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Optical properties of Ga₂O₃ thin films grown by atomic layer deposition using GaI₃ and O₃ as precursors

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Properties of Ga₂O₃ thin films grown by atomic layer deposition from GaI₃ and O₃ on Si(100) and amorphous SiO₂ substrates were investigated. The Ga₂O₃ films deposited on the bare Si and SiO₂ substrates at 450–550 °C contained the κ-Ga₂O₃ phase while it was not possible to exclude the presence of the ε-Ga₂O₃ phase in these films, either. On the substrates coated with α-Cr₂O₃, α-Ga₂O₃ was obtained at 275–550 °C. The formation of crystalline phases caused a marked increase in the density, roughness, and in the growth rate as well. The refractive indices, determined for the κ/ε-Ga₂O₃ and α-Ga₂O₃ films with thicknesses over 70 nm, were 1.96 ± 0.03 and 2.01 ± 0.02, respectively. Corresponding values of amorphous films, deposited on Si at 150–425 °C, on SiO₂ at 310 °C, and on α-Cr₂O₃/Si at 200–234 °C, were 1.86 ± 0.03 at 633 nm. The optical bandgap energies of amorphous Ga₂O₃, κ/ε-Ga₂O₃, and α-Ga₂O₃ were found to be 4.96, 5.22–5.28, and 5.28 eV in the approximation of direct optical transitions and 4.27, 4.43, and 5.09 eV, respectively, in the approximation of indirect optical transitions. The films of κ/ε-Ga₂O₃ and α-Ga₂O₃ served as effective antireflection coatings on the surface of silicon reducing the reflection down to 0.20% and 0.12%, respectively.

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1. Introduction

Gallium oxide (Ga₂O₃) has attracted marked interest as a promising material for high-voltage electronic devices,^{1–3} high electron-mobility transistors,⁴ resistive switching memories,^{5,6} solar-blind radiation detectors,^{7–9} and scintillators.¹⁰ Gallium oxide has also been studied as a relatively hard material^{11,12} that can, therefore, be used in protective coatings. Furthermore, possibilities for application of Ga₂O₃ for surface passivation of silicon solar cells have been recently investigated.¹³ Owing to appropriate refractive index values and the relatively wide transparency gap of Ga₂O₃ extending from the infrared to the ultraviolet spectral range,^{13–18} Ga₂O₃ thin films can also be used in antireflective coatings of solar cells and photodetectors that are based on silicon and III–V materials. Additionally, Ga₂O₃ films could be applied as antireflective coatings of light-emitting diodes and diode lasers as well. In all these applications, high hardness is highly beneficial to ensure improved durability of the functional coatings.

As shown previously, the optical properties of Ga₂O₃ thin films significantly depend on the crystal structure and phase composition formed in the deposition or post-deposition annealing process. Ga₂O₃ can be amorphous or form at least

six crystalline phases: α-, β-, γ-, δ-, ε-, and κ-Ga₂O₃.^{19,20} A marked number of studies including the characterization of refractive index (*n*) and optical bandgap (*E_g*) have been conducted for amorphous films.^{13–18,20–26} The results obtained indicate that the optical properties of the amorphous films markedly depend on the deposition method¹³ as well as deposition process parameters.²¹ For instance, the bandgap values of 4.05–5.47 eV^{13–15,17,18,20,21,23–26} have been reported for amorphous Ga₂O₃ films from the (*αhν*)² versus *hν* plots, where *α* is the absorption coefficient and *hν* is the photon energy. The refractive index values reported for amorphous films range from 1.75 to 1.90 at 633 nm.^{13–18,21,22,24,25}

In the list of crystalline phases, β-Ga₂O₃ with the monoclinic structure (space group *C2/m*) has attracted the most significant interest that is evidently related to the higher stability of this phase compared to the stabilities of other crystalline phases.^{19,20} Optical bandgap energies of 4.26–5.24 eV published for β-Ga₂O₃^{14,16,24–31} are comparable to those of amorphous films while *n* values of 1.83–1.94 at 633 nm have been reported for β-Ga₂O₃.^{14,16,22,25,27,28,30}

A marked number of publications have also been focused on optical properties of α-Ga₂O₃ (space group *R3c*) because this phase has high density and *E_g* values.^{19,20} For instance, the *E_g* values ranging from 5.04 to 5.36 eV have been determined from the (*αhν*)² versus *hν* curves recorded for α-Ga₂O₃ thin films in the vicinity of the absorption edge.^{20,26,32–35} A similar value

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(5.46 eV) for the lowest band-to-band transition energy was obtained for α -Ga₂O₃ from the analysis based on spectroscopic ellipsometry (SE) measurements and density functional theory calculations.³⁶ The spectroscopic studies have also demonstrated that the absorption spectra of α -Ga₂O₃ have a more complex shape^{36–39} that has been interpreted assuming contribution of an exciton and two band-to-band transitions with bandgap energies of 5.58–5.62 and 6.18–6.44 eV, respectively.^{37–39}

The α -Ga₂O₃ polymorph has also relatively high n values of 1.97–2.01 as can be determined from the real parts of dielectric constants determined from SE data.^{36,39} However, the information concerning this parameter and, particularly, its dependence on the deposition process parameters is still limited.

Hexagonal ε -Ga₂O₃ (space group *P63mc*) and orthorhombic κ -Ga₂O₃ (space group *Pna2₁*) are also known as polymorphs with relatively high density.^{19,40,41} According to theoretical calculations, the bandgap energies of ε -Ga₂O₃ and κ -Ga₂O₃ should be 4.27 and 4.62 eV, respectively.⁴² However, the experimental characterization of optical parameters of pure ε - and κ -Ga₂O₃ polymorphs is a complex task because it is difficult to reveal the presence or absence of ε -Ga₂O₃ in the thin films that contain κ -Ga₂O₃.^{40,41} Moreover, the unambiguous determination of the κ -Ga₂O₃ phase in thin films by the X-ray diffraction (XRD) method needs rather complex measurements.^{43,44} This is probably one reason for the limited number of papers reporting the E_g values of ε -Ga₂O₃ and κ -Ga₂O₃. In these publications, E_g values of 4.6–5 eV for ε -Ga₂O₃^{45,46} and 4.9–5.14 eV for κ -Ga₂O₃^{9,29,47,48} have been reported. Notably, even less information can be found for n of these polymorphs while the value of 1.6 reported for ε -Ga₂O₃ does not seem to be consistent with the relatively high density of this phase.¹⁹ Therefore, additional studies focused on the optical properties of ε -Ga₂O₃ and κ -Ga₂O₃ as well as α -Ga₂O₃ polymorphs are evidently needed.

The self-limiting nature of atomic layer deposition (ALD) enables synthesis of thin films controlling the thickness with sub-nanometre resolution,^{15–18,24,44} fabrication of conformal coatings on substrates with complex shapes,^{14,15,22} and deposition of films with uniform thicknesses on large-area substrates.¹⁸ However, the deposition of crystalline Ga₂O₃ films on substrates that do not support epitaxial growth has been a problem for the majority of ALD processes studied so far. In a recent study, thin films containing α -Ga₂O₃ as well as those containing κ -Ga₂O₃ were grown by ALD at sufficiently low growth temperatures (T_G) using GaI₃ and O₃ as the precursors.⁴⁴ Therefore, this precursor system opens new possibilities for deposition and investigation of crystalline Ga₂O₃ thin films. Moreover, the GaI₃-O₃ precursor combination ensured relatively high growth rates as well as very low concentrations of residual impurities in the films, deposited in a wide range of T_G . For these reasons, the corresponding ALD process seems to be attractive for several applications, including technology of electronic devices, radiation detectors, waveguides, and optical coatings.

In electronics applications, the bandgap energy of a semiconductor dielectric material is a very important parameter, while in optical applications, bandgap energies as well as refractive indices and absorption coefficient values should be

known. All these parameters depend on the phase composition of a material. However, impurities, structural defects, and surface roughness that are all related to the material synthesis method may also influence the performance of materials and thin films in various applications. Hence, proceeding from the earlier promising results,⁴⁴ the application potential of the GaI₃-O₃ ALD process for the deposition of Ga₂O₃ thin films for optical applications was studied in the present work. For this purpose, films containing different Ga₂O₃ phases were deposited. The effect of substrates and ALD process parameters on the properties of the films was investigated. Significant effects of crystallization processes on the optical properties as well as growth rate were revealed. Application of Ga₂O₃ as a material of antireflection (AR) coatings was studied.

