Azimuthal Anisotropy of Rhombohedral (Corundum Phase) Heterostructures

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The corundum structure is rhombohedral/trigonal and thus has lower symmetry than the well-investigated hexagonal crystals such as wurtzite GaN- and ZnO-based materials. By investigating the growth of \(\alpha\)-phase \((\text{Al},\text{Ga})_2\text{O}_3\) alloy thin films on various orientations of \(\text{Al}_2\text{O}_3\) substrates, the anisotropy around the \([00.1]\)-axis is investigated. In particular, the pseudomorphic growth on the \(r\) plane \((01.2)\) and \(r'\) \((10.2)\) plane substrates is compared. The findings agree with elasticity theory. Also, different growth kinetics are found on these two planes in terms of growth rate and preferential cation incorporation.

1. Introduction

The growth of (corundum phase) \(\alpha\)-\(\text{Ga}_2\text{O}_3\)\(^{[1,2]}\) and \(\alpha\)-(\(\text{Al},\text{Ga})_2\text{O}_3\) alloys for buffer layers\(^{[3-6]}\) on sapphire has gained large interest. Also, the \((\text{Al},\text{Ga})_2\text{O}_3\) system is interesting as barrier layer for \(\text{Ga}_2\text{O}_3\) and \((\text{In},\text{Ga})_2\text{O}_3\)-based heterostructures.\(^{[7,8]}\) The corundum phase offers the larger band offsets compared with the monoclinc phase.\(^{[9]}\) In this work, we investigate the properties of strained heterostructures of rhombohedral thin films to investigate the particular effects of the trigonal symmetry on the epitaxial strain. \(\alpha\)-(\(\text{Al},\text{Ga})_2\text{O}_3\) thin films of various compositions are compared for epitaxial planes with inclination with respect to the \((00.1)\) \(c\) plane in two different azimuthal orientations. Predictions have been made in the studies by Grundmann et al.\(^{[10,11]}\) that in rhombohedral/trigonal heterostructures differences in epitaxial strain arise for different azimuths, whereas for hexagonal materials no differences are expected.

For hexagonal crystals, the elastic properties are cylindrically symmetric around the \(c\) axis, the so-called basal plane isotropy (Figure 1a for GaN). The threefold symmetry of the strain tensor in rhombohedral/trigonal crystals is visualized in Figure 1b for \(\alpha\)-\(\text{Ga}_2\text{O}_3\); the symmetry reduction is due to the elastic constant \(C_{14}\) being nonzero. We remark that the value for \(\text{Al}_2\text{O}_3\) is positive as determined from resonant ultrasound spectroscopy\(^{[12]}\) as well as from X-ray scattering.\(^{[13]}\) Also for \(\alpha\)-\(\text{Ga}_2\text{O}_3\), the coefficient is \(C_{14} > 0\).\(^{[14]}\) The material parameters used in this study are shown in Table 1.

![Image](https://example.com/image1)

In the study by Grundmann and Lorenz,\(^{[14]}\) it has been discussed and shown that the \(r\)-plane \((01.2)\) and the \(r'\)-plane are equivalent (as expected). Also, the \(m\) and \(\bar{m}\) planes are equivalent, whereas the \(a\) and \(\bar{a}\) planes are distinguished by some intricacies.\(^{[13]}\) In the study by Grundmann et al.,\(^{[11]}\) it has been calculated that the \(m\) and \(a\) planes have different elastic properties, whereas in a hexagonal crystal, they are strictly identical. However, the difference of out-of-plane strain on \(m\) and \(a\) planes is for \(\text{Al}_2\text{O}_3\) or \(\text{Ga}_2\text{O}_3\) quite small. The largest difference between the \(m\) azimuth \((01.0)\) and the azimuth \((10.0)\) (rotated by \(60^\circ\)) is given around the \(r\)-plane inclination;\(^{[14]}\) therefore, we investigate and compare here the \(r\)- and \(r'\)-planes (Figure 2).

2. Epitaxial Strain

As a primary sign of different stress–strain situation, we investigate the out-of-plane lattice spacing. The selection rules for space group R3c (No. 167)\(^{[15]}\) for allowed \((hkl)\) Bragg reflexes is \(-h+k+l = 3n\) \((n \in \mathbb{Z}_0)\). Thus the \((01.2)\) is an allowed reflection, but the \((10.2)\) is not. As shown in Figure 3, the only symmetric reflection for the \(r'\)-plane (accessible with copper anode) is the \((30.6)\) and allows us to determine the out-of-plane lattice spacing for this substrate orientation.

