Materials Physics and Mechanics. 2023;51(1): 1-9
Research article
http://dx.doi.org/10.18149/MPM.5112023_1

Submitted: November 11, 2022
Approved: November 16, 2022
Accepted: January 26, 2023

Epitaxial stabilization of α-Ga_2O_3 layers grown on r-plane sapphire

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Abstract. In this work, we study the thermal stabilization of metastable α-Ga_2O_3 in growth experiments. Gallium oxide films are grown on c- and r-plane sapphire substrates by halide vapor phase epitaxy (HVPE) at the temperature range of 450-690 °C. The surface morphology is investigated by scanning electron microscopy. The structural quality and phase composition of the grown films is studied by X-ray diffraction. It is found that the use of *r*-plane sapphire substrates prevents the formation of the orthorhombic κ-Ga_2O_3 and monoclinic *β*-Ga_2O_3 and thus extends the growth process window for the deposition of the rhombohedral *α*-phase of gallium oxide.

Keywords: gallium oxide, HVPE, epitaxial layers, *c*-plane and *r*-plane sapphire substrates

Acknowledgements. *The research was supported by Russian Science Foundation, Grant No. 19-19-00409.*

Citation: Nikolaev VI, Polyakov AY, Stepanov SI, Pechnikov AI, Guzilova LI, Scheglov MP, Chikiryaka AV. Epitaxial stabilization of α-Ga_2O_3 layers grown on r-plane sapphire. *Materials Physics and Mechanics*. 2023;51(1): 1-9. DOI: 10.18149/MPM.5112023_1.

Introduction

Gallium oxide is a prospective ultra-wideband gap semiconductor having a bandgap of about 5 eV. It has gained considerable interest recently for applications in high-power electronics, chemical sensors, and ultraviolet detectors [1]. Ga_2O_3 exists in many polymorphic forms denoted as monoclinic *β*, corundum *α*, defective spinel *γ*, orthorhombic (hexagonal) *κ(ε)*, and bixbyite *δ* polymorphs. In some early studies, the ε-phase was erroneously ascribed to a hexagonal P63mc space group. However, more recent studies revealed that the ε-phase actually consists of nanoscale domains of the orthorhombic structure rotated 120° relatively to each other [2]. The β-Ga_2O_3 polymorph is the most stable form and can be obtained by melt crystallization. However, the low symmetry of the monoclinic structure presents evident drawbacks for device applications.

Besides the monoclinic polymorph, other crystal forms of Ga_2O_3 such as the orthorhombic κ-phase and the rhombohedral corundum α-phase have attracted considerable interest due to their unique physical properties. The κ-phase has large spontaneous polarization which can be used to generate high-density two-dimensional electron gas. Among other polymorphs, *α*-Ga_2O_3 has the widest bandgap of 5.3 eV and is isostructural to sapphire substrates. Epitaxial stabilization can be used as an effective tool for the growth of metastable polymorphs of Ga_2O_3. Metastable polymorphs can be grown by epitaxial methods on foreign

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substrates. In most papers, *c*-plane sapphire was used as a substrate for the Ga_2O_3 growth, and only a few reports used *a, r*, and *m*-plane sapphire as the substrate.

The stability of α-Ga_2O_3 epitaxial films on sapphire substrates is governed by a large number of factors. On one hand, α-Ga_2O_3 is the best lattice-matched polymorph and has the same corundum structure as sapphire. The lattice mismatches between α-Ga_2O_3 and α-Al_2O_3 (sapphire) are only 4.81% and 3.54% in the *a*- and *c*-axis directions. For that reason, α-phase can be energetically more preferable to other polymorphs when grown epitaxially on sapphire substrates. On the other hand, the thermal stability of α-Ga_2O_3 is less than that of κ-Ga_2O_3 and β-Ga_2O_3. In the temperature range of 600-650 °C, all three phases can coexist and compete with each other.

In the previous studies, pressure, temperature, substrate type and orientation, gallium and oxygen precursors, additional hydrogen chloride flow, and doping with tin, silicon, and boron have been identified as the main factors which determine the preferential nucleation of one or another phase.

It has been observed by many authors that the growth of phase pure α-Ga_2O_3 on sapphire substrates is limited by the film thicknesses. High-resolution transmission electron microscopy studies revealed that independent of the growth method a few-monolayer thick α-Ga_2O_3 can be stabilized by strain during the growth of Ga_2O_3 on *c*-plane sapphire [3]. For thicker layers, the α-phase transforms to β-phase due to a large in-plane lattice mismatch between α-Ga_2O_3 and the sapphire substrate.

