Thermal stability of ε-Ga2O3 polymorph

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Abstract

The thermal stability of ε-Ga_2O_3 polymorph was studied by complementary methods. (0001)-oriented epitaxial films of ε-Ga_2O_3 were annealed at temperatures in the range 700-1000 °C and then investigated by X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM). In addition, Differential Scanning Calorimetry (DSC) up to 1100 °C was carried out on fragments of pure ε-Ga_2O_3 taken from a very thick layer. The results indicate that ε-Ga_2O_3 initiates modifying its crystallographic structure at about 680 °C as demonstrated by a mild endothermic bent of the DSC curve. However, the effective transition to β-phase occurs quite suddenly at 870-900 °C, depending of the heating rate. The XRD and TEM results confirm this evidence. TEM investigation in particular shows that after annealing at 1000 °C and rapid cooling the film is completely made of β-Ga_2O_3 grains, most of them with orientation (310) respect to the sapphire substrate. However, if the cooling rate is substantially reduced the converted β layer assumes the standard (-201) of β-Ga_2O_3 || to (001) of Al_2O_3 orientation.

1. Introduction

Oxides are materials with very high potential for novel generations of electronic devices, especially for sensing and energy applications. Among oxide semiconductors, sesquioxides (In_2O_3, Ga_2O_3, Al_2O_3 and their ternary alloys) have attracted much attention as they present a wide bandgap that ranges from 2.7 eV for In_2O_3 to 8.9 eV for Al_2O_3, which makes them in principle applicable as power diodes and transistors [1] [2] and solar-blind UV photodetectors [3] [4] [5]. Furthermore, they are generally hard and tolerate high temperatures and harsh environments, which allows their use as gas sensors [6] [7]. Most technological and scientific research so far focused on monoclinic β-Ga_2O_3, as it is the thermodynamically stable polymorph and available both as single crystal and thin epilayers. However, β-Ga_2O_3 generally presents anisotropic physical properties, and the single crystals are

prone to cleavage, which of course poses problems at the time of device manufacturing. For these reasons, there is an increasing interest about "novel" Ga_2O_3 polymorphs, for example the relatively unexplored phases (α, γ, δ, κ, ε) [8] [9] [10]. They generally present a crystallographic structure of higher symmetry than the β-phase (i.e. lower anisotropy), which makes them particularly attractive. However, they are metastable, which means that they tend to convert to β-phase upon high-temperature annealing.

The present paper focuses on the recently synthesized ε-Ga_2O_3 polymorph. Single-phase ε-Ga_2O_3 layers were reported for the first time by Oshima *et al.* by halide vapor phase epitaxy (HVPE) on GaN, AlN, and β-Ga_2O_3 substrates [11], and a little later by Boschi *et al.* [12] and Xia *et al.* [13] by means of Metal Organic Chemical Vapour Deposition (MOCVD), respectively on *c*-oriented sapphire and 6H-SiC.

The ε-phase was first observed in the middle of the last century in β-contaminated precipitates that had resulted from thermal decomposition of $Ga(NO_3)_3$ [8], while neutron diffraction studies showed that it belongs to hexagonal system with space group $P6_3mc$ [10], with a ratio of tetrahedral/octahedral gallium of 2.2:1 between close-packed oxygen layers. A later extensive crystallographic investigation of the real structure of ε-Ga_2O_3 showed that arrangement of tetrahedra and octahedra is not random, and that ordering actually occurs at the nanoscopic scale [14] [15]. The structure is made of a 4H (ABAC sequence) close-packed stacking of oxygen atoms along the c axis, whereby the Ga atoms occupy octahedral and tetrahedral sites forming two types of polyhedral layers parallel to (001). The edge-sharing octahedra and the corner-sharing tetrahedra form zig-zag ribbons along the [100] direction, resulting in orthorhombic $Pna2_1$ space group symmetry. This structure has an analogue among Al-oxides as well, the so-called κ-alumina. One should therefore be aware that ε-Ga_2O_3 may indeed show up a typical hexagonal (ε) or orthorhombic (κ) symmetry, according to the size of the ordered domains and resolution of the used characterization probe. Actually, due to the very small dimensions of the orthorhombic domains, they are clearly detected only by electron diffraction at the nanoscale. For the purpose of epitaxy and device technology ε-Ga_2O_3 can however be regarded as

an hexagonal semiconductor, with the same space group of gallium and aluminum nitride, which makes this material particularly attractive in view of developing novel nitride/oxide-based devices.

In this paper, we shall report for the first time on the results of complementary characterization methods (X-ray diffraction, XRD; Transmission Electron Microscopy, TEM; Differential Scanning Calorimetry, DSC) applied to a series of ε-Ga_2O_3 samples cut from the same wafer and submitted to thermal annealing at temperatures of 700-1000 °C in different atmospheres. From DSC, it appears that a minor change of the ε-Ga_2O_3 structure initiates already at 680-700 °C, although at present no conclusions about the actual nature of such modification can be drawn. On the other hand, a sudden and complete transition to β phase is detected by DSC at higher temperatures of 870-920 °C, this range being due to the inertia of the measurement system at different heating rates. The XRD and TEM results confirm this experimental evidence, as it will be discussed in detail below.