2. Experimental details

The Ga₂O₃ thin films were deposited on Si(100), amorphous SiO₂, α -Cr₂O₃/Si(100), and α -Cr₂O₃/SiO₂ substrates in a low-pressure flow-type ALD reactor described earlier.⁴⁹ The α -Cr₂O₃ seed layers that were needed to grow α -Ga₂O₃ films were also deposited by ALD. The seed layer thicknesses (d_{SL}) ranged from 0.7 to 9 nm. The ALD and post growth annealing processes employed to obtain α -Cr₂O₃ are described in a previous paper.⁵⁰

During ALD of Ga₂O₃, GaI₃ (99%, Strem Chemicals, Inc.) used as a metal precursor was kept at a temperature of 130 °C to volatilize the precursor. The GaI₃ vapour was transferred to the reaction zone with N₂ (AS Linde Gas, 99.999%) that was used as a carrier and purge gas. O₃ employed as an oxygen precursor was generated in a BMT Messtechnik 802N generator from O₂ (AS Linde Gas, 99.999%). The O₃ concentration, measured using a BMT Messtechnik 964 analyser at the output of the ozone generator, was set at 220–250 g m⁻³. An ALD cycle, repeated to obtain films with expected thicknesses (d), contained a GaI₃ pulse, purge, O₃ pulse, and another purge. Each of these reaction steps was 2 s in duration. For the deposition of Ga₂O₃ films studied in the present work, 500–2000 ALD cycles were used.

The elemental composition of the films was characterized using an X-ray fluorescence (XRF) spectrometer ZSX-400 (Rigaku Corp.). The phase composition, texture, density, and surface roughness were determined using an X-ray diffractometer Smartlab (Rigaku Corp.) with CuK α radiation generated at a tube power of 8.1 kW. Grazing incidence X-ray diffraction (GIXRD) carried out at an incidence angle $\omega = 0.5^\circ$, coplanar θ -2 θ -XRD and non-coplanar XRD were applied for phase composition and texture studies, while the X-ray reflection (XRR) method was used for the thickness, density, and surface roughness characterization. Crystalline phases observed in the films were identified on the basis of powder diffraction database ICDD PDF-2 (version 2023) and/or single crystal database ICSD (version 2022).

Optical properties were investigated using a spectroscopic ellipsometer GES-5E (Semilab, Inc.) and spectrophotometer V-570 (Jasco, Inc.). The n values were determined from the SE data as well as from the spectral oscillations of optical transmission spectra.⁵¹ To analyse the SE data for the Ga₂O₃ films



deposited on Si and SiO₂ substrates, one-layer fitting was used. In the case of films deposited on the α -Cr₂O₃ seed layers, an additional layer was added to the model that the fitting was based on. The thickness of this layer was calculated together with that of the Ga₂O₃ film. The absorption spectra were calculated from the transmission and reflection spectra⁵² measured at normal incidence in a wavelength (λ) range of 190–800 nm.

3. Results and discussion

3.1. Phase composition

Consistent with the results of earlier studies,⁴⁴ the X-ray diffractograms depicted in Fig. 1(a) and (b) demonstrate that

the films deposited on Si at $T_G \geq 425$ °C and on α -Cr₂O₃/Si at $T_G \geq 275$ °C contained crystalline phases, while the films deposited at lower T_G were amorphous. The crystalline phases, identified on the basis of diffractograms presented in Fig. 1(a) and (b), were ϵ -Ga₂O₃ and/or κ -Ga₂O₃ on bare Si substrates and α -Ga₂O₃ on α -Cr₂O₃/Si. The same phases were obtained on bare SiO₂ and α -Cr₂O₃/SiO₂ substrates, respectively (Fig. 1(c) and (d)). Regardless of the film thickness, which varied from 74 to 210 nm, and T_G , which varied from 450 to 550 °C, the highly developed preferential (0 0 1) orientation of ϵ -Ga₂O₃ and/or κ -Ga₂O₃ was formed in the films deposited on Si (Fig. 1(a)) as well as on SiO₂ (Fig. 1(c)).

On α -Cr₂O₃/Si and α -Cr₂O₃/SiO₂ substrates, the (0 0 1) orientation of α -Ga₂O₃ was the prevalent one, especially in

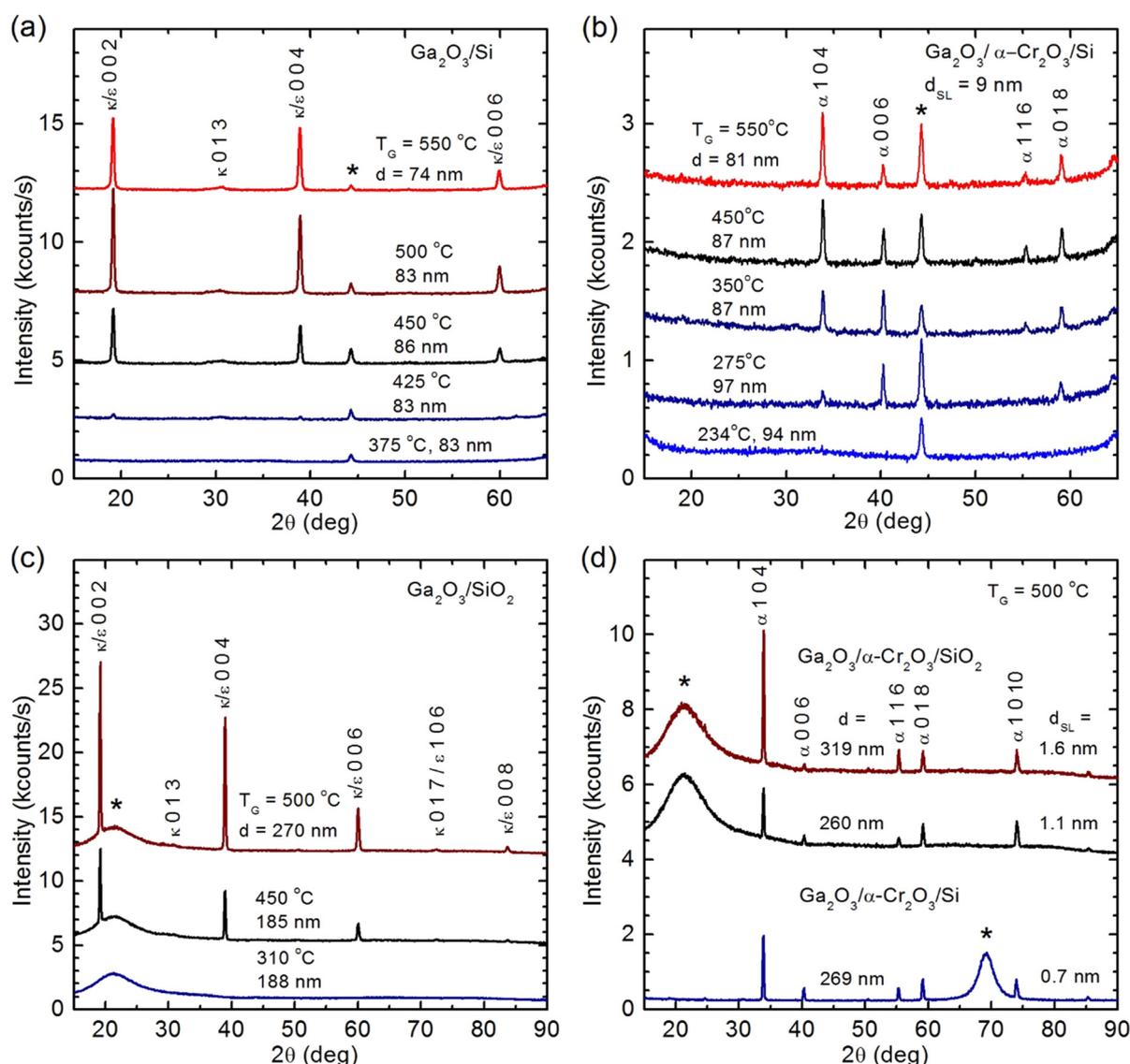


Fig. 1 Coplanar θ - 2θ -XRD diffractograms of (a), (b) 74–97 nm thick Ga₂O₃ films grown on (a) bare Si and (b) α -Cr₂O₃/Si substrates, and (c), (d) 185–319 nm thick Ga₂O₃ films grown on (c) SiO₂ and (d) α -Cr₂O₃/SiO₂ and α -Cr₂O₃/Si substrates. Growth temperatures and film thicknesses are shown at corresponding diffractograms. (b) The α -Cr₂O₃ seed layer thicknesses (d_{SL}) were 9 ± 3 nm. Miller indices of α -Ga₂O₃ (α) and κ -Ga₂O₃ (κ) are added to corresponding XRD reflections. Reflections attributable to the substrates and/or sample stage of diffractometer are marked with asterisks.



the thinner films grown at lower temperatures (Fig. 1(b)). This conclusion is based on the result that the reflection 0 0 6, which has an intensity of 3% relative to the 1 0 4 reflection of an ideal polycrystalline material (PDF-2 file 01-074-1610), is the most intense one in the diffractograms of the films grown at 275–350 °C (Fig. 1(b)). However, with increasing T_G and film thickness, the relative intensity of the 0 0 6 reflection decreased (Fig. 1(b) and (d)) and approached the corresponding value of a powder material.