The thermal stability of α-$(Al_xGa_{1-x})_2O_3$ is expected to be higher than that of pure α-Ga_2O_3 because α-phase is the stable polymorph of Al_2O_3. Surprisingly, even a small Al doping is sufficient to increase the growth temperature and resistance to thermal annealing. According to Lee *et al.*, slight doping with Al (1-2.5%) allows the growth at higher temperatures (e.g. 50–150 °C higher) without the marked appearance of the β-phase and enhances thermal stability for successive thermal treatments [4].

Several research groups reported that the Sn doping growth could facilitate the preferential growth of the κ-phase [5-7]. This phenomenon was observed with MBE, PLD, and mist-CVD. Kang *et al.* investigated the Sn-induced phase stabilization of κ-Ga_2O_3 and the thermal stability of the films grown by mist chemical vapor deposition [7]. They found that Sn doping promotes the κ-phase even under low temperature (T_g = 450 °C) growth conditions that strongly favor the α-phase. The post-growth annealing tests at 800−1000 °C showed that the thermal stability of the κ-phase also depends on the Sn concentration. The higher the Sn concentration, the more stable the phase. The one with the highest Sn content showed no phase transition from κ to β after annealing at 800 °C, 900 °C, and 1000 °C for 30 min each. The exact mechanism of the Sn-induced phase stabilization of κ-Ga_2O_3 remains elusive.

The addition of boron stabilizes the MOVPE growth of the α-phase on *c*-, *a*-, and *r*-plane sapphire substrates [8]. A preferred growth of the α-phase without boron addition could only be observed on *r*-plane Al_2O_3. While most of the growths of α-Ga_2O_3 thin films have been investigated on *c*-plane sapphire substrates, there are a few publications of α-Ga_2O_3 on sapphire substrates of other orientations.

Cheng *et al.* systematically investigated the differences of α-Ga_2O_3 films grown on *a*-, *c*-, and *r*-plane sapphire substrates using the mist-CVD method [9]. They reported that the quality of *c*-plane α-Ga_2O_3 films is better than both *a*-plane and *r*-plane epilayers, corresponding to the results of XRD 2θ scans and optical absorption. They claimed to have a higher growth rate on the *c*-plane (11.44 nm/min) than on the *a*- and *r*-plane sapphire (5.74 and 5.26 nm/min).

Oshima *et al.* reported the growth of ten-period binary α-Al_2O_3/Ga_2O_3 superlattices on *r*-plane sapphire substrates by plasma-assisted molecular beam epitaxy [10]. The superlattice with α-Ga_2O_3 thickness up to >1 nm had coherent interfaces without misfit dislocation despite

the large lattice mismatches.

Hu *et al.* studied the growth of Ga_2O_3 thin films on various oriented (*c*-, *a*-, *m*-, *r*-plane) sapphire substrates by plasma-enhanced chemical vapor deposition (PECVD) is investigated using high-purity metallic Ga and oxygen (O_2) as precursor materials and argon (Ar) as carrier gas. The film grown on the c-plane sapphire substrates exhibits the *β*-phase with a preferred growth plane of ($\bar{2}01$), while these grown on the *m*- and *r*-planes are amorphous.

The achievable film thickness of phase pure *α*-Ga_2O_3 is limited by the formation of c-plane facets on the α-Ga_2O_3 surface.

Phase stabilization of *α*-Ga_2O_3 on *r*-plane sapphire was studied by Kracht *et al.* who observed no indication for *β*-Ga_2O_3 in *α*-Ga_2O_3 layers on r-plane sapphire with a thickness up to 117 nm thickness [11]. This layer thickness is much higher than the values reported for MBE growth on the *a* and *c* planes, respectively. If growth time is further extended the nucleation of β-Ga_2O_3 on *c*-plane facets that are increasingly exposed during the growth of α-Ga_2O_3 is observed.

Here, we investigate the effect of substrate temperature on the growth in the α-Ga_2O_3 on *c*- and *r*-plane sapphire substrates.

Experiment

Ga_2O_3 films were grown by HVPE on (0001) *c*-plane and ($10\bar{1}2$) *r*-plane single-side polished sapphire substrate of 400 μm thickness. Oxygen gas (O_2) and gallium chloride (GaCl) were used as precursors with argon (Ar) used as a carrier gas. The GaCl vapor was synthesized *in situ* through the chemical reaction between metallic gallium and gaseous hydrogen chloride upstream in the reactor. The growth of the Ga_2O_3 films was performed at temperatures varying from 450 ºC to 690 ºC and a fixed O/Ga mole flow ratio of 4.2. The growth rate varied from 1.7 to 6.9 μm/hr. The overall thickness of the films was 1-5 μm. A more detailed description of the epitaxial growth procedures can be found in our earlier papers [12-14].

