mitigate the following drawbacks: (i) the (010) surface has been shown to be unstable under metal-rich growth conditions, i.e., resulting in the formation of (110)-facets,\(^9\) and (ii) it is not a cleavage plane and therefore currently more challenging to be prepared with respect to the (001), (201), and (100) surfaces, at least without considering the possible need of defined substrate offsets. Consequently, there is a need to increase the growth rate for crystal orientations other than (010) and interest in exploring growth conditions that so far have prevented layer growth by MBE, i.e., high \(T_g\) and metal-rich conditions.

MBE growth using metal-exchange catalysis\(^23,24\) (MEXCAT) is a promising avenue to overcome these limitations. This process is based on the collaborative effect of kinetically favored formation of intermediate In\(_2\)O\(_3\) (which can grow at lower O-flux and higher \(T_g\) than Ga\(_2\)O\(_3\))\(^12,18\) and the subsequent thermodynamically driven exchange of its In-atoms by Ga (due to stronger Ga–O than In–O bonds).\(^9\) In-mediated MEXCAT-MBE has been shown to enable a high Ga\(_2\)O\(_3\) growth rate with limited In-incorporation under conditions (Ga-rich, high \(T_g\)) prohibitive for growth of Ga\(_2\)O\(_3\) due to severe Ga\(_2\)O desorption.\(^24\) Likewise, Sn-flux mediated Ga\(_2\)O\(_3\) heteroepitaxy by MEXCAT-MBE\(^21\) lead to the same qualitative results, demonstrating the generality of the MEXCAT approach for MBE. Both Sn- and In-mediated MEXCAT-MBE performed on top of a buffer layer of (201)-oriented \(\bar{\beta}\)-Ga\(_2\)O\(_3\) on c-plane sapphire substrates resulted in the formation of the metastable \(\bar{k}\)-phase of Ga\(_2\)O\(_3\).\(^23,24,26\) Recently, In-mediated MEXCAT on \(\bar{\beta}\)-Ga\(_2\)O\(_3\) (010) substrates has been demonstrated to triple the Ga\(_2\)O\(_3\) growth rate under Ga-rich conditions at \(T_g = 900^\circ\mathrm{C}\) preserve the monoclinic structure, and maintain a low surface roughness (rms < 0.5 nm) while limiting the In-incorporation (not detectable X-ray diffraction XRD peak shift and no In-signals from energy dispersive x-ray spectroscopy EDX).\(^26\) Furthermore, the concept of In-mediated MEXCAT has been extended to the deposition of \(\bar{\beta}\)-(Al\(_x\)Ga\(_{1-x}\))\(_2\)O\(_3\) alloys on (010) substrates, allowing for stabilization of up to \(x = 0.2\) incorporation at high \(T_g\).\(^20\)

In this experimental work, we investigate the In-mediated MEXCAT on all the available orientations of \(\bar{\beta}\)-Ga\(_2\)O\(_3\) substrates, aiming at insights in the crystal quality and future perspective of Ga\(_2\)O\(_3\) homoepitaxy by MBE on different surfaces. In particular, we show that MEXCAT allows for homoepitaxial growth under deposition conditions otherwise prohibitive on all the major \(\bar{\beta}\)-Ga\(_2\)O\(_3\) orientations. The synthesis parameters that allow for layer growth (i.e., \(T_g\), \(O_2/ga\)-flux ratio) as well as the growth rates are found to depend on the surface orientation, which we explain by the relation between surface free energy from \textit{ab initio} calculations (Ref. 9) and ad-atom binding energy extracted from our data using the growth model for MEXCAT-MBE presented in Ref. 23. Furthermore, we show that the (201)-orientation is challenging for \(\bar{\beta}\)-Ga\(_2\)O\(_3\) homoepitaxy due to the formation of twins. MEXCAT, however, allows for the homoeptaxy of high quality \(\bar{\beta}\)-Ga\(_2\)O\(_3\) layers on both (100) 6°-offcut and (001) substrates (no structural defects identified, rms < 0.5 nm), with low In incorporation (In < 0.1 cation cat. %). In particular, the (001)-orientation also allowed for growth rates comparable to the ones obtainable in (010) homoepitaxy (i.e., 2.3 nm/min).

The (201) and (010) \(\bar{\beta}\)-Ga\(_2\)O\(_3\) orientated substrates for this study were unintentionally doped and Fe-doped, respectively, and were both purchased from the Tamura company, while the (100) and (001) oriented wafers were Mg-doped and prepared from bulk crystals obtained from the Czechralski method at the Leibniz-Institut für Kristallzüchtung. To prevent the formation of twin domains, the (100)-substrates were offcut by 6° toward the c-direction. Before being loaded into the MBE chamber, the substrates were chemically etched in phosphoric acid (85 wt. % H\(_3\)PO\(_4\); \(T = 130^\circ\mathrm{C}\), \(t = 15\) min) to remove potential polishing damage in the first 100 nm from the substrate surface; the process was then followed by an \(O_2\)-annealing treatment (\(p = 1\) bar, \(T = 950^\circ\mathrm{C}, t = 60\) min) in a tube furnace. The experiments were performed in a MBE chamber equipped with an O-plasma source run at a plasma power \(P = 300\) W. Before the deposition, all the substrates were in situ oxygen-plasma treated at an O-flux of 1 standard cubic centimeter per minute (sccm) at a substrate temperature \(T_g = 875^\circ\mathrm{C}\) for \(t = 30\) min. All growth runs were performed for a fixed deposition time of 30 min. The beam equivalent pressure of Ga was fixed to \(\text{BEPr}_\text{Ga} = 1.27 \times 10^{-7}\) mbar, equivalent to a particle flux of \(\Phi_{\text{Ga}} = 2.2\) nm\(^2\) s\(^{-1}\) (determined from the measured growth rate under O-rich deposition conditions on c-plane sapphire substrates)—i.e., full Ga incorporation \(\approx 100\) nm (i.e., growth rate 3.3 nm/min).