As the reflections of ϵ -Ga₂O₃ overlap with those of κ -Ga₂O₃,^{40,41,43,44} it is not possible to conclude on the basis of the coplanar θ -2 θ XRD diffractograms presented in Fig. 1(a) and (c), which of these two phases was formed on bare Si and SiO₂ substrates. However, there are a few κ -Ga₂O₃ reflections, for instance reflections 0 1 3 and 1 2 2, that do not have counterparts in the diffractogram of ϵ -Ga₂O₃.^{40,43,44} Unfortunately, in the case of κ -Ga₂O₃ films with highly developed (0 0 1) preferential orientation of crystallites, these reflections cannot be recorded by XRD using the coplanar θ -2 θ geometry. Therefore, non-coplanar XRD analysis was performed to obtain more information about the phase composition of the films grown on bare Si and SiO₂. In this analysis, the sample inclination angle (χ) was varied, while the θ -2 θ XRD diffractograms for selected 2 θ ranges were recorded (Fig. 2).

According to the results of this analysis, the reflection observed in the coplanar diffractograms at around 30.5° (Fig. 1(a) and (c)) peaked at $\chi = 20.5^\circ$ in the diffractogram of the film grown on Si and at $\chi = 20.2^\circ$ in the diffractogram of the film grown on SiO₂ (Fig. 2). The 2 θ value of 30.7°, refined from the non-coplanar analysis, matched with the 0 1 3 reflection position of κ -Ga₂O₃. As β -Ga₂O₃ could also contribute to the reflection at these 2 θ values, a χ scan was also recorded at 48.7°

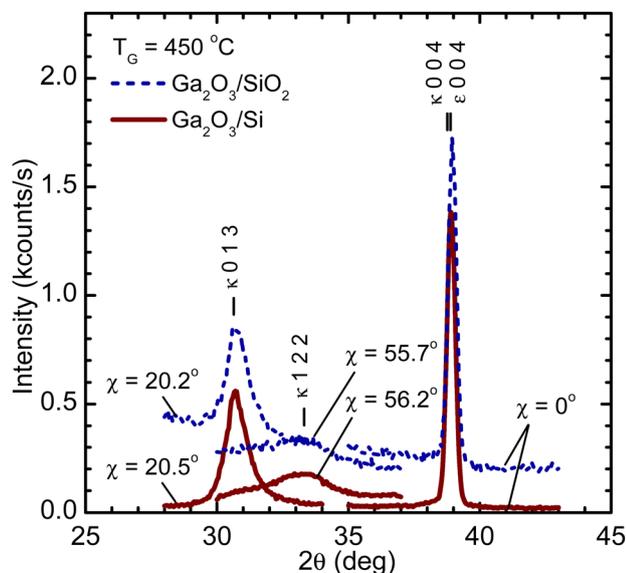


Fig. 2 Selected XRD reflections recorded in non-coplanar θ -2 θ geometry at different inclination angles χ for a 210 nm thick Ga₂O₃ film grown on bare Si (solid lines) and 180 nm thick Ga₂O₃ film grown on bare SiO₂ (dotted lines). The films were grown at 450 °C.

where the 5 1 0 reflection of β -Ga₂O₃ with a relative intensity of 20% was expected to appear (ICSD coll. code 83645) provided that this phase was present in the films. However, the χ scan did not reveal this reflection. Thus, there were no detectable amounts of β -Ga₂O₃ in these films. Consequently, the reflection observed at 30.7° belonged to κ -Ga₂O₃. Additionally, a reflection attributable only to (1 2 2) atomic planes of κ -Ga₂O₃ appeared at $2\theta = 33.3^\circ$ and χ values of 56.2° and 55.7° in the diffractograms of films grown on bare Si and SiO₂, respectively (Fig. 2). Within a precision of 1.0–1.6°, these χ values observed were equal to the angle between the (1 2 2) and (0 0 1) planes of κ -Ga₂O₃ (54.6°). Hence, the appearance of the (1 2 2) reflection in non-coplanar and (0 0 l) reflections in coplanar analysis confirmed the presence of κ -Ga₂O₃ in these films. Unfortunately, the XRD analysis did not allow us to exclude the presence of ϵ -Ga₂O₃ in the films deposited on bare Si and SiO₂. Therefore, the phase of these films is denoted as κ/ϵ -Ga₂O₃ in the following sections of this paper.

The growth of κ/ϵ -Ga₂O₃ on substrates (such as Si and amorphous SiO₂) that do not support epitaxial growth is one of the main advantages of the GaI₃-O₃ ALD process. In previous studies, the κ - and ϵ -Ga₂O₃ have mainly been observed in the films epitaxially grown on α -Al₂O₃ (0 0 1) (c-cut sapphire) substrates,^{7,9,20,25,31,41,45–48} whereas only in a few cases have the substrate temperatures below 500 °C been sufficient for formation of these phases.^{25,48} Moreover, a relatively complex method, that is, epitaxial lateral overgrowth, including the deposition of the TiO₂ seed layer on c-sapphire and a following lithography process to form a pattern that supports the κ -Ga₂O₃ growth, has been developed⁵³ and applied⁵⁴ for improving the quality of κ/ϵ -Ga₂O₃ films. However, even in these cases, substrate temperatures of 540–570 °C have been used for deposition of the films by halide vapour phase epitaxy.^{53,54} Hence, the thermal ALD based on GaI₃ and O₃ provides a much simpler approach for deposition of films containing κ -Ga₂O₃.

Low concentration of impurities in the films deposited by ALD from GaI₃ and O₃ was probably a key factor that enabled growth of crystalline phases at relatively low temperatures. For instance, according to the results of XRF analysis, the iodine concentration did not exceed 0.01 at% in the 160–320-nm-thick films deposited on Si and SiO₂ substrates at 450–500 °C. With decreasing T_G , the iodine concentration increased reaching 0.05 at% at 310 °C and 1.5 at% at 200 °C.

3.2. Influence of crystallization on density, surface roughness, and growth rate

Expectedly, the densities as well as surface roughness values significantly depended on the formation of crystalline phases in the deposition process. The growth of α -Ga₂O₃ at $T_G \geq 275$ °C and κ/ϵ -Ga₂O₃ at $T_G \geq 450$ °C caused a marked increase in density (Fig. 3(a)) and roughness values (Fig. 3(b)) compared to the corresponding values of amorphous films.

As can be seen in Fig. 3(a), the densities of X-ray-amorphous films did not depend on the film thickness and substrates, and showed only minor increase (from 5.25 ± 0.11 g cm⁻³ to 5.55 ± 0.16 g cm⁻³) with the T_G increase from 150 to 400 °C.