The phase composition and crystal structure of the produced Ga_2O_3 films were investigated by X-ray diffraction (XRD). The surface morphology and the cross-section of the films were studied by scanning electron microscopy (SEM).

Results and discussion

The comparison of the surface morphology for different samples was performed by SEM imaging (Fig. 1,2). Compared to specimens grown on r-plane sapphire, Ga_2O_3 films grown on c-plane substrates exhibit flatter surface morphology. This tendency becomes even more pronounced at higher growth temperatures. For example, it can be seen that Ga_2O_3 grown on *c*-plane sapphire at 670 °C forms a continuous film. Most of the film is composed of oriented crystal blocks of 120° symmetry, a few crystallites with hexagonal symmetry can be also observed. In contrast, the specimen grown on *r*-plane sapphire is clearly polycrystalline composed of agglomerated prismatic crystallites of various orientations. The observed crystal habit is typical for the monoclinic polymorph.

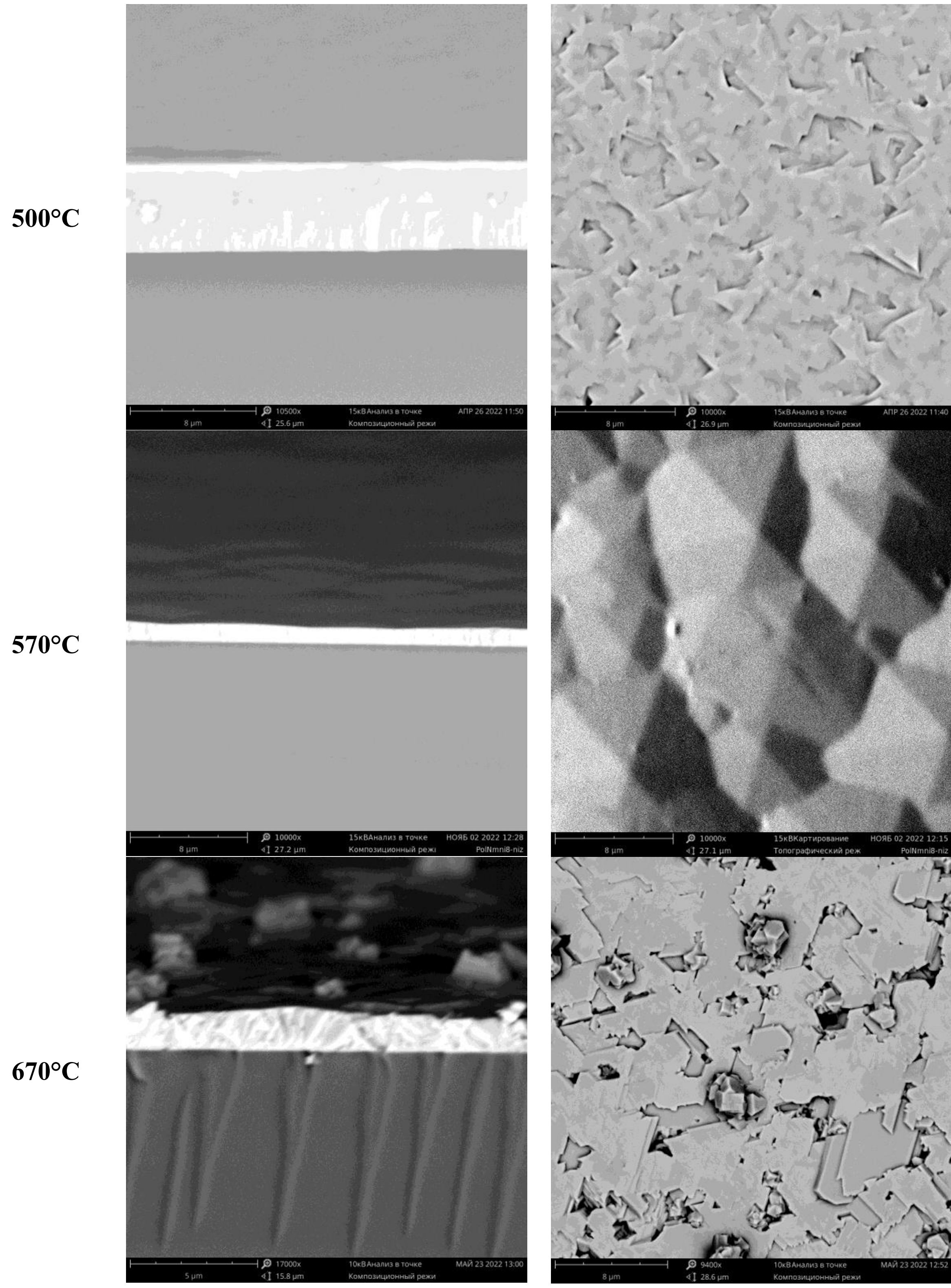

Fig. 1. Cross-sectional and plan view SEM images for Ga_2O_3 layers on c-plane sapphire at different temperatures

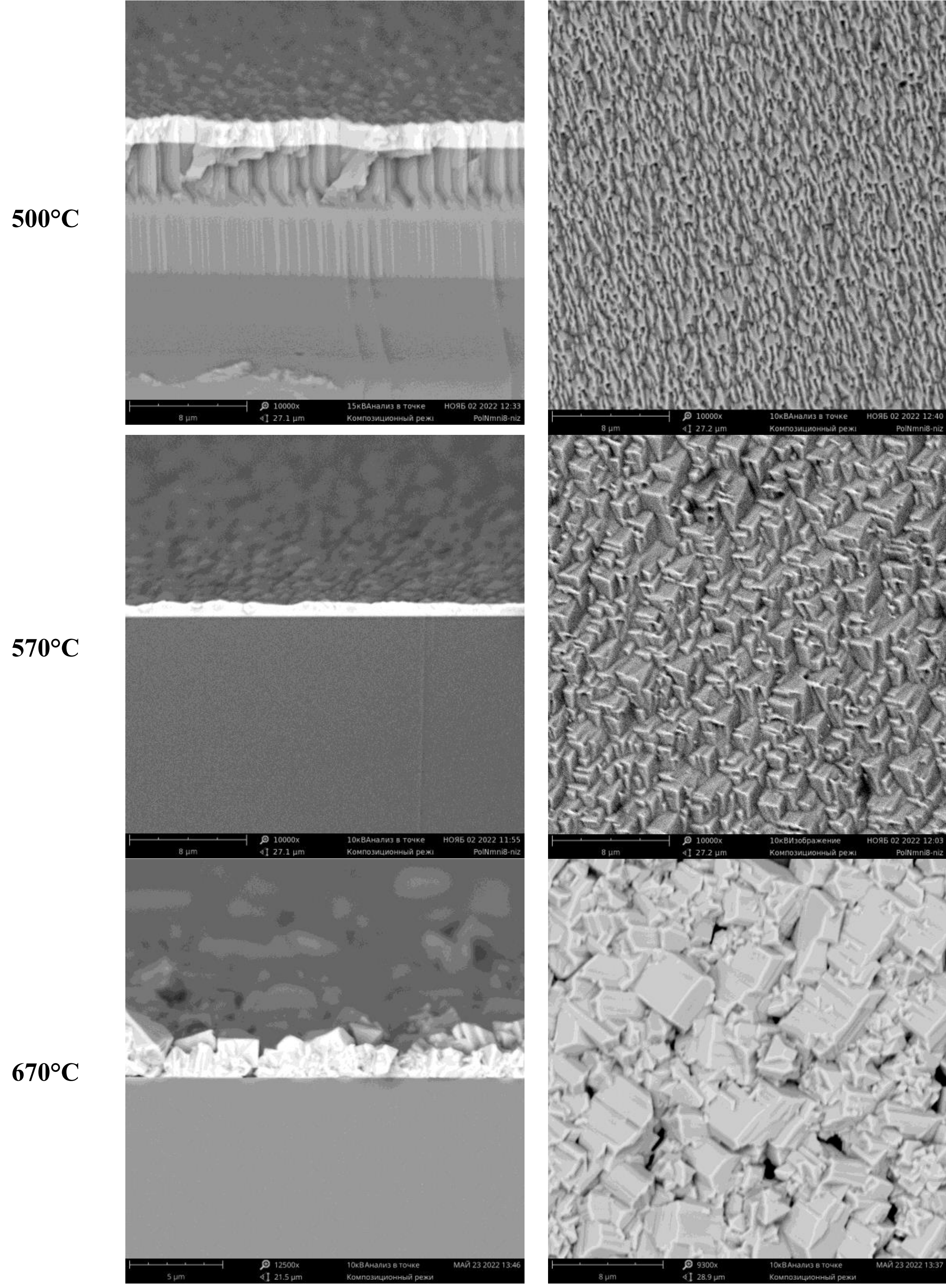

Fig. 2. Cross-sectional and plan view SEM images for Ga_2O_3 layers on r-plane sapphire at different temperatures