The particle flux of In for the catalyzed growths was fixed to \(\Phi_\text{In} = 1.3\) \(\Phi_{\text{Ga}}\) (\(\text{BEPr}_\text{In} = 5.2 \times 10^{-8}\) mbar). The \(T_g\) was measured by an optical pyrometer. For some of the depositions, an additional thin (Al\(_x\)Ga\(_{1-x}\))\(_2\)O\(_3\) marker layer was deposited at the substrate-layer interface. The growth parameters for the interlayer were maintained.
the same regardless of the different investigated surfaces, with \( T_g = 720 \, ^\circ C \), an O-flux of 1 sccm, Al cell temperature = 1008 \, ^\circ C \) (BEP\textsubscript{Al} \( \approx 4 \times 10^{-8} \) mbar), and deposition time = 80 s (targeted Al composition \( \approx 5 \) cat. \%, thickness \( \approx 1–5 \) nm). The surface morphology was characterized by atomic force microscopy (AFM, Bruker Dimension Edge) in PeakForce tapping mode. The homoepitaxial layers were monitored by XRD symmetric, out-of-plane 2\( \theta \)-\( \omega \) scans (PANalytical X'Pert Pro MRD using Cu K\( _{\alpha} \) radiation), and their composition was investigated by means of time-of-flight secondary ion mass spectrometry (SIMS) using ToF-SIMS IV from IONTOF GmbH. The quantitative ToF-SIMS calibration of the In-concentration was obtained from pulsed laser deposited \((\text{In}_x\text{Ga}_{1-x})_2\text{O}_3\) reference films on c-plane sapphire substrates analyzed by EDX in a scanning electron microscope (5 samples with In content 1–40 c at. %—Oxford Instruments GmbH/JEOL GmbH). Depth profiling of SIMS craters was performed by interference microscopy (Veeco Instruments, Inc.). Selected samples were investigated by transmission electron microscopy (TEM—aberration corrected FEI Titan 80–300 operating at 300 kV). Scanning TEM (STEM) images were recorded with a high-angle annular dark-field (HAADF) detector with an inner acceptance angle of 35 mrad and a camera length of 196 nm. TEM samples were prepared and studied in the cross section view perpendicular to the [010] direction for the (100), (001), and (201) growth orientations.

We initially applied on all the substrate orientations the nominal deposition parameters that we previously reported to be effective for the In-mediated MEXCAT-MBE of (010)-oriented layers, i.e., \( T_g = 900 \, ^\circ C \), \( \Phi_{\text{In}} = 1/3 \, \Phi_{\text{Ga}} \), and O-flux = 0.33 sccm\textsuperscript{21}. With the formation of (110)-facets, the resulting (010)-homoepitaxial layer shows the typical morphology previously highlighted for metal-rich deposition conditions (see Ref. 21). Its thickness of 50 nm (detected by XRD thickness fringes, not shown) signifies an effective incorporation of \( \approx 50\% \) of the incoming Ga flux; the thickness reduction with respect to what we have previously reported\textsuperscript{21} can be attributed to a slightly different efficiency of our O-plasma source. More importantly, no layer growth was detected on all the other substrate orientations (not shown), indicating a substrate-orientation dependence of In-mediated MEXCAT for \( \beta\text{-Ga}_2\text{O}_3 \) homoepitaxy. The mean surface roughness of the substrates after these growth experiments are reported in Tables I–III for (\( \bar{2}01 \)), (100), and (001), respectively. We point out that when no growth takes place, the rms values might be altered by localized Ga-etching effects that cause a roughening of the surfaces with respect to an untreated substrate.

In the following, we report the results of growth on the different substrate orientations under various growth conditions (\( T_g \), O-flux).

**MEXCAT on (201)**. Growth of homoepitaxial layers on this substrate orientation was found to require much lower \( T_g \) and/or higher O-fluxes with respect to the (010) one. A decrease of \( T_g \) down to 735 \, ^\circ C \) resulted in a rough morphology (rms = 2.45 nm) characterized by elongated features oriented along the [010] direction [Fig. 1(a)].