The pseudomorphic growth (of thin films with sufficiently low Ga content) is deducted from reciprocal space maps (RSMs). Two films on \(r\)- and \(r'\)-planes with almost identical Al concentration \(x \approx 0.905\) are compared in Figure 4 for the \((41.6)\) reflex for \(r\)-plane substrate and the \((rotated\ by\ 60^\circ)\) corresponding \((5-4.6)\) reflex for the \(r'\) substrate. The different splitting of film and substrate peaks is also present for this reflex. Supporting Information\(^{[17]}\) shows the complete set of X-ray diffraction (XRD) RSMs around the asymmetric \((41.6)/(5-4.6)\) reflections of all \(r\) and \(r'\)-sample pairs considered in this work and for the skew-symmetric \((00.6)\) reflex for selected sample pairs.
peak separation of the (03.6) reflex of rhombohedral (R3c, α-phase) alumina (experimental values) and gallia (theoretical values) (same parameters as used in the study by Grundmann and Lorenz[14]).

| Material | a (nm) | c (nm) | C_{11} | C_{12} | C_{13} | C_{14} | C_{15} |
|----------|--------|--------|--------|--------|--------|--------|--------|
| Al₂O₃    | 0.4759 | 1.2991 | 4.97   | 1.63   | 1.16   | 5.01   | 0.22   |
| Ga₂O₃    | 0.49825 | 1.3433 | 3.815  | 1.736  | 1.26   | 3.458  | 0.173  |

Figure 1. Shape of the Young’s module of a) GaN and b) α-Ga₂O₃, with the c-axis pointing upwards. While the hexagonal material has cylindrical rotation symmetry around the c-axis, the trigonal system exhibits a threefold symmetry.

Figure 2. Schematic of facets of the corundum structure. The spherical coordinate system (θ, ϕ) is shown; the arrow “c” is at θ = 0, the arrow “a” belongs to (θ, ϕ) = (π/2, 0), and arrow “m” points to (θ, ϕ) = (π/2, π/2). For Al₂O₃, the (01.2) r-plane (blue) is at (θ, ϕ) = (57.6°, 90°) and the (10.2) r’ plane (red) at the same θ but ϕ = 30°.

From the 2θ peak separation of the (03.6) reflex, the out-of-plane lattice mismatch of film (F) and substrate (S) lattice spacing Δd/d = (d_F – d_S)/d_S is calculated, using the Al₂O₃ parameters of Table 1. The dependence is shown in Figure 5a for various samples grown with the same number of 30 k pulsed laser deposition (PLD) pulses on both r- and r’-planes together with the pseudomorphic elastic strain theory. For high Al concentrations, the data points are on the lines, indicating pseudomorphic growth. For smaller Al concentration, the out-of-plane strains are smaller due to strain relaxation. For the same composition, the out-of-plane strain on r’-plane is always smaller than on r-plane as predicted in the studies by Grundmann et al.[11,14] In the inset of Figure 5a, the out-of-plane mismatch is normalized to (1 – x), getting rid of the linear dependency (the small nonlinearity in the theory is mostly due to the composition dependence of elastic constants). The pseudomorphic samples for x > 0.8 are very close to the theoretical expectation.

Samples from the same (AlₓGa_{1-x})₂O₃ PLD target (35 wt% Al₂O₃, x = 0.4975) grown with different thicknesses (using 3 k, 10 k, and 30 k PLD pulses) are shown in Figure 5b. The high growth temperature of 1000 °C has been chosen as it promotes stronger strain relaxation[18]. The depositions resulted in layer thickness for the samples of about 100, 220, and 600 nm, respectively. With increasing thickness, the growth rate decreases in agreement with our previous findings that plastic strain relaxation favors lower growth rate.[18] This is connected with reduced gallium incorporation, explaining the slight increase of Al concentration of the films with increasing thickness. Most importantly, for smaller thickness, the strain state approaches the pseudomorphic theory lines.

A compilation of known out-of-plane strains for various substrate orientations is shown in Figure 6. To normalize to the lattice mismatch and eliminate the linear dependence on (1 – x), we depict (Δd/d)/(1 – x) interpolated for x = 0.9. The threefold symmetric dependence for the inclined r/r’-plane is fairly strong and matches our experimental result. For c plane, naturally no angular dependence exists. For the m/a azimuth, results on m plane[19] and a plane[20] have been included and are very similar.

