Structural and Elastic Properties of $\alpha$-(Al$_x$Ga$_{1-x}$)$_2$O$_3$ Thin Films on (11.0) Al$_2$O$_3$ Substrates for the Entire Composition Range

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1. Introduction

During the last decade, ultrawide bandgap semiconductors and specifically the group-III sesquioxides attracted increasing scientific interest, especially monoclinic $\beta$-Ga$_2$O$_3$ triggered by demonstration of a Ga$_2$O$_3$ based metal–semiconductor field-effect transistor by Higashiwaki et al. in 2012.[11] Its exceptional material properties, such as a wide bandgap of 4.6–5.0 eV, a large Baliga’s figure of merit, and a large breakdown field of 8 MV cm$^{-1}$ make Ga$_2$O$_3$ a viable candidate for next-generation power electronic devices. Further applications within solar-blind and quantum-well infrared photodetectors were proposed.[2–5]

Apart from the well-studied and thermodynamic stable monoclinic $\beta$-gallia structure, Ga$_2$O$_3$ can crystallize in various polymorphs.[6] The second-most stable structure is the orthorhombic $\alpha$-phase, for which ternary PLD thin films were already reported.[7–11] The third-most stable polymorph is the rhombohedral $\alpha$-phase.

In comparison to the $\beta$-polymorph, $\alpha$-Ga$_2$O$_3$ has a trifle higher bandgap of 5.0–5.3 eV.[12–16] N-type conductivity can be achieved by an additional Sn-doping[17] enabling the preparation of highly rectifying Schottky barrier diodes.[17–19] Consequently, devices operating at high voltages with low on-resistance were already demonstrated.[13] As the corundum structure is the thermodynamically most stable phase of Al$_2$O$_3$, the growth of ternary (Ga$_x$Al$_{1-x}$)$_2$O$_3$ is feasible without miscibility gap, potentially enabling bandgap engineering between 5.0 and 8.8 eV.[20] The rhombohedral unit cell exhibits six Ga$_2$O$_3$ formula units and has space group R3c. Due to the smaller ionic radii of Al (0.57 Å) compared to that of Ga (0.62 Å), the lattice parameter $a$ ($c$) can be increased from 4.7617 Å (12.995 Å) for $\alpha$-Al$_2$O$_3$ to 4.9825 Å (13.433 Å) for $\alpha$-Ga$_2$O$_3$.

Successful fabrication of rhombohedral Ga$_2$O$_3$ was reported by mist chemical vapor deposition (CVD).[13,17,19,21–23] halide vapor phase epitaxy (HVPE),[14,16,24] metallographic vapor phase epitaxy (MOVPE),[15] mist epitaxy,[19] and the sol–gel method[12] whereas ternary $\alpha$-(Al$_x$Ga$_{1-x}$)$_2$O$_3$ has been realized by mist CVD,[25–28] PLD,[29,30] and molecular beam epitaxy (MBE)[31] until now. As substrates, a-, c-, m-, or r-plane sapphire are possible to use. Typically, the rhombohedral structure forms under high pressures and/or temperatures.[13,32]

In this study, we present the growth of binary $\alpha$-Ga$_2$O$_3$ and ternary $\alpha$-(Al$_x$Ga$_{1-x}$)$_2$O$_3$ thin films by PLD using two different combinatorial approaches on a-sapphire. The binary $\alpha$-Ga$_2$O$_3$ thin film was deposited utilizing a single Ga$_2$O$_3$ ceramic target. By means of a twofold azimuthally segmented target (Ga$_2$O$_3$/Al$_2$O$_3$) we created an $\alpha$-(Al$_x$Ga$_{1-x}$)$_2$O$_3$ thin film with a laterally varying cation composition on a 2 inch in diameter wafer. The continuous composition spread approach (CCS–PLD) was introduced by von Wenckstern et al.[33] and the resulting cation gradient ranges between $x = 0.13$ and $x = 0.84$ as measured by energy-dispersive X-ray spectroscopy (EDX). The thin-film thickness was determined by spectroscopic ellipsometry and ranges between 230 and 280 nm across the wafer. Further laterally...
homogeneous $\alpha$-(Al$_x$Ga$_{1-x}$)$_2$O$_3$ thin films were grown utilizing radially segmented ceramic targets. The usage of such targets allows the creation of a discrete material library and in this case of (Al$_x$Ga$_{1-x}$)$_2$O$_3$ thin films with a well-defined Al content by changing the radial position of the laser spot.[34] As thin films with a laterally homogeneous, discrete cation composition can thereby be produced, samples fabricated using radially segmented targets are referred to as discrete cation composition samples (DCCS) in the following. Another application of this approach is the synthesis of a thin film having a vertically varying cation composition, and that is why this method is abbreviated with VCCS-PLD. Further information about the implemented PLD approaches can be found in ref. [35].