The cross-sectional STEM HAADF images of this sample [Figs. 1(b) and 1(c)] confirm the growth of a (\( \bar{2}01 \)) homoepitaxial layer and allow us to relate its AFM morphology to the presence of facetted surface features.
of islands along the [010] direction. Due to the irregular height and distribution of the islands, it is difficult to identify a precise layer thickness (range 15–30 nm, i.e., \( \approx 20\% \) incorporation of the incoming Ga-flux). Under these deposition conditions, the presence of well-defined facets on the side of the islands [white dotted lines in Fig. 1(b)] is visible. Figure 1(c) shows an atomically resolved STEM HAADF image of a part of an island, which reveals three kinds of defects, i.e., twin lamellae on the (201) plane, twins on the (100) plane, and a defect induced by a lateral shift of a part of the layer with respect to the other on the (201) growth surface. All of these defects can be explained by the 2D-island growth on the respective growth surfaces. Evidence for these defects comes from the analysis of Fast Fourier Transformations (FFTs) of Fig. 1(c) [Fig. 1(d)] and corresponding inverse FFTs. The extra-reflections (I) and the streaks (II) in the FFT [Fig. 1(d)] correspond to a twinning of the lattice on the (201) plane and are revealed by high intensity in the inverse FFT in Fig. 1(e) [inverse FFT extracted from region (III) in Fig. 1(d)]. Within this twinned island, additional twins on the (100) planes appear as dark lines. These dark lines correspond to half unit cell high twin lamellae. The image pattern in the region marked IV [green arrow Fig. 1(c)] has already been observed in homoepitaxial layers grown on the (100) plane of \( \beta\text{-Ga}_2\text{O}_3 \). It is explained by the overlap of two different grains, whose lattices have been shifted in the (201) plane with respect to each other.

The ToF-SIMS measurement performed on a twin sample deposited under the same conditions independently confirms the presence of a layer consisting of islands with broad height distribution, as visible from the double-peak in the In-intensity profile [red dots in Fig. 2(a)]. From the calibration, the In-concentration in this sample is found to be around \( C_{\text{In}} \approx 2 \times 10^{19} \text{ cm}^{-3} \) [i.e., \( \approx 0.05 \text{ cat. \%} \)] at a depth of \( x \approx 5 \text{ nm} \). Si impurities are usually found as a contaminant in \( \text{Ga}_2\text{O}_3 \) homoepitaxy at the substrate-layer interface and can therefore be used as an interface marker [blue dots in Fig. 2(a)]. The absence of a second Si-peak at \( x \approx 20 \text{ nm} \) is related to its lower intensity with respect to the In one (near the detection limit). The layer thickness can be estimated around 10–25 nm from the SIMS profile, in line with TEM results [Fig. 1(b)].

For comparison, another layer was deposited under the very same conditions (i.e., \( T_g = 735 \text{ °C} \) and O-flux \( \approx 0.33 \text{ sccm} \)) without providing an additional In-flux. The SIMS profile of this sample [Fig. 2(b)] shows Si impurities only at the surface, clearly indicating the absence of a deposited layer. Since no In-flux was provided during this growth run, the presence of a certain amount of In in the first nanometers of the substrate (\( C_{\text{In}} \approx 2 \times 10^{18} \text{ cm}^{-3} \)) has to be considered as a surface impurity most likely coming from the sample holder, which has been the same for all the deposition runs.

Further deposition conditions were screened aiming at improving the quality of the homoepitaxial (201) layers. In-catalyzed growth with an increased O-flux of 0.5 sccm resulted in a nonhomogeneous rough surface (rms \( \approx 9.81 \text{ nm} \)) with high incorporation of the incoming Ga-flux \( \approx 85 \text{ nm} \) thick layer, not shown) and \( C_{\text{In}} \approx 5 \times 10^{20} \text{ cm}^{-3} \) (i.e., \( \approx 1.3 \text{ cat. \%} \), not shown). Increasing incorporation of In with increasing O-flux and/or decreasing \( T_g \) has already been reported for the heteroepitaxy of \( (\text{In},\text{Ga}_{1-x})_2\text{O}_3 \).

A higher \( T_g \) of 800 °C required to increase the O-flux up to 0.75 sccm to detect layer growth with In-catalysis (i.e., no growth detected for 0.33 and 0.5 sccm). With these growth conditions, a 60–70 nm layer was deposited: the \( C_{\text{In}} \) as a function of probed depth [Fig. 3(a)] shows that after an initial broad peak detected at the substrate-layer interface (max \( C_{\text{In}} \approx 7.2 \times 10^{17} \text{ cm}^{-3} \), i.e., \( \approx 0.19 \text{ cat. \%} \) ), the \( C_{\text{In}} \) stabilizes to a value of \( \approx 9.8 \times 10^{18} \text{ cm}^{-3} \), i.e., \( \approx 0.03 \text{ cat. \%} \). The presence of an In-peak at the substrate-layer interface has been generally identified in all the samples and is probably related to the first stages of the catalytic growth. An AFM image of this sample [inset of Fig. 3(a)] shows a rough surface (rms \( \approx 6.99 \text{ nm} \)) dominated by islands oriented along the [010] direction, similarly to the ones shown in Fig. 1(a). A reference sample deposited without In-catalysis under the very same growth conditions resulted in no layer growth (not shown).
A further increase of the O-flux to 1 sccm at $T_g = 800 \degree C$ with In-catalysis resulted in almost full Ga-flux incorporation and a surface characterized by several micrometers large islands with an irregular shape and a typical height of $\approx 50$–$80$ nm [similar morphology to Fig. 4(d)]. In contrast to what has been previously reported in Ga$_2$O$_3$ heteroepitaxy on $c$-plane sapphire substrates with a $(\overline{2}0\overline{1})$-oriented $\beta$-Ga$_2$O$_3$ seed layer,\textsuperscript{23} In-mediated MEXCAT in $(\overline{2}0\overline{1})$-homoepitaxy never resulted in the formation of the metastable $\varepsilon/k$-phase\textsuperscript{26} in our layers.