3. Growth Kinetics

As another point we would like to discuss is the differences in growth kinetics. We draw the attention to the fact that thin films grown side-by-side under the same growth conditions at 750 °C (with substrate rotation) on r- and r’-planes exhibit different Al-concentration. As typical for the (AlₓGa_{1-x})₂O₃ PLD growth at low oxygen pressure,[14,21] the gallium concentration in the film is much lower than in the PLD target. This is compared in Figure 7 for three pairs of samples from different targets. For epitaxy on r’-plane, the gallium incorporation is stronger (and the Al concentration smaller). Correlated with this, also the film thickness (and the growth rate) was larger on r’-plane...
than for $r$-plane. The $x(x_t)$ dependence can be fitted with the model from the study by Grundmann and Lorenz\cite{14}

$$x = \frac{x_t}{q + (1 - q)x_t} \tag{2}$$

with the parameters $q_r = 0.096$ and $q_0 = 0.164$ that are independent of target composition for growth at 750°C. Generally, $q$ summarizes the probability of Ga versus Al incorporation.\cite{14,18}

Thus, Ga incorporation is about 70% more probable on $r_0$-plane than on $r$-plane (under the given growth conditions and at 750°C).

The $q$ values, calculated from (2) as $q = (x_t/x) \times (x - 1)/ (x_t - 1)$ are shown for various samples grown sequentially under similar conditions at 1000°C in Figure 8. As already reported in the study by Grundmann et al.,\cite{18} at this growth temperature, $q$ decreases linearly with $x_t$. Clearly, $q$ is systematically larger for growth on the $r'$-plane than on $r$-plane, maintaining the trend found for deposition at 750°C.

The competition between chemisorption and desorption of volatile gallium suboxides\cite{21,22} is in general in favor of crystal

![Figure 3](image3.png)

Figure 3. XRD 2θ–ω scans of $\alpha$-(Al$_{x}$Ga$_{1-x}$)$_2$O$_3$ thin films on Al$_2$O$_3$ grown at 750°C with almost identical composition, $x \approx 0.859$, grown on the $r$ and $r'$-planes. On the $r$ plane (blue, shifted × 10 for clarity), the (0n,2n) reflexes for $n = 1, 2, 3, 4$ appear, on the $r'$-plane (red), only the (30.6) reflex appears. Inset: The (03.6)/(30.6) reflexes in magnified angular scale; the dashed lines indicate the film peak maxima. The small peak at about 44.4° is due to the stainless steel sample holder.

![Figure 4](image4.png)

Figure 4. Corresponding RSMs of pseudomorphic $\alpha$-(Al$_{x}$Ga$_{1-x}$)$_2$O$_3$ thin films on Al$_2$O$_3$ with almost identical $x = 0.905$ grown at 750°C on the $r$ (left, [41.6] reflex) and $r'$-plane (right, [5 -4.6] reflex). (The double peaks are due to the Kα1,2 splitting).

![Figure 5](image5.png)

Figure 5. Out-of-plane lattice mismatch $\Delta d/d$ of $\alpha$-(Al$_{x}$Ga$_{1-x}$)$_2$O$_3$ thin films on $r$-plane (blue) and $r'$-plane (red) Al$_2$O$_3$. The lines are the prediction from elastic strain theory as reported in the study by Grundmann and Lorenz.\cite{14} a) Samples grown with 30 000 PLD pulses from different targets. The squares and diamonds are from samples grown at 750°C in two different reactors (W and A chambers, respectively), the circles are for samples grown at 1000°C (A chamber). Inset: $(\Delta d/d)/(1 - x)$, experimental data (symbols) and theory (lines). b) Samples grown at 1000°C from PLD target with 35 wt% Al ($x_t = 0.4975$) and different thickness (30k, 10k, and 3k PLD pulses as labeled).
Polar plot of the mismatch of the out-of-plane lattice spacing divided by \((1 - x)\) of \(\alpha-(Al, Ga)_2O_3\) layers for \(x = 0.9\) on \(r\)-plane (blue), \(r'\)-plane (red), \(a\) plane (purple square, from the study by Hassa et al.), \(c\) plane (green), \(\alpha\) plane (purple diamond, from the study by Kneiss et al.), and \(\theta\) plane (green) \(Al\) plane (purple diamond, from the study by Kneiss et al.). The lines are the expectations from elastic strain theory for \(\theta = 0\) (green), \(\theta = \theta_i\) (black), and \(\theta = \pi/2\) (purple).

Figure 6. Polar plot of the mismatch of the out-of-plane lattice spacing divided by \((1 - x)\) of \(\alpha-(Al, Ga)_2O_3\) layers for \(x = 0.9\) on \(r\)-plane (blue), \(r'\)-plane (red), \(a\) plane (purple square, from the study by Hassa et al.), \(c\) plane (green) \(Al\) plane (purple diamond, from the study by Kneiss et al.), and \(\theta\) plane (green) \(Al\) plane (purple diamond, from the study by Kneiss et al.). The lines are the expectations from elastic strain theory for \(\theta = 0\) (green), \(\theta = \theta_i\) (black), and \(\theta = \pi/2\) (purple).