The XRD ω–2θ scans of Ga_2O_3 films grown on *c*-plane sapphire at different temperatures are shown in Fig. 3. All XRD spectra show reflexes from the sapphire substrate that can be indexed as 0006 at 2θ ≈ 41.65° and 00012 at 2θ ≈ 90.85°. The other two well-pronounced diffraction peaks can be assigned to the 0006 and 00012 reflections of *α*-Ga_2O_3. The specimens grown at temperatures below 530 °C showed diffraction peaks which can be assigned to 004 and 006 reflections of *κ*-Ga_2O_3. The specimens grown at higher temperatures exhibit *β*-Ga_2O_3 peaks that can be indexed as 402 at 2θ ≈ 38°, 603 at 2θ ≈ 59° and 804 at 2θ ≈ 82°. Interestingly, the intensity of diffraction peak related to *κ*-Ga_2O_3 decrease with increasing temperature, on the contrary, the intensity of *β*-Ga_2O_3 diffraction peaks increases as the growth temperature increases. The XRD pattern from the specimen grown at 670 °C also shows a variety of minor peaks which can be attributed to *β*-Ga_2O_3 phase. The growth temperature is a key factor in controlling the balance between *α*, *β*, and *κ* phases. Under the given growth conditions, the HVPE deposition of α-Ga_2O_3 on c-plane sapphire substrates is possible only within a very narrow temperature window at about 530 °C. It can be speculated that low growth temperature conditions result in *κ*-Ga_2O_3 because this phase has a smaller lattice mismatch with c-plane sapphire. On the other hand, at a higher temperature, the diffusion length is longer, and atoms reach the step edges. Therefore, the formation of the *α*-Ga_2O_3 phase which has the same structure as the sapphire substrate becomes energetically more favorable.

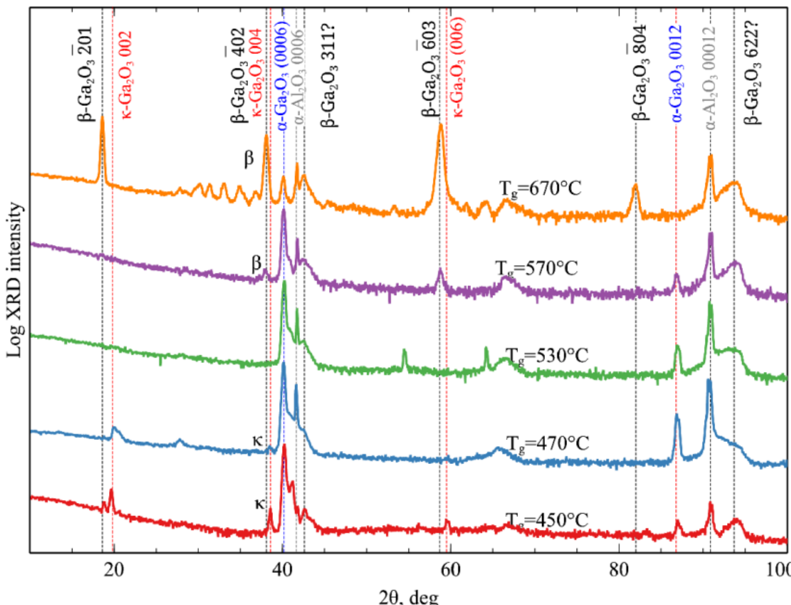

Fig. 3. Symmetrical ω-2θ XRD scans of Ga_2O_3 epilayers grown on *c*-plane sapphire substrates at different growth temperatures

The upper-temperature limit is in line with previous publications, as metastable *α*-Ga_2O_3 has the propensity to revert to the stable β-phase upon heating. The transition temperature to the *β*-phase is from 600 °C to 650 °C and depends on the film thickness. As reported by Lee et al., *α*-Ga_2O_3 films thicker than 1 μm on c-plane sapphire substrates remained α-phase upon annealing up to 550 °C but gradually changed to *β*-phase at a temperature higher than 600 °C [15]. The phase stability of α-Ga_2O_3 on c-plane sapphire can be enhanced by decreasing the film thickness. According to Jinno *et al.*, an α-Ga_2O_3 film around 20 nm thick maintained the corundum structure at an annealing temperature of 750 °C [16].