As summarized in Table I, we show that In-mediated MEXCAT allows us to widen the growth window in $(\overline{2}0\overline{1})$ homoepitaxy to regimes otherwise prohibitive for $\beta$-Ga$_2$O$_3$ growth, enabling large Ga-flux incorporation (up to $\approx 65\%$) with limited In-incorporation ($<0.1$ cat. %). Nonetheless, our results suggest that obtaining $(\overline{2}0\overline{1})$ layers with high structural quality would require a proper choice of the substrate offcut to prevent the formation of twin lamellae due to the possibility of double positioning during growth. Twin lamellae can limit the electrical transport properties and results in considerable surface roughness in our deposited layers.

**MEXCAT on (100) $6^\circ$-offcut.** The In-assisted synthesis conditions that allowed for growth at the lowest $T_g$ for the $(\overline{2}0\overline{1})$ homoepitaxial samples. For easier comparison among different substrate orientations, we highlight (in bold) the deposition conditions that were investigated on all the substrate orientations.

| $T_g$ (°C) | O-flux (sccm) | Growth rate' (nm/min) | rms (nm) | In incorporation (cm$^{-3}$) |
|-----------|--------------|----------------------|---------|--------------------------|
| 735       | 0.33         | $\approx 0.65$ [Figs. 1(b)–2(a)] | 2.45 [Fig. 1(a)] | $2 \times 10^{19}$ [Fig. 2(a)] |
| 735—no MEXCAT | 0.33       | No growth             | 0.31    | ...                       |
| 735       | 0.5          | $\approx 2.8$        | 9.81    | $5 \times 10^{20}$       |
| 800       | 0.33         | No growth             | 0.58    | ...                       |
| 800       | 0.5          | No growth             | 0.62    | ...                       |
| 800       | 0.75         | $\approx 2.2$ [Fig. 3(a)] | 6.99 [Fig. 3(a)] | $1 \times 10^{19}$ [Fig. 3(a)] |
| 800—no MEXCAT | 0.75       | No growth             | 1.08    | ...                       |
| 800       | 1            | $\approx 3.3$        | 23.30   | $1.5 \times 10^{21}$     |
| 900       | 0.33         | No growth             | 1.15    | ...                       |

\textsuperscript{a}Full incorporation 3.3.

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![AFM micrographs of samples deposited on $6^\circ$ offcut (100) with In-mediated MEXCAT](image-url)
orientation—i.e., $T_g = 735$ °C and O-flux = 0.33 sccm—did not result in layer growth on the (100) substrates. The AFM image of this tentative growth [Fig. 4(a)] shows the presence of a smooth surface (rms = 0.28 nm) with a morphology related to the 6° offcut along the c-direction, and the ToF-SIMS profile highlights the absence of a layer [black dots in Fig. 4(e)].

Thus, we tested conditions that previously resulted in higher growth rates for (201) homoepitaxy, i.e., $T_g = 800$ °C and O-fluxes $\geq 0.75$ sccm. For these samples, an additional (Al$_{x}$Ga$_{1-x}$)$_2$O$_3$ interlayer was deposited at the substrate-film interface. The highest tested O-flux (2 sccm) resulted in a rough surface containing irregularly shaped islands with a typical height of about 150 nm [Fig. 4(d)], similar to the one previously discussed for the (201)-oriented layer deposited at 1 sccm. ToF-SIMS of this sample (not shown) suggests an almost full incorporation of the Ga$_2$O$_3$ layer with additional In-incorporation of about 21.4 cat. % (i.e., 65% of the total provided In-flux, $C_{\text{In}} \approx 8.2 \times 10^{11}$ cm$^{-2}$). Just for this sample, we detected an additional XRD reflection that we attribute to bixbyite In$_2$O$_3$ (not shown). The coexistence of both monoclinic and bixbyite phase in the (In$_{x}$Ga$_{1-x}$)$_2$O$_3$ alloy system is expected for such a large amount of In$_x$Ga$_{1-x}$.

A lower O-flux of 1 sccm resulted in a smoother surface (rms = 1.07 nm), with a morphology compatible with step bunching along the substrate offcut direction [Fig. 4(c)]. ToF-SIMS shows that the layer is $\approx$30 nm thick [green dots in Fig. 4(e)] with an estimated $\approx$2 nm thick (Al$_{x}$Ga$_{1-x}$)$_2$O$_3$ interlayer at the substrate interface. $C_{\text{In}}$ as a function of depth is showing a similar trend as the one of thick layers, with a peak at the interlayer-interface ($C_{\text{In}} \approx 2.2 \times 10^{12}$ cm$^{-2}$, i.e. 5.7 cat. %) followed by a plateau region with limited In incorporation ($C_{\text{In}} \approx 2.2 \times 10^{11}$ cm$^{-2}$, i.e., 0.006 cat. %).