Al-concentration \(x\) of \(\alpha-(Al, Ga)_2O_3\) thin films grown at 750 °C (W chamber) side-by-side on \(r\)-plane (blue) and \(r'\)-plane (red) \(Al_2O_3\) versus \(Al\) concentration \(x_i\) in the PLD target. The dashed lines are fits with a simple growth model \(a_0 = 0.096\) and \(a_1 = 0.164\).

Figure 7. Al-concentration \(x\) of \(\alpha-(Al, Ga)_2O_3\) thin films grown at 750 °C (W chamber) side-by-side on \(r\)-plane (blue) and \(r'\)-plane (red) \(Al_2O_3\) versus \(Al\) concentration \(x_i\) in the PLD target. The dashed lines are fits with a simple growth model \(a_0 = 0.096\) and \(a_1 = 0.164\).

\(q\) values for \(\alpha-(Al, Ga)_2O_3\) thin films grown at 1000 °C (A chamber) on \(r\)-plane (blue) and \(r'\)-plane (red) \(Al_2O_3\) as a function of concentration \(x_i\) in the PLD target. The dashed lines are linear fits with slopes 0.31 and 0.37.

Figure 8. \(q\) values for \(\alpha-(Al, Ga)_2O_3\) thin films grown at 1000 °C (A chamber) on \(r\)-plane (blue) and \(r'\)-plane (red) \(Al_2O_3\) as a function of concentration \(x_i\) in the PLD target. The dashed lines are linear fits with slopes 0.31 and 0.37.

growth on the \(r'\)-plane, possibly representing an advantage in the fabrication of Ga-containing alloy thin films. It seems interesting to further investigate this effect also for other cations such as indium and to find out its microscopic origin with an atomistic modeling approach for the growth kinetics.

4. Conclusion

In summary, we have presented experimental evidence of the trigonal symmetry of the strain tensor in the \(\alpha-(Al, Ga)_2O_3\) system which is relevant for strained heteroepitaxy on planes inclined to the \(c\) plane. Quantitative agreement exists between the experimental film strain and continuum elastic theory. High-quality \(\alpha-(Al, Ga)_2O_3\) thin films were grown on \(r\)- and \(r'\)-plane substrates. The growth kinetics have been studied and a more efficient gallium incorporation on the \(r'\)-plane has been found.

5. Experimental Section

We fabricated thin-film samples using PLD on \(r\)-plane, (01.2) or \(r'\)-plane, (10.2) \(Al_2O_3\) substrates. The epipolished 2 in. diameter \(r\) and \(r'\)-plane wafers were cut from the same raw crystal by Cryscore Optoelectronic Ltd., Jiaozuo, Henan, China. The substrates were used as delivered. The targets were pressed and sintered from high purity (4N7) \(Al_2O_3\) and (5N) \(Ga_2O_3\) powders provided by Alfa Aesar. Samples were fabricated in two different growth chambers with resistive heating (W chamber) and IR laser diode heating (A chamber). The substrate temperature has been set \(\approx 750\) °C (W and A chambers) or 1000 °C (A chamber only). In the study by Grundmann et al., it has been shown that the higher growth temperature leads to stronger strain relaxation for thin films above the critical thickness. The oxygen partial pressure was \(10^{-1}\) mbar. All samples have been grown with 30 000 PLD pulses. In addition, we have grown films with 10 000 and 3000 PLD pulses from the same target to investigate different thicknesses. For the direct comparison of growth on the two substrate types, samples were fabricated side-by-side with a rotating substrate holder (this was only possible at 750 °C). Energy dispersion X-ray analysis (EDX) was recorded with a FEI Nanolab 200 system. XRD \(2\theta-\omega\) scans were recorded using a PANalytical X’pert PRO materials research diffractometer equipped with either a parabolic mirror (Cu K\(_\alpha\)) or a hybride monochromator (Cu K\(_\alpha\)) as incident optics. RSMs around symmetric and asymmetric substrate and film reflections were measured using the fast frame-based option of the PI Xcel\(_\text{TM}\) area detector. RSMs around the skew-symmetric (00.6) peak were measured with (time consuming) \(\omega-2\theta\) versus \(\omega\) area scans in triple-axis configuration.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

heterostructures, rhombohedral, strain, stress

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