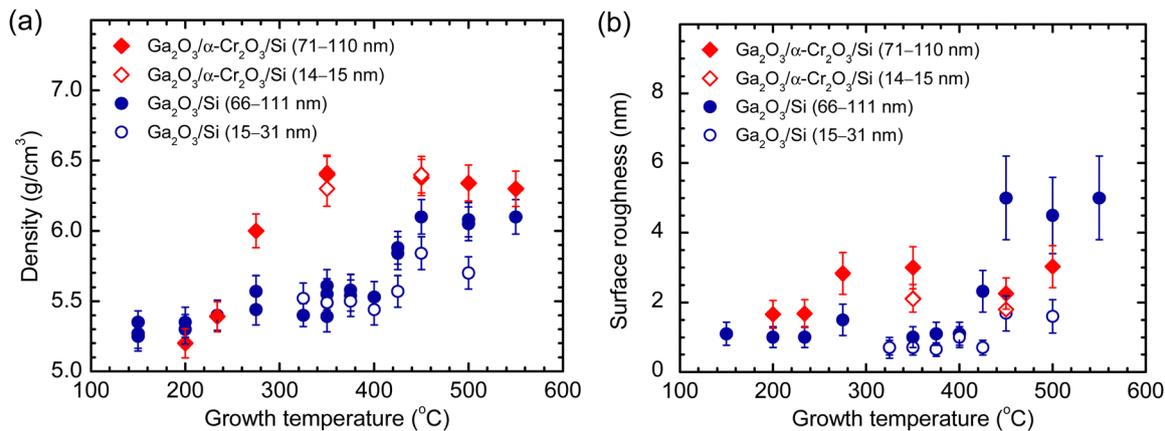


Fig. 3 (a) Density and (b) surface roughness recorded by XRR as a function of growth temperature for 14–15 nm and 71–110 nm thick Ga_2O_3 films grown on $\alpha\text{-Cr}_2\text{O}_3/\text{Si}$ substrates, and for 15–31 nm and 66–111 nm thick Ga_2O_3 films grown on bare Si substrates. The thicknesses of $\alpha\text{-Cr}_2\text{O}_3$ seed layers were 9 ± 3 nm.

In contrast, the densities of films containing $\kappa/\varepsilon\text{-Ga}_2\text{O}_3$ formed on bare Si substrates at 450–550 °C were 5.93–6.10 g cm^{-3} , while those of the $\alpha\text{-Ga}_2\text{O}_3$ films obtained on the $\alpha\text{-Cr}_2\text{O}_3/\text{Si}$ substrates at 350–550 °C reached 6.40 g cm^{-3} (Fig. 3(a)). Notably, the densities recorded for the $\alpha\text{-Ga}_2\text{O}_3$ and 66–111 nm thick $\kappa/\varepsilon\text{-Ga}_2\text{O}_3$ films were very close to the corresponding values calculated from the crystal structure parameters (6.11 g cm^{-3} for $\kappa\text{-Ga}_2\text{O}_3$ and 6.47 g cm^{-3} for $\alpha\text{-Ga}_2\text{O}_3$), and reported in the XRD database (PDF-2 files 01-074-1610 and 01-082-3196) and earlier papers.^{40,41} Somewhat lower densities were determined for thinner (15–31 nm) films deposited on the bare Si substrates (Fig. 3(a)) at temperatures enabling growth of $\kappa/\varepsilon\text{-Ga}_2\text{O}_3$ (Fig. 1(a)). This result is in agreement with the results of earlier GIXRD studies⁴⁴ and indicates that on bare Si substrates, the growth started with formation of amorphous or another low-density phase whereas the $\kappa/\varepsilon\text{-Ga}_2\text{O}_3$ phase gradually developed with increasing film thickness. In contrast, the densities close to the XRD database values of $\alpha\text{-Ga}_2\text{O}_3$ were obtained even for 14–15 nm films deposited on $\alpha\text{-Cr}_2\text{O}_3/\text{Si}$ substrates at temperatures allowing crystallization of Ga_2O_3 on these substrates. Consequently, on these substrates, the growth of $\alpha\text{-Ga}_2\text{O}_3$ started from the very beginning of deposition as it can also be concluded from the data of GIXRD studies described in our previous work.⁴⁴

The growth of $\kappa/\varepsilon\text{-Ga}_2\text{O}_3$ caused more significant surface roughening than the growth of $\alpha\text{-Ga}_2\text{O}_3$ did (Fig. 3(b)). The relatively small roughness increase related to the growth of $\alpha\text{-Ga}_2\text{O}_3$ was evidently due to the uniform nucleation of this phase on $\alpha\text{-Cr}_2\text{O}_3$. On the other hand, high roughness values and strong dependence of roughness on the film thickness, observed for the $\kappa/\varepsilon\text{-Ga}_2\text{O}_3$ films (Fig. 3(b)), were probably related to low concentration of nucleation centres on the bare Si substrates and faster growth of $\kappa/\varepsilon\text{-Ga}_2\text{O}_3$ compared to that of amorphous phase and different growth rates of crystallites with different orientations.

The results depicted in Fig. 4 confirm the conclusion about the faster growth of $\kappa/\varepsilon\text{-Ga}_2\text{O}_3$ compared to that of the amorphous phase. Fig. 4 clearly demonstrates that the growth per cycle (GPC) determined for films deposited with 600–700 ALD

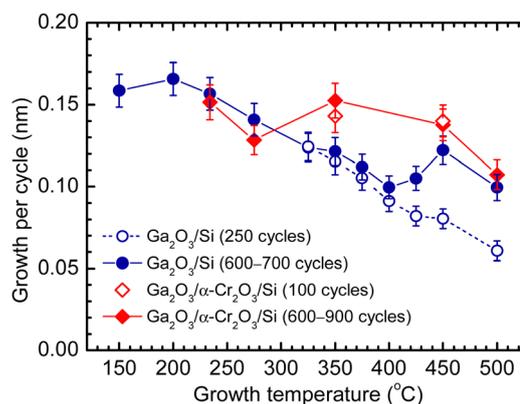


Fig. 4 Growth per cycle as a function of growth temperature for Ga_2O_3 films grown with 250 and 600–700 ALD cycles on bare Si substrates and with 100 and 600–900 ALD cycles on $\alpha\text{-Cr}_2\text{O}_3/\text{Si}$ substrates. The thicknesses of $\alpha\text{-Cr}_2\text{O}_3$ seed layers were 9 ± 3 nm.

cycles markedly increased, when T_G increased from 400 to 450 °C causing transition from the growth of amorphous phase to that of $\kappa/\varepsilon\text{-Ga}_2\text{O}_3$ (Fig. 1(a)). Interestingly, this kind of change in GPC was not observed in the case of markedly thinner films grown with 250 ALD cycles (Fig. 4). Considering the density (Fig. 3(a)) and surface roughness (Fig. 3(b)) values as well as the results of GIXRD studies reported earlier,⁴⁴ it was possible to conclude that the crystal structure was less developed in the films grown on bare Si with 250 ALD cycles than that in the corresponding films grown with 600–700 ALD cycles.

Notably, the T_G increase from 275 to 350 °C, causing considerable improvement in crystallinity of the films deposited on $\alpha\text{-Cr}_2\text{O}_3$ also led to increase in GPC (Fig. 4). Therefore, the GPC of $\alpha\text{-Ga}_2\text{O}_3$ was also higher than that of amorphous Ga_2O_3 . However, no effect of the film thickness on GPC was observed in this case. As can be seen in Fig. 4, the GPC values of films grown with 100 ALD cycles on $\alpha\text{-Cr}_2\text{O}_3$ were very close to the GPC values of films grown with 600–900 cycles on these substrates. This result confirms the conclusion about uniform



nucleation of α -Ga₂O₃ on α -Cr₂O₃ that is obviously related to epitaxial growth of α -Ga₂O₃ on α -Cr₂O₃.

In the T_G ranges, where no transitions from amorphous to crystal growth were observed, the growth per cycle decreased with increasing T_G . This kind of decrease in GPC can be caused by an increase in the I/Ga atomic ratio in the surface species formed during GaI₃ adsorption. According to the results of a previous study,⁴⁴ this ratio was as small as 0.7 at $T_G = 200$ °C. Therefore, the possible I/Ga increase of up to 3 could lead to a marked increase in the steric hindrance of Ga adsorption and, correspondingly, to significantly smaller amount of Ga₂O₃ formed during an ALD cycle. A possible reason for the increase in the I/Ga ratio is the re-adsorption of gaseous I₂, formed during the adsorption of GaI₃. As discussed in an earlier publication,⁵⁵ the re-adsorption of gaseous reaction products can explain the decrease in GPC as well as the thickness gradients that are similar to those observed in the case of films deposited from GaI₃ and O₃ at $T_G \geq 450$ °C.⁴⁴ In contrast, at the precursor pulse durations used in our experiments, a considerable contribution of the thermal decomposition of GaI₃ to the formation of thickness gradients was unlikely at temperatures of up to 500 °C because the precursor pulse duration increase from 2 to 5 s caused marked reduction in thickness gradients but no considerable increase in GPC in the substrate areas that were close to the outlet of the precursor supply line. Simulations of chemical reactions with the HSC Chemistry 7.0 software (Outotec Research Oy), indicating that significant thermal decomposition of GaI₃ could start at temperatures exceeding 500–550 °C, confirmed this conclusion.