A further decrease in the O-flux to 0.75 sccm resulted in a smoother layer [rms = 0.32 nm, Fig. 4(b)] with a morphology resembling the one of the offcut substrate [Fig. 4(a)], and a thickness of 8–10 nm determined by ToF-SIMS [red dots in Fig. 4(c)]. Due to the limited thickness of the layer though, it is not possible to identify a clear plateau of $C_{\text{In}}$ in the deposited layer; nonetheless, the $C_{\text{In}}$ peak at the interlayer-layer interface is $\approx 9.5 \times 10^{10}$ cm$^{-2}$ (i.e., 0.25 cat. %), while the lowest detected $C_{\text{In}}$ in the layer is $\approx 3.5 \times 10^{10}$ cm$^{-2}$ (i.e., 0.01 cat. %). A deposition under the same conditions without In-flux did not result in a Ga$_2$O$_3$ layer growth, but just in a slight incorporation of In in the (Al$_{x}$Ga$_{1-x}$)$_2$O$_3$ marker layer ($\approx$2 nm thick, see blue dots in Fig. 4(e)).

No extended defects are visible both in bright field and STEM images of the layer [Figs. 5(a) and 5(b), respectively]. The high crystal quality of the deposited layer is also apparent from the FFT image reported in Fig. 5(c), as no unexpected spots or streaks appear from the β-Ga$_2$O$_3$ ones are observed. Due to the Z-contrast in the HAADF-STEM image, the (Al$_{x}$Ga$_{1-x}$)$_2$O$_3$ interlayer can be identified as a dark line compared to the Ga$_2$O$_3$ substrate and layer. The respective thicknesses of the (Al$_{x}$Ga$_{1-x}$)$_2$O$_3$ and Ga$_2$O$_3$ layer are estimated to range between 2–3 and 7–9 nm [Fig. 5(c)], in good agreement with the SIMS results [red dots in Fig. 4(e)]. The step edges due to the 6°-offcut in the c-direction are resulting in (201)-planes [purple dotted lines in Fig. 5(d)]. While the substrate surface presents only half-unit cell steps ($\approx 0.62$ nm), the layer surface presents steps of different heights as illustrated in the high-magnification STEM images in Fig. 5(d). All step heights correspond to multiples of half a unit cell in the a-direction, with the largest steps of 2.5 unit cells ($\approx 1.1$ nm). This points towards step bunching in some parts of the layer during growth, although this is not influencing the crystalline quality of the film.

As summarized in Table II, In-mediated MEXCAT is a fundamental ingredient to grow β-Ga$_2$O$_3$ layers on (100)-oriented substrates in the presence of an offcut along the c-direction. We have shown that the growth of high quality (100)-homoepitaxial layers is not just limited to MOVPE but can be also extended to MBE.

**MEXCAT on (001).** We tested two deposition conditions that were previously investigated for the other two discussed orientations, i.e., $T_g = 735$ °C–O-flux = 0.33 sccm and $T_g = 800$ °C–O-flux = 0.75 sccm. The In-mediated growth run at the lowest $T_g$ resulted in a $\approx$32 nm thick layer with a $C_{\text{In}}$ peak at the substrate-layer interface of $\approx 7.5 \times 10^{10}$ cm$^{-2}$ (i.e., 0.07 cat. %) and a constant intralayer $C_{\text{In}}$ of $\approx 1.0 \times 10^{10}$ cm$^{-2}$ (i.e., 0.03 cat. %) [Fig. 6(a)], highlighting a
TABLE II. Summary results for the (100) homoepitaxial samples on 6°-offcut substrates. We highlight (in bold) the deposition conditions that were investigated on all the substrate orientations.

| \( T_g \) (°C) | O-flux (sccm) | Growth rate (nm/min) | rms (nm) | In incorporation (cm\(^{-3}\)) |
|----------------|---------------|-----------------------|-----------|-----------------------------|
| 735            | 0.33          | No growth [Fig. 4(e)]  | 0.28 [Fig. 4(h)] | \ldots |
| 800            | 0.75          | \( \approx 0.27 \) [Figs. 4(e) and 5] | 0.32 [Figs. 4(h) and 5] | 4 \times 10^{18} [Fig. 4(e)] |
| 800 – no MEXCAT| 0.75          | No growth             | 0.20      | \ldots |
| 800            | 1             | \( \approx 1 \) [Fig. 4(e)] | 1.07 [Fig. 4(c)] | 2.2 \times 10^{18} [Fig. 4(e)] |
| 800            | 2             | \( \approx 3.3 \)     | 59.60 [Fig. 4(d)] | 8.2 \times 10^{21} |
| 900            | 0.33          | No growth             | 0.45      | \ldots |

*Full incorporation 3.3.

larger growth rate than on the (201) and (100) orientations (respectively, Tables I and II). The AFM micrograph of this layer [inset of Fig. 6(a)] shows (i) the presence of \( \approx 100 \) nm large and \( \approx 10 \) nm high dots on the surface whose origin is not currently understood, and (ii) elongated features along the [010] direction as already reported in other homoepitaxial growths on this orientation.\(^{16,33}\) The resulting rms surface roughness is 3.11 nm.