The rhombohedral crystal structure of the thin films was confirmed by X-ray diffraction (XRD) $2\theta$-$\omega$ scans. Furthermore, epitaxial growth as well as the $a$- and $c$-lattice constants were studied in dependence on the Al content by XRD reciprocal space map (RSM) measurements.

2. Results and Discussion
2.1. Chemical Composition

To identify the cation ratio of the 2 inch in diameter large (Al$_x$Ga$_{1-x}$)$_2$O$_3$ CCS–PLD thin film, EDX was conducted on 49 positions across the wafer. The measurement points are marked as black dots in Figure 1a; the composition between these data points was interpolated and the resulting cation ratio represented as false color map. Along the cation gradient direction, marked with a black arrow, additional EDX measurements were performed in 1 mm steps to obtain the spatial Al dependency with high lateral resolution as shown in Figure 1b. The Al incorporation covers a range of $0.13 \leq x \leq 0.84$.

2.2. Structural Analysis

The crystal structure of each sample was investigated by XRD. In Figure 2a, an exemplary $2\theta$-$\omega$ scan of the binary Ga$_2$O$_3$ thin film is presented and confirms the rhombohedral $\alpha$-phase with reflection peaks at $2\theta = 35.96^\circ$ and $76.35^\circ$, which can be assigned to the (110)- and (220)-lattice planes. The substrates reflection peaks appear at slightly higher angular positions of $2\theta = 37.80^\circ$ and $80.52^\circ$. The XRD $\phi$-scans of the asymmetric (113) reflection of the thin film as well as of the substrate confirm single crystalline, epitaxial growth without rotational domains as the reflections occur on the same $\phi$-angles for layer and substrate.

To analyze the shift of the (110)- and (220)-lattice plane reflections with increasing Al content, $2\theta$-$\omega$ patterns were recorded every 1 mm along the cation gradient of the 2 inch long (Al$_x$Ga$_{1-x}$)$_2$O$_3$ thin film shown in Figure 1 and subsequently, the spatial positions were associated with the chemical composition shown in Figure 1b. The resulting false color map is presented in Figure 2c and reveals the crystallization in the rhombohedral phase in the entire investigated Al range. The angular positions of the (110)- and (220)-reflection peaks shift from $2\theta = 36.22^\circ$ and $77.0^\circ$ for $x = 0.13$ to $2\theta = 37.34^\circ$ and $79.56^\circ$ for $x = 0.84$, as expected, as the ionic radius of Al is smaller compared to that of Ga. For $x = 1$, the reflection peaks will potentially merge into the substrate peaks detected at $2\theta = 37.80^\circ$ and $80.52^\circ$.

2.3. Lattice Constants

RSMs of the asymmetric (226)-reflex were measured as function of the ternary alloy composition to determine in-plane lattice constants as well. Exemplary RSMs of the CCS $\alpha$-(Al$_x$Ga$_{1-x}$)$_2$O$_3$ sample are shown in Figure 3 revealing relaxed growth for $x = 0.14$ and pseudomorphic growth for $x = 0.84$. To determine the transition point from relaxed to pseudomorphic growth as well as the behavior of the lattice constants, 25 RSMs were recorded on various positions along the thin-film gradient. Furthermore, RSMs of the binary Ga$_2$O$_3$ thin film as well as of the bare substrate were examined. Hence, the reflection peak positions were identified and are shown in Figure 4a in reciprocal space units ($q_x$, $q_y$). The variation of the chemical composition is marked in false colors. Based on the reflection peak positions, the out-of-plane $a$- as well as the in-plane $c$-lattice constants were identified and shown in Figure 4b,c as a function of the Al content. In Figure 4b, the $a$-lattice constants of the lateral homogeneous $\alpha$-(Al$_x$Ga$_{1-x}$)$_2$O$_3$ thin films deposited via the DCCS–PLD technique are included additionally. Based on the graphs shown in Figure 4, a distinction of three different
cation regimes is suggested: 1) $0 \leq x \leq 0.55$, 2) $0.55 < x < 0.6$, and 3) $x \geq 0.6$.