3.3. Optical properties

Absorption spectra of Ga₂O₃ films grown on SiO₂ and α -Cr₂O₃/SiO₂ substrates were calculated from transmission (Fig. 5(a)) and reflection (Fig. 5(b)) spectra. The transmission spectra (Fig. 5(a)) as well as the absorption spectra (Fig. 6(a)) demonstrate that the films were transparent or weakly absorbing at the wavelengths down to 290 nm and $h\nu$ values of up to 4.3 eV,

approximately. The decrease in the intensities of transmission maxima observed with decreasing wavelength in this range was evidently related to the contribution of light scattering caused by the surface roughness and material inhomogeneities. According to XRR analysis, the surface roughness values of these films exceeded 5–6 nm. This kind of roughness was estimated to be sufficient to explain the transmission decrease observed at wavelengths down to 290–300 nm. This decrease in the transmission resulted in the modest increase in the absorption coefficient determined at $h\nu$ values of up to 4.2–4.4 eV for films grown on bare SiO₂ and of up to 4.9 eV for a film grown on the α -Cr₂O₃/SiO₂ substrate (Fig. 6(a)).

Expectedly, the absorption spectra depended on the phase composition of Ga₂O₃ (Fig. 6(a)). The absorption onset of amorphous films deposited on SiO₂ at $T_G = 310$ °C was observed at markedly lower $h\nu$ values than those of κ/ϵ -Ga₂O₃ deposited on SiO₂ at 450–500 °C and, particularly, that of α -Ga₂O₃ grown on α -Cr₂O₃/SiO₂ at 500 °C (Fig. 6(a)). In the absorption spectrum of α -Ga₂O₃, two-step onset of absorption, causing a feature at 5.5–5.6 eV, was recorded (Fig. 6(a)). A similar feature, has been observed in earlier studies of α -Ga₂O₃^{36–39} as well as monoclinic ZrO₂⁵⁶ and HfO₂.^{53,57} In all three cases, contribution of excitonic effects and specific electron band structures of these materials have been considered as possible reasons for this kind of feature.^{36–39,56,57} For instance, in the case of α -Ga₂O₃, an exciton band peaking at 5.5–5.6 eV and two different bandgap energies (5.61–5.62 and 6.18–6.52 eV) have been applied to fit the experimental curve recorded for the ordinary beam.^{38,39} Notably, the absorption onsets that appeared at around 5.1 and 5.8 eV in the absorption spectra of our α -Ga₂O₃ films coincided with those reported by Segura *et al.*,³⁷ Kracht *et al.*³⁸ and Feneberg *et al.*³⁹ indicating that the bandgap energies of these films were very similar to each other.

However, in a number of applications, the performance of α at the optical absorption edge rather than in the range of strong absorption is of importance. Therefore, the E_g values are frequently determined from the $(\alpha h\nu)^2$ versus $h\nu$ or $(\alpha h\nu)^{1/2}$

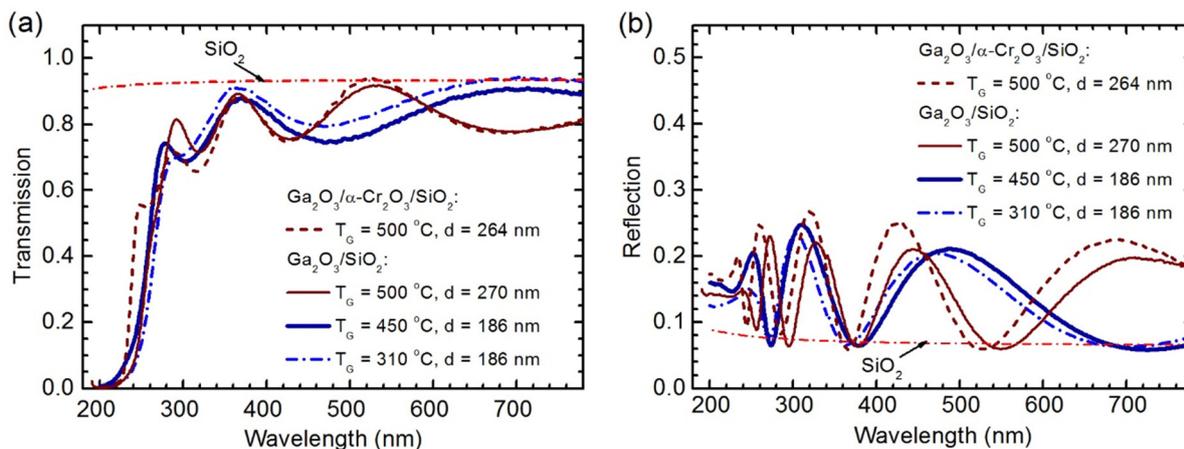


Fig. 5 Optical (a) transmission and (b) reflection spectra of Ga₂O₃ films grown at different temperatures on SiO₂ and α -Cr₂O₃/SiO₂ substrates. The thickness of the α -Cr₂O₃ layer was 1.1 ± 0.4 nm.



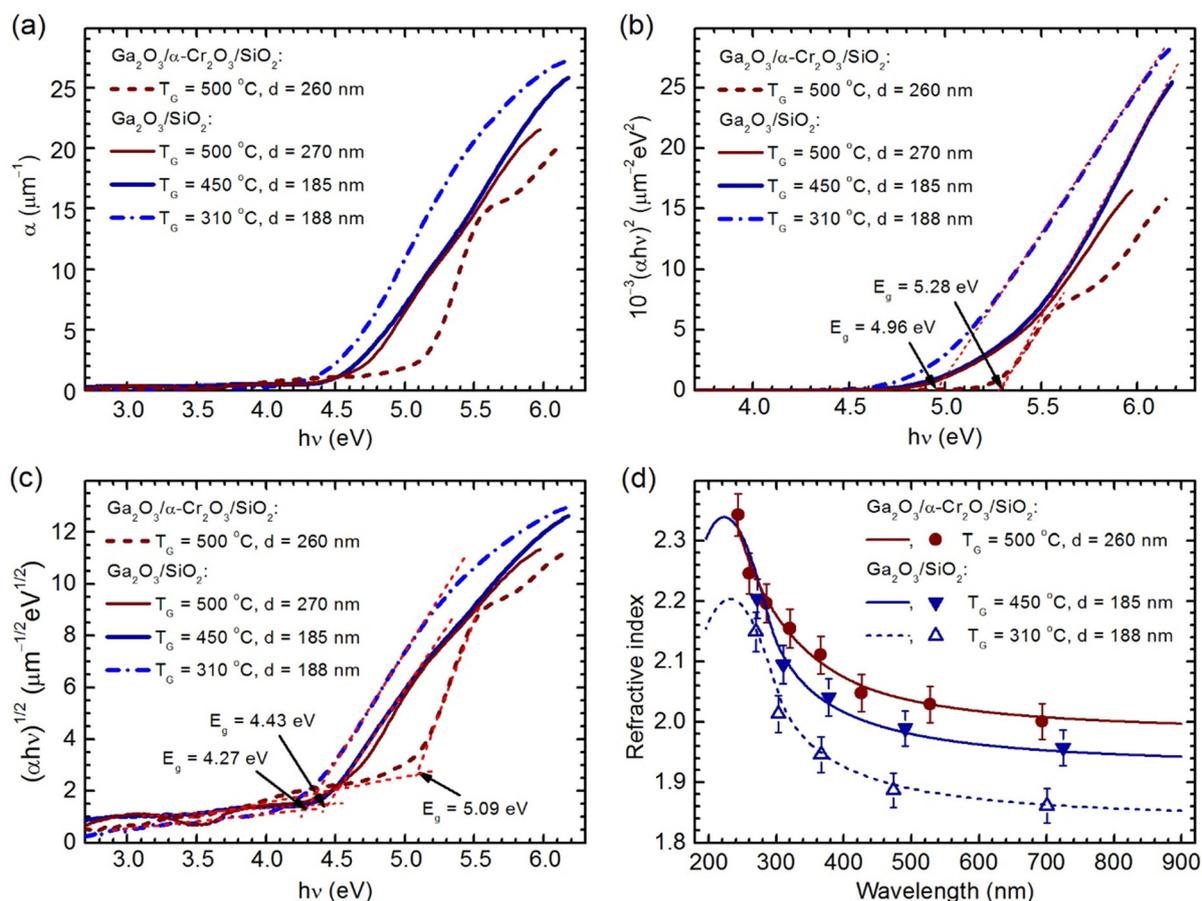


Fig. 6 (a) Absorption coefficient, (b) $(\alpha h\nu)^2$, and (c) $(\alpha h\nu)^{1/2}$ as a function of $h\nu$, and (d) refractive index as a function of wavelength determined for Ga_2O_3 films grown at different temperatures on SiO_2 and $\alpha\text{-Cr}_2\text{O}_3/\text{SiO}_2$ substrates. The thickness of the $\alpha\text{-Cr}_2\text{O}_3$ layer was 1.1 ± 0.4 nm.