For the growth at \( T_g = 800 \) °C and O-flux = 0.75 sccm, an approximately 2 nm thick (Al\(_x\)Ga\(_{1-x}\))\(_2\)O\(_3\) marker layer was intentionally deposited at the substrate-layer interface. The thickness of the \( \beta\)-Ga\(_2\)O\(_3\) layer is estimated from ToF-SIMS as \( \approx 65 \) nm, with a \( C_{Ga} \) peak at the substrate-layer interface of \( \approx 1.1 \times 10^{20} \) cm\(^{-3}\) (i.e., 0.29 cat. %) and a constant intralayer \( C_{Ga} \) of \( \approx 3 \times 10^{19} \) cm\(^{-3}\) (i.e., 0.08 cat. %) [Fig. 6(b)]. Under these deposition conditions, the layer is smooth (rms = 0.41 nm), still presenting elongated features oriented along the [010] direction [AFM in the inset of Fig. 6(b)]. The presence of well-defined XRD fringes in the vicinity of the (002) diffraction peak [facilitated by the (Al\(_x\)Ga\(_{1-x}\))\(_2\)O\(_3\) marker layer] allows us to precisely determine the thickness of the layer = 70 nm, i.e., 70% incorporation of the Ga total flux—growth rate = 2.3 nm/min [Fig. 6(c) red line], in line with the thickness range previously extracted from the SIMS profile [Fig. 6(b)]. Even though we are not maximizing the Ga-flux for our deposition runs, we highlight that the growth rate obtained here is exceeding what has been so far reported in the literature for this orientation with MBE (\( \approx 0.9 \) nm/min).\(^{16,33}\) A layer deposited under the same deposition conditions without additional In-flux resulted in no layer growth [black line in Fig. 6(c)].

A cross-sectional TEM analysis along [010] of the In-catalyzed sample grown at \( T_g = 800 \) °C–O-flux = 0.75 sccm is reported in Fig. 7. The absence of contrast features in the dark field image in Fig. 7(a) (except for the TEM specimen thickness gradient related fringes) as well as the undisturbed appearance of the atomic pattern in high resolution STEM images [Figs. 7(b) and 7(d)] indicate a high crystalline quality of the film without extended defects (e.g., twinning, stacking faults), as can be also seen by the regular FFT as expected for perfect \( \beta\)-Ga\(_2\)O\(_3\) [Fig. 7(c)]. The red arrows in Figs. 7(a) and 7(b) highlight the presence of the \( \approx 2 \) nm thick (Al\(_x\)Ga\(_{1-x}\))\(_2\)O\(_3\) marker layer and the overall layer thickness of approximately 70 nm is confirmed. The surface of the layer appears smooth with a roughness peak-to-valley value of \( \approx 1–2 \) \( \delta \) lattice parameters [i.e., 0.5–1 nm, Fig. 7(d)] in line with the AFM micrographs [inset of Fig. 6(b)]. The presence of elongated features along the [010] direction seems to be related to a partial faceting of the surface.

As summarized in Table III, we show that In-mediated MEXCAT allows us to obtain smooth (001) layers with a large incorporation of the provided Ga-flux with similar efficiency as previously reported for [010]\(^{12}\) although at a lower substrate temperature. Our experiments suggest that (001) is a promising surface for \( \beta\)-Ga\(_2\)O\(_3\) homoepitaxy because of the high quality of the deposited layers.

![](https://example.com/figure6.png)

**FIG. 6.** \( C_{Ga} \) evaluated from ToF-SIMS measurements as a function of probed depth for (001) homoepitaxy at (a) \( T_g = 735 \) °C with an O-flux = 0.33 sccm and (b) \( T_g = 800 \) °C with an O-flux = 0.75 sccm; in the insets of the graphs, the respective AFM micrographs are shown. (c) (002) XRD peak of the samples deposited at \( T_g = 800 \) °C with an O-flux = 0.75 sccm with (red) and without (black) In-mediated MEXCAT.
It is important to highlight that the In-concentrations in the In-mediated MEXCAT deposited layers should not affect their electrical properties: In is energetically favorably replacing Ga in the octahedral site of the monoclinic cell, and their isovalent nature excludes electrically active doping and ionized impurity scattering. We electrically characterized two unintentionally doped 50 nm thick Ga$_2$O$_3$ layers deposited with optimized In-mediated MEXCAT conditions on (001)- and (010)-oriented insulating substrates. Hg-contact capacitance-voltage measurements did not show any free carriers on both layers (even under forward bias the measured capacitance corresponded to the parasitic capacitance measured on an insulating glass slide). Additional 2-terminal current-voltage measurements between annealed Ti/Au contacts confirmed the presence of insulating layers (resistance >1 GΩ). These results confirm that, similar to Ga$_2$O$_3$ layers grown by MBE, undoped Ga$_2$O$_3$ layers grown by MEXCAT-MBE are insulating. A separate dedicated study is needed to understand the interplay of the catalytic growth with $n$-type extrinsic doping, particularly with respect to the conflicting role of Sn as catalyst (i.e., not incorporated in the film) and donor during In-mediated MEXCAT.