In regime (1) the peak positions of the (226)-thin film reflection in reciprocal space increases along a straight connecting the $\alpha$-Ga$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ binary endpoints indicating relaxed growth of the thin film on the substrate for regime (1). Here, the $a$- and $c$-constants both decrease nearly linearly. Linear fits of the lattice constants yields

$$a_{\text{bulk}}(x) = a_0 + x \cdot (a_1 - a_0)$$

and

$$c_{\text{bulk}}(x) = c_0 + x \cdot (c_1 - c_0)$$

with $a_0 = 4.9825$ Å and $c_0 = 13.433$ Å denoting the lattice constants of $\alpha$-Ga$_2$O$_3$\footnote{[21]} as well as $a_1 = 4.759$ Å and $c_1 = 12.991$ Å of $\alpha$-Al$_2$O$_3$\footnote{[16]}. The experimentally determined lattice constants of the binary sample are with $a = 4.976$ and $c = 13.455$ Å in excellent agreement with literature values\footnote{[21]}. In the second identified regime (2), the reflection peaks broaden strongly as observed in Figure 3b. The evaluation of the peak positions reveals that $q_\perp$ decreases slightly while $q_k$ increases up to the value of binary $\alpha$-Al$_2$O$_3$, indicating compressive in-plane stress of the lattice. Here, the $\alpha$-$(\text{Al}_{x} \text{Ga}_1-x)_2$O$_3$ lattice adjusts in-plane to the substrate’s lattice, which causes the rapid drop of $c$ to approximately 12.99 Å, corresponding to the lattice constant of binary $\alpha$-Al$_2$O$_3$. The rapid change is compensated out-of-plane by a small increase in $a$. For even higher Al contents ($x \geq 0.6$), the out-of-plane crystal

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{a) XRD $2\theta$-$\omega$ scan of an $\alpha$-Ga$_2$O$_3$ thin film. b) XRD $\phi$-scans of the skew-symmetric (113) reflection of the $\alpha$-Ga$_2$O$_3$ layer and the $a$-plane substrate. c) 55 single $2\theta$-XRD scans presented as false color maps of the $\alpha$-$(\text{Al}_{x} \text{Ga}_1-x)_2$O$_3$ thin film in dependence on the cation composition recorded along the composition gradient indicated in Figure 1a. Note, that the low-intensity peak at $2\theta = 44.48^\circ$ is caused by the XRD sample holder and can be neglected.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{RSMs of the CCS wafer recorded in the vicinity of the $\alpha$-Al$_2$O$_3$ (226) peak for Al contents of a) $x = 0.14$, b) $x = 0.58$, and c) $x = 0.84$.}
\end{figure}
lattice contracts leading to an increasing $q_{\perp}$ value, while $q_{\parallel}$ remains constant. Thinking of lattice constants, this means that $a$ decreases to the $\alpha$-$\text{Al}_2\text{O}_3$ data point while $c$ stays constant at around 12.99 Å. A change in relaxed to pseudomorphic growth with increasing Al content was also reported by Grundmann and Lorenz[30] for $\alpha$-(Al$_{x}$Ga$_{1-x}$)$_3$O$_3$ thin films on r-plane sapphire. Based on this study, the theoretical out-of-plane strain[30,37] given by

$$a = a_{\text{bulk}} \left(1 - \frac{C_{12} \epsilon_a + C_{13} \epsilon_c}{C_{11}}\right)$$  \hspace{1cm} (3)

with $\epsilon_a = a_{\parallel}/a_{\text{bulk}} - 1$, $\epsilon_c = c_{\parallel}/c_{\text{bulk}} - 1$, and the elastic constants $C_{11}$, $C_{12}$, and $C_{13}$ of the rhombohedral structure.[30] is included in Figure 4b coinciding with the experimental pseudomorphic out-of-plane $a$-lattice constants. The observable theoretical bowing is caused by the concentration dependence of the elastic constants and fits reasonably well with the experimental data.