versus $h\nu$ plots, while the former plots assuming direct optical transitions have mainly been used to determine optical bandgap energies of $\alpha\text{-Ga}_2\text{O}_3$,^{20,26,32–35} $\epsilon\text{-Ga}_2\text{O}_3$,^{45,46} $\kappa\text{-Ga}_2\text{O}_3$,^{9,47} and amorphous Ga_2O_3 .^{13–15,17,18,20,21,23–26} Extrapolating the linear parts of the $(\alpha h\nu)^2$ versus $h\nu$ plots of our films (Fig. 5(b)) yielded the optical bandgap energies in the approximation of direct optical transitions (E_{dg}) at 4.96 eV for amorphous Ga_2O_3 , 5.22–5.28 eV for $\kappa/\epsilon\text{-Ga}_2\text{O}_3$, and 5.28 eV for $\alpha\text{-Ga}_2\text{O}_3$ (Table 1). The E_{dg} values of amorphous Ga_2O_3 and $\alpha\text{-Ga}_2\text{O}_3$ were consistent with corresponding values of 4.05–5.47 eV^{13–15,17,18,20,21,23–26} and 5.04–5.36 eV^{20,26,32–35} reported in earlier publications. In contrast, the E_{dg} values determined for $\kappa/\epsilon\text{-Ga}_2\text{O}_3$ exceeded those of 4.6–5 eV^{45,46} and 4.9–5.14 eV^{9,29,47,48} published for $\epsilon\text{-Ga}_2\text{O}_3$ and $\kappa\text{-Ga}_2\text{O}_3$, respectively. It is also worth mentioning that E_{dg} obtained for our amorphous Ga_2O_3 films were very close to the most typical values of 4.80–5.00 eV obtained for amorphous Ga_2O_3 films grown by ALD previously.^{13–16,18,24}

Comparing the absorption spectra (Fig. 6(a)) and E_{dg} values obtained from the results depicted in Fig. 6(b), one can see that the absorption was relatively strong at the E_{dg} values determined from the $(\alpha h\nu)^2$ versus $h\nu$ curves. Consequently, the direct transition analysis was not sensitive enough to the absorption at the photon energies close to the absorption edges

Table 1 Optical bandgap values E_{dg} determined from the $(\alpha h\nu)^2$ versus $h\nu$ plots and E_{ig} determined from the $(\alpha h\nu)^{1/2}$ versus $h\nu$ plots for 185–270 nm thick Ga_2O_3 films grown on SiO_2 and $\alpha\text{-Cr}_2\text{O}_3/\text{SiO}_2$ substrates

T_{G} (°C)	Substrate	d (nm)	Phase	E_{dg} (eV)	E_{ig} (eV)
310	SiO_2	188	Amorphous	4.96 ± 0.03	4.27 ± 0.03
450	SiO_2	185	$\kappa/\epsilon\text{-Ga}_2\text{O}_3$	5.28 ± 0.03	4.43 ± 0.03
500	SiO_2	270	$\kappa/\epsilon\text{-Ga}_2\text{O}_3$	5.22 ± 0.05	4.43 ± 0.04
500	$\alpha\text{-Cr}_2\text{O}_3/\text{SiO}_2^a$	260	$\alpha\text{-Ga}_2\text{O}_3$	5.28 ± 0.03	5.09 ± 0.03

^a The thickness of the $\alpha\text{-Cr}_2\text{O}_3$ layer was 1.1 ± 0.4 nm.

of these materials. Furthermore, the linear parts in the $(\alpha h\nu)^2$ versus $h\nu$ plots of the films deposited on SiO_2 at 450–500 °C were relatively short and appeared at photon energies significantly exceeding the E_{dg} values determined from these plots (Fig. 6(b)). This obviously resulted in additional uncertainty in the determination of E_{dg} for these films. Therefore, the optical bandgap energies were also determined from the $(\alpha h\nu)^{1/2}$ versus $h\nu$ plots (Fig. 6(c)) assuming indirect optical transitions between the valence and conduction bands. The E_{ig} values obtained in this approximation were 4.27 eV for amorphous Ga_2O_3 , 4.43 eV for $\kappa/\epsilon\text{-Ga}_2\text{O}_3$, and 5.09 eV for $\alpha\text{-Ga}_2\text{O}_3$ (Table 1). These energies correspond well to the absorption onsets



(Fig. 6(a)). Therefore, it is possible that the Ga_2O_3 phases studied in this work have indirect bandgaps as it has been predicted for $\alpha\text{-Ga}_2\text{O}_3$ in theoretical calculations.^{58–60} Notably, the $E_{\text{dg}} - E_{\text{ig}}$ value of 0.19 eV, determined from the absorption spectra of $\alpha\text{-Ga}_2\text{O}_3$ in this work is close to the corresponding values of 0.21–0.25 eV obtained from the first-principles calculations.^{58–60}

Alternatively, there is a possibility that the bandgap is direct but the electron transitions do not follow the momentum selection rule, when the photon energies causing the transitions are close to the bandgap energies. The latter effect might be related to the structural defects, impurities, and/or band tails that can contribute to the electron transitions at photon energies close to the bandgap values.⁶¹ Therefore, it is not surprising that the recent experimental results of Ma *et al.*,⁶² yielding an E_{ig} value of 5.02 eV for $\alpha\text{-Ga}_2\text{O}_3$ from the $(\alpha h\nu)^{1/2}$ versus $h\nu$ plots, also indicate that contribution of indirect transitions to the shapes of absorption spectra at the absorption edge of this phase cannot be neglected.

Refractive indices determined as a function of wavelength for the Ga_2O_3 films deposited on SiO_2 and $\alpha\text{-Cr}_2\text{O}_3/\text{SiO}_2$ substrates are depicted in Fig. 6(d). The experimental points with error bars correspond to the n values determined from the spectrophotometry data, while the curves were calculated from the results of SE measurements. Expectedly, the n values of $\kappa/\epsilon\text{-Ga}_2\text{O}_3$ and $\alpha\text{-Ga}_2\text{O}_3$ films grown on SiO_2 and $\alpha\text{-Cr}_2\text{O}_3/\text{SiO}_2$ at 450 and 500 °C, respectively, were markedly higher than those of an amorphous film deposited on SiO_2 at 310 °C (Fig. 6(d)). Very similar results, obtained for the 80–107 nm thick films on Si and $\alpha\text{-Cr}_2\text{O}_3/\text{Si}$, are shown in Fig. 7.

The data presented in Fig. 7 demonstrate that the variation of T_{G} from 200 to 375 °C and from 450 to 550 °C did not cause considerable changes in the n values and dispersion curves of the films grown on Si substrates. However, the T_{G} increase from 375 to 450 °C causing the transition from the growth of

Table 2 Comparison of refractive index values determined by spectroscopic ellipsometry at 365 and 633 nm for Ga_2O_3 films grown on Si, SiO_2 , $\alpha\text{-Cr}_2\text{O}_3/\text{Si}$, and $\alpha\text{-Cr}_2\text{O}_3/\text{SiO}_2$ substrates

T_{G} (°C)	Substrate	d (nm)	Phase	n at 365 nm	n at 633 nm
310	Si	188	Amorphous	1.95 ± 0.02	1.86 ± 0.02
310	SiO_2	188	Amorphous	1.95 ± 0.02	1.86 ± 0.02
450	Si	189	$\kappa/\epsilon\text{-Ga}_2\text{O}_3$	2.01 ± 0.03	1.93 ± 0.02
450	SiO_2	185	$\kappa/\epsilon\text{-Ga}_2\text{O}_3$	2.02 ± 0.03	1.94 ± 0.02
500	Si	273	$\kappa/\epsilon\text{-Ga}_2\text{O}_3$	2.06 ± 0.03	1.98 ± 0.02
500	SiO_2	270	$\kappa/\epsilon\text{-Ga}_2\text{O}_3$	2.04 ± 0.03	1.98 ± 0.02
500	$\alpha\text{-Cr}_2\text{O}_3/\text{Si}^a$	269	$\alpha\text{-Ga}_2\text{O}_3$	2.06 ± 0.03	2.01 ± 0.03
500	$\alpha\text{-Cr}_2\text{O}_3/\text{SiO}_2^b$	260	$\alpha\text{-Ga}_2\text{O}_3$	2.09 ± 0.03	2.02 ± 0.03

^a The thickness of the $\alpha\text{-Cr}_2\text{O}_3$ layer was 0.7 ± 0.3 nm. ^b The thickness of the $\alpha\text{-Cr}_2\text{O}_3$ layer was 1.1 ± 0.4 nm.

amorphous phase to the growth of $\kappa/\epsilon\text{-Ga}_2\text{O}_3$ led to a marked increase in n (Fig. 7). In line with the results presented in Fig. 6(d), even higher n values were measured for the $\alpha\text{-Ga}_2\text{O}_3$ films deposited on the $\alpha\text{-Cr}_2\text{O}_3/\text{Si}$ substrates.