From our results, it is clear that In-mediated MEXCAT allows us to widen the growth window on all the major substrate orientations (see Tables I–III). Nonetheless, there are visible differences in the growth rates $\Gamma$ on the different $\beta$-Ga$_2$O$_3$ surfaces. Figure 8(a) allows for a direct comparison of $\Gamma$ obtained with MEXCAT on different substrate orientations under three selected growth conditions as a function of their respective surface free energies from first principle calculations of Ref. 9.

Comparing the three sets of data collected in this work [blue, red, and green points Fig. 8(a)], we notice a monotonically increasing growth rate with increasing surface free energy of the different orientations, following the order $\Gamma$ (001) > $\Gamma$ (010) > $\Gamma$ (010). We relate these experimental findings to the mechanism of the In-catalytic growth, which relies on the presence of In ad-atoms on the growth surface (i.e., Ga$_2$O$_3$) that can either form the catalyzing In$_2$O$_3$ (kinetically driven steps of the catalysis) or desorb off the surface. Once In$_2$O$_3$ is formed on the surface, its In atoms can be exchanged by Ga (thermodynamically driven step of the catalysis) forming Ga$_2$O$_3$ layer material and surface In ad-atoms that can re-enter the catalytic cycle or desorb. In the simple, quantitative, rate-equation based model for the In-mediated MEXCAT-MBE put forward in Ref. 23, the growth-rate limiting step is the thermally activated desorption of the In ad-atoms. Hence, the growth rate can be described as a function of all growth parameters [Eq. (6) in Ref. 23] and the activation energy $\Delta$ for In-desorption [Eq. (7) in Ref. 23] from the Ga$_2$O$_3$ surface. Providing the growth rate $\Gamma$ observed in our experiments (and expressed in incorporated Ga-atoms per unit area and time) together with the used growth conditions (growth temperature $T_g$, In-flux $\Phi_{\text{In}}$, Ga-flux $\Phi_{\text{Ga}}$, and active O-flux for the oxidation of In to In$_2$O$_3$ $\Phi_{\text{O}}$), we can use Eqs. (6) and (7) from Ref. 23 to calculate this activation energy as $\Delta = \kappa T_g \ln(\sqrt{\Phi_{\text{Ga}}^2 \Phi_{\text{O}}^2 (T_g-1) - \Phi_{\text{In}}^2})/f_0$ with pre-exponential factor $f_0$ arbitrarily fixed at $10^{14}$ nm$^{-2}$ s$^{-1}$. The resulting values are shown in Fig. 8(b) as a function of surface free energy of the investigated Ga$_2$O$_3$ surface orientations. Larger $\Delta$ correspond to a larger barrier for the desorption of the In ad-atoms. Figure 8(b) shows that for given growth conditions, $\Delta$ increases with increasing surface free energy of the Ga$_2$O$_3$, suggesting that the stronger bonds/higher bond densities reflected by higher surface free energies also correspond to stronger bonds of this surface to the In ad-atoms. For example, the presence of low

| $T_g$ (°C) | O-flux (sccm) | Growth rate$^a$ (nm/min) | rms (nm) | In incorporation (cm$^{-3}$) |
|----------|--------------|----------------------|---------|-------------------------|
| 735      | 0.33         | $\approx$1.1 [Fig. 6(a)] | 3.11 [Fig. 6(a)] | $1 \times 10^{19}$ [Fig. 6(a)] |
| 800      | 0.75         | $\approx$2.3 [Figs. 6(b), 6(c), and 7] | 0.41 [Fig. 6(b)] | $3 \times 10^{19}$ [Fig. 6(b)] |
| 800 – no MEXCAT | 0.75 | No growth [Fig. 6(c)] | 0.18 . . . |
| 900      | 0.33         | No growth [Fig. 6(d)] | 0.17 . . . |

$^a$Full incorporation 3.3.
investigated (010) surface (2.3 nm/min, i.e., 70% incorporation of the impinging Ga-flux). In this regard, we would like to remark that the present work is not aiming at maximizing the absolute value of the growth rate, which could be scaled up with the provided metal and oxygen fluxes. Moreover, we demonstrate that the limited incorporation of In associated with MEXCAT-MBE depositions (10^{13}–10^{15} cm^{-2}) is not changing the insulating characteristics of unintentionally doped layers. Our experimental findings therefore suggest that (001) is a strong candidate for the homoepitaxial deposition of high quality layers on large area substrates. For practical purposes, future MEXCAT-MBE studies should aim at maximizing the growth rates, particularly on the (100) orientation, while maintaining a high crystalline quality.