The constants derived for the $\alpha$-(Al$_{x}$Ga$_{1-x}$)$_3$O$_3$ thin films coincides for $0 \leq x \leq 0.55$ with literature values[25,28] and follow Vegard’s law. The transition to pseudomorphic growth at around $x = 0.55$ is influenced by the thin-film thickness (here 240 nm) and will occur at higher Al concentrations for thicker thin films. In contrast to this current study, Ito et al., Dang et al., and Fujita et al. reported growth of relaxed $\alpha$-(Al$_{x}$Ga$_{1-x}$)$_3$O$_3$ thin films in the entire composition range, pseudomorphic growth was not[25,28,38] Grundmann et al. reported a similar transition composition for thin films in r-plane sapphire, which might be due to different relaxation mechanisms, e.g., for (01.2)-oriented thin films relaxation may occur via prismatic glide planes which is not possible for the (11.0)-oriented thin films discussed here.

3. Conclusion

In the present study, we investigated the growth as well as the evolution of the lattice parameters with varying Al content of $\alpha$-(Al$_{x}$Ga$_{1-x}$)$_3$O$_3$ thin films. The samples were synthesized by different combinatorial PLD approaches on a-plane $\text{Al}_2\text{O}_3$ and the rhombohedral crystal structure was confirmed by XRD 20–ω measurements. RSMs reveal a change of relaxed to pseudomorphic growth for an Al content of $x = 0.55$. For $x < 0.55$ the out-of-plane $a$- and in-plane $c$-lattice constants decreases with increasing Al content following Vegard’s law confirming relaxed growth. For the pseudomorphic thin films, the c-constant align at around 12.99 Å corresponding to $\alpha$-$\text{Al}_2\text{O}_3$ and the out-of-plane $a$-lattice constant first increases step-like ($x \approx 0.6$) and decreases subsequently to the value of $\alpha$-$\text{Al}_2\text{O}_3$.

4. Experimental Section

In this study, we investigated thin films deposited by using various combinatorial pulsed laser deposition (PLD) techniques. A Coherent LPX Pro 305 KrF excimer laser beam (248 nm) with an energy density of 2.6 J cm$^{-2}$ on the target surface is utilized. The target-to-substrate distance is 10 cm. An $\alpha$-$\text{Ga}_2\text{O}_3$ thin film was deposited at a growth temperature ($T_g$) of $\approx 640$ °C and an oxygen pressure ($p(O_2)$) of 0.01 mbar using a single $\text{Ga}_2\text{O}_3$ (purity 99.999%, Alfa Aesar) ceramic target. Further lateral homogeneous thin films were deposited utilizing an elliptically segmented $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$ target (corresponds to Al contents of $x < 0.75$) or an $(\text{Al}_0.4\text{Ga}_0.6\text{O}_3)/\text{Al}_2\text{O}_3$ ($x > 0.75$) target. The cation composition was varied by changing the radial position of the laser spot on the PLD target based on the VCCS–PLD technique.[34] The growth parameters are $T_g = 715$ °C and $p(O_2) = 0.0006$ mbar. As substrates $5 \times 5$ mm$^2$ large a-sapphire was used, 10,000 laser pulses were applied with a repetition rate of 10 Hz.

The ternary thin film obtaining a lateral varying cation composition was fabricated by using the CCS approach for PLD.[33,35] The sample was grown at $T_g = 640$ °C and $p(O_2) = 0.006$ mbar on a 2 inch in diameter large a-sapphire wafer. For this purpose, a twofold segmented ceramic target consisting of one $\text{Ga}_2\text{O}_3$ segment and one $\text{Al}_2\text{O}_3$ (purity 99.997%, Alfa Aesar) segment was rotated simultaneously with the 2 inch in diameter large substrate. Both segments were additionally doped with 0.1 wt% SiO$_2$. The applied pulse number was 25 000 with a repetition rate of 10 Hz.

The chemical cation distribution of the 2 inch in diameter large wafer was determined by EDX using a FEI Nova Nanolab 200 equipped with an Ametek EDAX detector. XRD (2θ–ω, θ, ρSM) measurements were conducted using a PANalytical X’pert PRO MRD diffractometer equipped
with a PIxcel3D detector operating in 1D scanning line mode with 255 channels (for 2\(\omega\)-scans), receiving slit mode (\(\phi\)-scans), and fast 2D frame based mode (RSMs). The thin-film thickness was deduced by spectroscopic ellipsometry using a dual rotating compensator ellipsometer (RC2, J.A. Woollam M2000) with a spot size of about 300 \(\times\) 500 \(\mu\)m\(^2\).

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

combinatorial synthesis, pulsed laser deposition, X-ray diffraction, \(\alpha\)-(Al\(_{1-x}\)Ga\(_x\))\(_2\)O\(_3\), \(\alpha\)-Ga\(_2\)O\(_3\)

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