As it was expected, the films grown on Si and $\alpha\text{-Cr}_2\text{O}_3/\text{Si}$ substrates had n values that were very similar to those of the films deposited on SiO_2 and $\alpha\text{-Cr}_2\text{O}_3/\text{SiO}_2$, respectively (Table 2). The minor differences observed did not exceed the experimental uncertainty. Comparing the results presented in Table 2 and Fig. 8, one can see that at $d > 80$ nm, the dependence of n on d was weak. However, at lower film thicknesses, n decreased with decreasing d (Fig. 8(a)).

As an one-layer model was used to analyse the SE data, one probable reason for the decrease in n observed with decreasing d at lower film thicknesses was the increasing contribution of surface roughness, causing the formation of surface layer with lower density and, correspondingly, a decrease in the mean value of n calculated from the SE results. For instance, the XRR analysis yielded surface roughness values of 0.9 and 1.0 nm for the 59 and 85 nm thick films grown on Si at 350 °C, 4.5 and 5.0 nm for the 44 and 85 nm thick films grown on Si at 450 °C, and 2.5 nm for the 43 and 83 nm thick films grown on $\alpha\text{-Cr}_2\text{O}_3/\text{Si}$ at 450 °C. Therefore, with the thickness decrease in these d ranges, the surface roughness decreased insignificantly or did not decrease at all. Correspondingly, the relative amount of material with lower n increased with decreasing film thickness leading to the decrease in the mean value of n .

To characterize the effect of T_{G} on n in more detail, the values of n determined at wavelengths of 365 and 633 nm for films with thicknesses of 79–107 nm deposited on Si and $\alpha\text{-Cr}_2\text{O}_3/\text{Si}$ substrates are displayed in Fig. 8(b) as a function of T_{G} . Comparison of the results presented in Fig. 1(a), (b) and 8(b) leads to a conclusion that the effect of T_{G} on n is insignificant in the T_{G} ranges where no phase transitions take place. For instance, no considerable influence of T_{G} was observed on n of amorphous films grown on bare Si at 150–425 °C, $\kappa/\epsilon\text{-Ga}_2\text{O}_3$ films grown on bare Si substrates at 450–550 °C, and $\alpha\text{-Ga}_2\text{O}_3$ films grown on $\alpha\text{-Cr}_2\text{O}_3/\text{Si}$ at 350–550 °C. In contrast, marked increase in n of films deposited on bare Si and $\alpha\text{-Cr}_2\text{O}_3/\text{Si}$ is observed with the T_{G} increase from 425 to 450 °C and from 230 to 350 °C, respectively (Fig. 8(b)), that is,

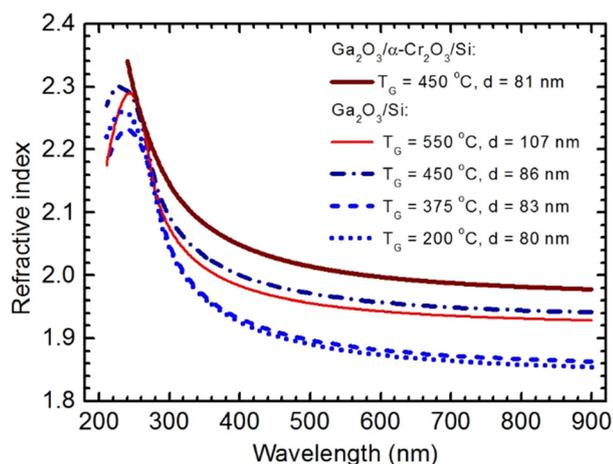


Fig. 7 Refractive index as a function of wavelength determined by spectroscopic ellipsometry for Ga_2O_3 films grown at different temperatures on Si and $\alpha\text{-Cr}_2\text{O}_3/\text{Si}$ substrates. The thickness of the $\alpha\text{-Cr}_2\text{O}_3$ layer was 1.1 ± 0.4 nm.



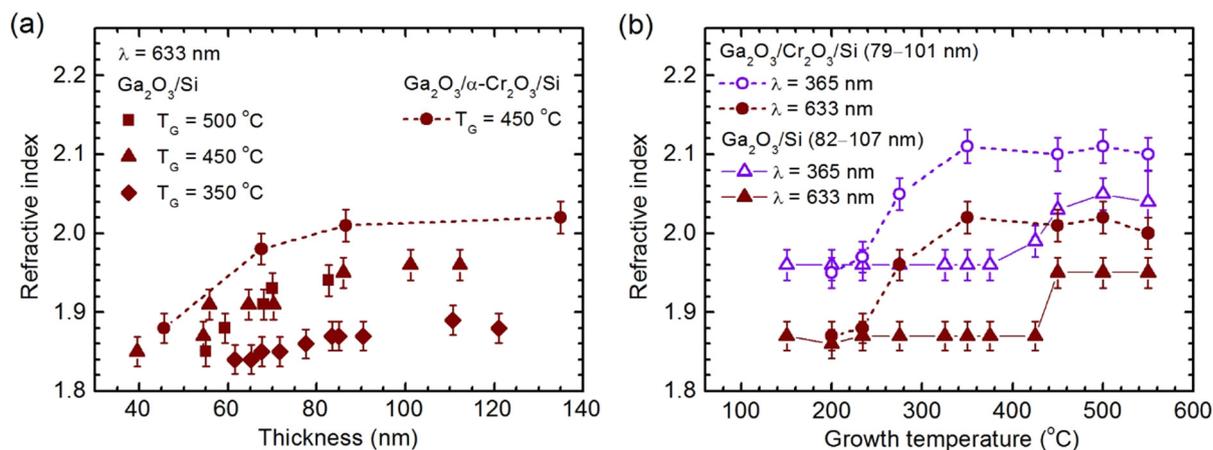


Fig. 8 Refractive index as a function of (a) thickness of films grown at 350, 450 and 500°C and (b) growth temperatures of 82–107 nm thick films grown on Si and 79–101 nm thick films grown on $\alpha\text{-Cr}_2\text{O}_3/\text{Si}$ substrates. The $\alpha\text{-Cr}_2\text{O}_3$ seed layer thicknesses were $9 \pm 3\text{ nm}$. The refractive indices were calculated at wavelengths of (a) 633 nm and (b) 365 and 633 nm from the spectroscopic ellipsometry data.

with the transition from the growth of amorphous to that of crystalline films (Fig. 1(a) and (b)).

The n values, obtained for amorphous Ga_2O_3 in this work (Table 2 and Fig. 8(b)), were well comparable to the highest values (1.84–1.87 at $\lambda = 633\text{ nm}$) reported for amorphous films in previous ALD studies.^{13,14,16,18} In addition, the n values obtained for the films grown on $\alpha\text{-Cr}_2\text{O}_3/\text{Si}$ and $\alpha\text{-Cr}_2\text{O}_3/\text{SiO}_2$ in this work (Table 2 and Fig. 8(b)) were close to a value of 2.00 that can be determined from the ellipsometry data of Feneberg *et al.*³⁹ published for the epitaxial films grown on $\alpha\text{-Al}_2\text{O}_3$ (0 0 0 1) by ultrasonic mist chemical vapour epitaxy.