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REFERENCES

1. J. Pearton, J. Yang, P. H. Cary, F. Ren, J. Kim, M. J. Tadjer, and M. A. Mastro, Appl. Phys. Rev. 5, 011301 (2018).
2. J. Pearton, F. Ren, M. Tadjer, and J. Kim, J. Appl. Phys. 124, 220901 (2018).
3. A. Kuramata, K. Koshi, S. Watano, Y. Yu, T. Masui, and S. Yamakoshi, Jpn. J. Appl. Phys., Part 1 55, 1202A2 (2016).
4. Z. Galazka, R. Uecker, D. Klimm, K. Irmscher, M. Naumann, M. Pietsch, A. Kwasniewski, R. Bertram, S. Ganschow, and M. Bickerman, ECS J. Solid State Sci. Technol. 6, Q3007 (2017).
5. S. Geller, J. Chem. Phys. 33, 676 (1960).
6. G. Wagner, M. Baldini, D. Gogova, M. Schmidbauer, R. Schewski, M. Albrecht, Z. Galazka, D. Klimm, and R. Fornari, Phys. Status Solidi A 211, 27 (2014).
7. Z. Cheng, M. Hanke, Z. Galazka, and A. Trampert, Nanotechnology 29, 395705 (2018).
8. A. Fiedler, R. Schewski, M. Baldini, Z. Galazka, G. Wagner, M. Albrecht, and K. Irmscher, J. Appl. Phys. 122, 165701 (2017).
9. R. Schewski, K. Lion, A. Fiedler, C. Wouters, A. Popp, S. V. Levcenchko, T. Schulz, M. Schmidbauer, S. Bin Anooz, R. Grüneberg, Z. Galazka, G. Wagner, K. Irmscher, M. Scheffler, C. Draxl, and M. Albrecht, APL Mater. 7, 022515 (2018).
10. K. Sasaki, A. Kuramata, T. Masui, E. G. Villora, K. Shimamura, and S. Yamakoshi, Appl. Phys. Express 5, 035502 (2012).
11. M.-Y. Tsai, O. Bierwagen, M. E. White, and J. S. Speck, J. Vac. Sci. Technol., A 28, 354 (2010).
12. P. Vogt and O. Bierwagen, Phys. Rev. Mater. 2, 120401 (2018).
13. P. Vogt and O. Bierwagen, Appl. Phys. Lett. 109, 062103 (2016).
14. P. Vogt and O. Bierwagen, Appl. Phys. Lett. 106, 081910 (2015).
15. P. Vogt and O. Bierwagen, Appl. Phys. Lett. 108, 072101 (2016).
16. Y. Oshima, E. Ahsadni, S. Kaun, F. Wu, and J. S. Speck, Semicond. Sci. Technol. 33, 015013 (2018).
17. M. Baldini, M. Albrecht, A. Fiedler, K. Irmscher, R. Schewski, and G. Wagner, ECS J. Solid State Sci. Technol. 6, Q3040 (2017).
18. T. Zacherle, P. C. Schmidt, and M. Martin, Phys. Rev. B 87, 235206 (2013).
19. S. Lany, APL Mater. 6, 041610 (2018).
20. P. Vogt, A. Mauze, F. Wu, B. Bonet, and J. S. Speck, Appl. Phys. Express 11, 062103 (2018).
21. P. Mazzolli, P. Vogt, R. Schewski, C. Wouters, M. Albrecht, and O. Bierwagen, APL Mater. 7, 022511 (2018).
22. D. Blewins, K. Stevens, A. Lindsey, G. Foundos, and L. Sande, IEEE Trans. Semicond. Manuf. 32, 466 (2019).
25 P. Vogt, O. Brandt, H. Riechert, J. Lähnemann, and O. Bierwagen, Phys. Rev. Lett. 119, 196001 (2017).
26 M. Kracht, A. Karg, J. Schörmann, M. Weinhold, D. Zink, F. Michel, M. Rohrke, M. Schowalter, B. Gerken, A. Rosenauer, P. J. Klar, J. Janek, and M. Eichhoff, Phys. Rev. Appl. 8, 054002 (2017).
27 P. Vogt and O. Bierwagen, APL Mater. 4, 086112 (2016).
28 I. Cora, F. Mezzadri, F. Boschi, M. Bosi, M. Čaplovičová, G. Calestani, I. Dódony, B. Pécz, and R. Fornari, CrystEngComm 19, 1509 (2017).
29 T. Oshima, T. Okuno, N. Arai, Y. Kobayashi, and S. Fujita, Jpn. J. Appl. Phys., Part 1 48, 040208 (2009).
30 R. Schewski, M. Baldini, K. Irmscher, A. Fiedler, T. Markurt, B. Neuschulz, T. Remmele, T. Schulz, G. Wagner, Z. Galazka, and M. Albrecht, J. Appl. Phys. 120, 225308 (2016).
31 D. Gogova, G. Wagner, M. Baldini, M. Schmidbauer, K. Irmscher, R. Schewski, Z. Galazka, M. Albrecht, and R. Fornari, J. Cryst. Growth 401, 665 (2014).
32 E. Ahmadi, O. S. Koksalci, X. Zheng, T. Mates, Y. Oshima, U. K. Mishra, and J. S. Speck, Appl. Phys. Express 10, 071101 (2017).
33 M. R. Maccioni, F. Ricci, and V. Fiorentini, Appl. Phys. Express 8, 021102 (2015).
34 S. Bin Anooz, A. Popp, R. Grüneberg, C. Wouters, R. Schewski, M. Schmidbauer, M. Albrecht, A. Fiedler, M. Ramsteiner, D. Klimm, K. Irmscher, Z. Galazka, and G. Wagner, J. Appl. Phys. 125, 195702 (2019).
35 S.-H. Han, A. Mauze, E. Ahmadi, T. Mates, Y. Oshima, and J. S. Speck, Semicond. Sci. Technol. 33, 045001 (2018).
36 M. H. Wong, K. Sasaki, A. Kuramata, S. Yamakoshi, and M. Higashiwaki, Appl. Phys. Lett. 106, 032105 (2015).