On the other hand, the lower temperature limit defined by the formation of the *κ*-phase is apparently of a less fundamental nature and is related to the particular features of the employed

growth technique. For example, mist-CVD shows the opposite trend where the low-temperature growth (<550 °C) favors the formation of *α*-Ga_2O_3, while higher temperatures result in the deposition of κ-Ga_2O_3 films. A similar trend has been reported for the HVPE technique, where deposition at a relatively high temperature (T_g = 650 °C) resulted in κ-Ga_2O_3 [17]. On the other hand, Son *et al*. Reported that the growth at 470–650 °C resulted in preferentially *α*-phase epilayers, while the deposition at 450 °C produced a mixture of *α*- and *κ*-Ga_2O_3 polymorphs [18]. In the case of the MOCVD technique, the balance between *α* and *κ* polymorphs is governed not solely by temperature, but by multiple factors. Typically, MOCVD growth at low temperatures (550 °C) results in polycrystalline Ga_2O_3 because precursors do not have sufficient energy to form crystalline Ga_2O_3 film.

Figure 4 presents XRD ω–2θ scans of Ga_2O_3 films grown on *r*-plane sapphire at different temperatures. The specimens grown in the temperature range 450 °C – 650 °C showed only 1012, 2024, and 3036 reflexes of the *r*-plane α-Al_2O_3 and *α*-Ga_2O_3. Therefore, the film is composed mainly of the (1012)-oriented *α*-Ga_2O_3 phase, with little or no detectable admixture of other polymorphic phases.

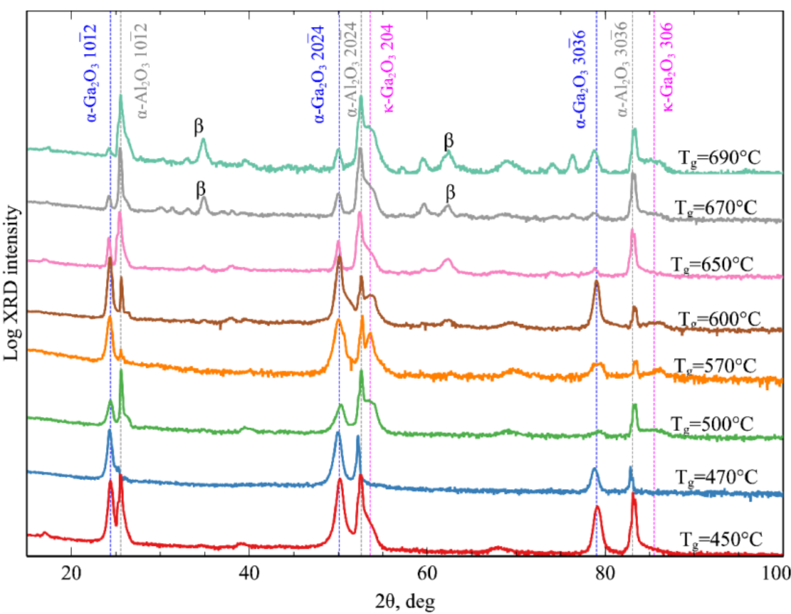

Fig. 4. Symmetrical ω-2θ XRD scans of Ga_2O_3 epilayers grown on *r*-plane sapphire substrates at different growth temperatures

It should be noted that the growth of *α*-Ga_2O_3 layers on the *r*-plane of sapphire is characterized by a much wider temperature process window. First, in contrast to the Ga_2O_3 films on the *c*-plane sapphire, specimens on the *r*-plane do not exhibit the inclusion of the *κ*-phase. Secondly, the upper temperature limit which is marked by the onset of the *β*-phase formation is increased from 570 °C to 670 °C.

Conclusion

In summary, the HVPE growth of Ga_2O_3 on *c* and *r*-plane sapphire substrates has been studied. We show that the use of *r*-plane sapphire substrates facilitates the growth of phase-pure *α*-Ga_2O_3 films. At low temperatures, Ga_2O_3 films grown on *r*-plane sapphire do not exhibit an inclusion of the κ-phase. At high temperatures, up to about 700 °C the use of r-plane sapphire substrates prevents the thermal decomposition of the *α*-Ga_2O_3 and its transformation into *β*-Ga_2O_3.

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