When comparing the results of our experiments with those of earlier studies, one can see that the n values of $\kappa/\epsilon\text{-Ga}_2\text{O}_3$ films recorded at 633 nm (Table 2 and Fig. 8) are somewhat higher than the corresponding values of 1.83–1.94 at 633 nm reported for stoichiometric $\beta\text{-Ga}_2\text{O}_3$.^{14,16,22,25,27,28,30} One can also notice that refractive indices of 2.00–2.02 obtained for $\alpha\text{-Ga}_2\text{O}_3$ at 633 nm in this work (Table 2 and Fig. 8) and by

Feneberg *et al.*³⁹ are close to that of 2.04 determined at 633 nm for $\gamma\text{-Ga}_2\text{O}_3$.^{58,63} However, the E_{dg} and E_{ig} values of $\alpha\text{-Ga}_2\text{O}_3$ (Table 1) are markedly higher than the respective values of 5.0 and 4.4 eV^{58,63} reported for $\gamma\text{-Ga}_2\text{O}_3$.

In agreement with theoretical considerations and results obtained earlier for other materials,^{64–66} the refractive index values (Fig. 8) increase together with the material densities (Fig. 3(a)). Additionally, our data demonstrate that the E_g values are in positive correlation with the densities of Ga_2O_3 phases studied in this work. The latter result is not common for other materials. For instance, high-density rutile and $\text{TiO}_2\text{-II}$ phases of TiO_2 have narrower bandgaps compared to that of the low-density anatase phase.⁶⁶ An explanation for this difference can be deduced from the results of Ohta *et al.*,⁶⁷ who investigated phase transition of anatase to $\text{TiO}_2\text{-II}$ at high hydrostatic pressures. They observed a predictable shift of the optical absorption edge of anatase to higher energies, caused by the reduction of average bond length and corresponding increase

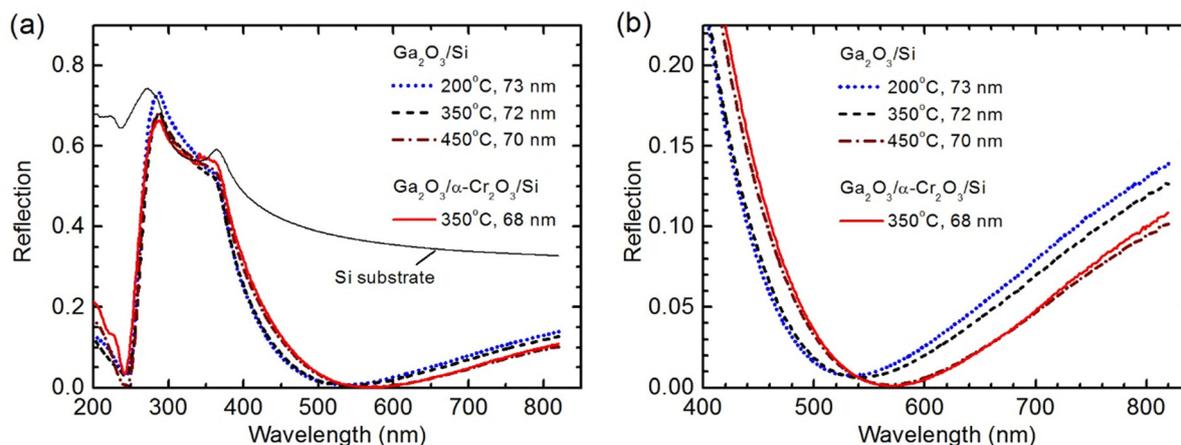


Fig. 9 Reflection spectra recorded in wavelength ranges of (a) 200–820 nm and (b) 400–820 nm for silicon substrates coated with Ga_2O_3 and $\text{Ga}_2\text{O}_3/\alpha\text{-Cr}_2\text{O}_3$ antireflection coatings. (a) Reflection spectrum of bare silicon substrate is shown for comparison. The thickness of $\alpha\text{-Cr}_2\text{O}_3$ was $1.5 \pm 0.5\text{ nm}$.



Table 3 Properties of Ga₂O₃ and Ga₂O₃/α-Cr₂O₃ antireflection coatings deposited on Si substrates

T _G (°C)	Phase	Thickness (nm)	λ _{min} (nm)	R _{min} (%)
200	Amorphous	73 ± 3	533 ± 5	0.75 ± 0.08
350	Amorphous	72 ± 3	540 ± 5	0.68 ± 0.07
450	κ/ε-Ga ₂ O ₃	70 ± 3	570 ± 5	0.20 ± 0.05
350	α-Ga ₂ O ₃ /α-Cr ₂ O ₃	68 ± 3/1.5 ± 0.5	570 ± 5	0.12 ± 0.04

in the material density under the increasing hydrostatic pressure. However, at pressures causing the phase transformation from anatase to TiO₂-II, an abrupt absorption-spectrum shift to lower energies appeared because of the atomic rearrangement. Therefore, the higher E_g values, recorded for Ga₂O₃ phases with higher densities in our experiments, indicate that the differences of the atomic arrangements in these phases from those in the Ga₂O₃ phases with lower densities do not cause bandgap shrinking that would be comparable to the E_g increase due to the decrease in the average bond length or unit cell volume.^{60,68}

In the visible range of spectrum, the n^2 values calculated on the basis of data depicted in Table 2 and Fig. 8 were close to the refractive index value of silicon.⁶⁹ Therefore, the Ga₂O₃ films studied in this work were expected to be suitable for highly efficient single-layer antireflection (AR) coatings of silicon-based optoelectronic devices, for instance, solar cells and photodiodes. The reflection spectra, measured for silicon substrates coated with Ga₂O₃ and Ga₂O₃/α-Cr₂O₃ thin films at different temperatures, demonstrate that at wavelengths (λ_{min}) corresponding to the reflection minima, the reflection values (R_{\min}) below 1% can be obtained for all coatings studied (Fig. 9 and Table 3). The lowest R_{\min} values that reached 0.12% were recorded for the α-Ga₂O₃/α-Cr₂O₃ AR coatings. However, the R_{\min} of the κ/ε-Ga₂O₃-coated Si was also very low (Table 3).

It is also worth noting that the light transmission through the α-Ga₂O₃/α-Cr₂O₃ AR coatings is sufficiently high only at wavelengths exceeding 400 nm. At lower wavelengths, the absorption of light in the α-Cr₂O₃ seed layer might become significant. For instance, using the data published for α-Cr₂O₃ thin films,⁷⁰ the absorption in a 1 nm thick seed layer was estimated to increase from ≤0.2% at 400 nm to 1.5% at 350 nm, 3.8% at 300 nm, and 8% at 200 nm. Hence at wavelengths below 400 nm, the κ/ε-Ga₂O₃-AR coatings are evidently more efficient than the α-Ga₂O₃/α-Cr₂O₃ AR coatings.

4. Conclusions

The results of this work confirm significant influence of the crystal growth and phase composition on the density and optical properties of Ga₂O₃. Notably the formation of phases with higher densities caused an increase in both the optical bandgap energies and refractive indices. The bandgap energies, estimated from the $(\alpha h\nu)^2$ versus $h\nu$ plots for the amorphous, κ/ε, and α phases of Ga₂O₃ with the densities of 5.2–5.6, 5.9–6.1, and 6.2–6.4 g cm⁻³, were 4.96, 5.22–5.28, and 5.28 eV, respectively. These values were consistent with previous data, obtained using the same approach that assumed domination of

direct optical transitions in the absorption process. However, the bandgap values of 4.27, 4.43, and 5.09 eV, respectively, determined from the $(\alpha h\nu)^{1/2}$ versus $h\nu$ plots corresponding to the indirect transitions, characterized the optical absorption edge energies even better. This result indicates that most probably, the electron transitions, caused by absorption of radiation with photon energies close to the absorption edge, do not follow the momentum selection rule although most of the Ga₂O₃ phases have generally been considered to be direct bandgap materials. Influence of impurities and/or structural defects on optical transitions can be a possible reason for this effect. The refractive index values of amorphous Ga₂O₃, κ/ε-Ga₂O₃, and α-Ga₂O₃ films, measured at 633 nm for films with thicknesses exceeding 70 nm, were 1.86 ± 0.03, 1.96 ± 0.03 and 2.01 ± 0.02, respectively. Because of appropriate refractive index values, these Ga₂O₃ phases appeared to be suitable for applications in AR coatings allowing the reduction of reflection from the silicon surface down to 0.12–0.20%.

The results of this work also reveal that the crystallization processes markedly influence GPC. Moreover, on the substrates that do not support epitaxial growth of a crystalline phase, the spontaneous crystallization may lead to considerable dependence of GPC on the Ga₂O₃ film thickness. These effects should also be considered when designing ALD processes for the deposition of optical coatings because, as a rule, the thickness is an important parameter of a thin film deposited for optical applications.

Data availability

Data are available upon request from the authors.

Conflicts of interest

There are no conflicts to declare.

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