2. Experimental

For the annealing experiments, we selected a set of square specimens, with size of about 6 x 6 mm^2, cut from epilayers deposited by MOCVD at 650 °C on (0001)-oriented sapphire, following the procedure described in [12]. The samples were cleaned with organic solvents, before placing them within a tubular furnace with controlled inner atmosphere. Either pure nitrogen or pure oxygen were flushed inside the furnace during the entire annealing and cooling periods. Table I reports the parameters for the series of annealing experiments. A preliminary check by XRD showed that all as-grown films were c-oriented single-phase ε-Ga_2O_3, as demonstrated by the presence of sharp peaks at 19.17°, 38.85°, and 59.87°, corresponding to (002), (004), and (006) reflections, respectively.

The samples were measured by XRD before and after thermal treatments by using a Thermo ARL X'tra diffractometer equipped with a Si(Li) Thermo Electron solid-state detector and making use of Cu K_α radiation.

Additionally, some samples were investigated by TEM. Cross-sectional samples were thinned by conventional Ar ion beam milling. As charging of samples was significant, a few nm thin amorphous

carbon layer was evaporated on sample surface to prevent this effect. The prepared samples were examined by a Philips CM20 transmission electron microscope operating at 200 kV, and bright- field (BF) images and selected area electron diffraction (SAED) patterns were taken onto imaging plate detector. HR-TEM images, SAED patterns were acquired using a JEOL 3010 operating at 300 kV and equipped with LaB_6 cathode and Gatan Orius CCD camera.

DSC analysis was carried out on a very thick ε-Ga_2O_3 film (thickness of about 10 μm) grown exactly under the same conditions of the epilayers used for thermal annealing, but for a much longer time. DSC measurements were performed with a NETZSCH STA 449C "Jupiter" equipment. To obtain the highest sensitivity, samples (30-35 mg each) were put directly onto the sensor of a DSC-c_p sample carrier without using a crucible, and the measurements were performed in flowing helium (20 ml/min).

3. Results and Discussion

The basic characterization included X-ray diffraction of the films, before and after annealing. The as-grown sample consists of pure ε-phase Ga_2O_3 epitaxially grown with (001) orientation onto sapphire, as shown in Figure 1. This is confirmed by the peak positions, namely 2θ = 19.17°, 38.85°, 59.87°, corresponding to the (002), (004) and (006) reflections, respectively. It should be noted that the typical (-201) orientation of β-phase grown on sapphire gives rise to a similar peak sequence, however positioned at slightly different 2θ values (18.97, 38.46, 59.2°), according to the larger interplanar spacing. The annealing process modifies the structure of the films: after treatment at 700 °C one can note the appearance of new weak reflections (Figure 2), but complete conversion to β-Ga_2O_3 is observed only after thermal treatment above 900 °C. Noteworthy, in the fully converted β films, a precise epitaxial relation seems to be established during transition. A clearly dominant (-201) orientation is always detected for the β-phase, despite a broadening of the peaks with respect to as-grown samples. This actually indicates that the lattice re-arrangement is imperfect and that the phase transition leaves behind a somewhat defected structure.

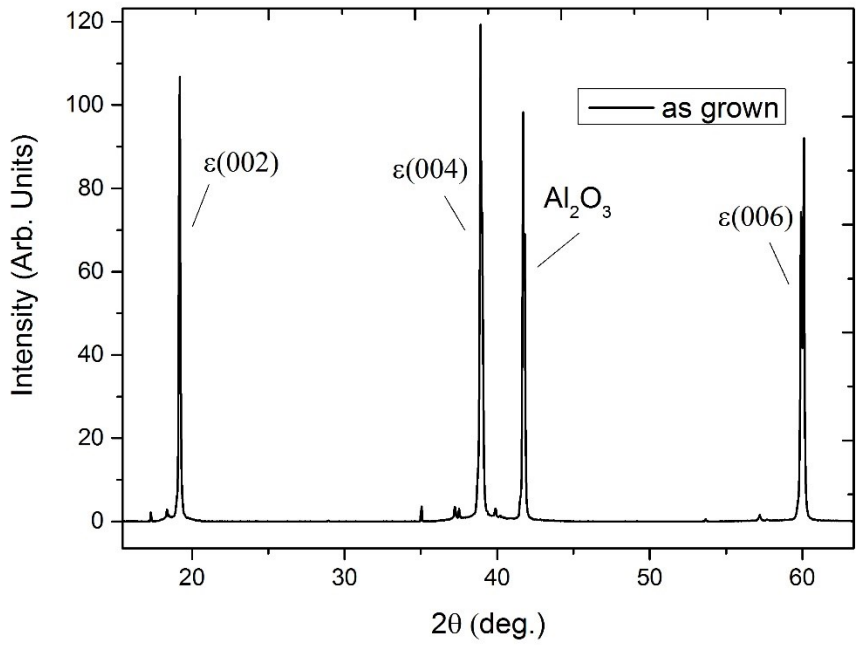


Fig.1: X-Ray powder diffraction pattern of as-grown ε-Ga_2O_3 thin film.

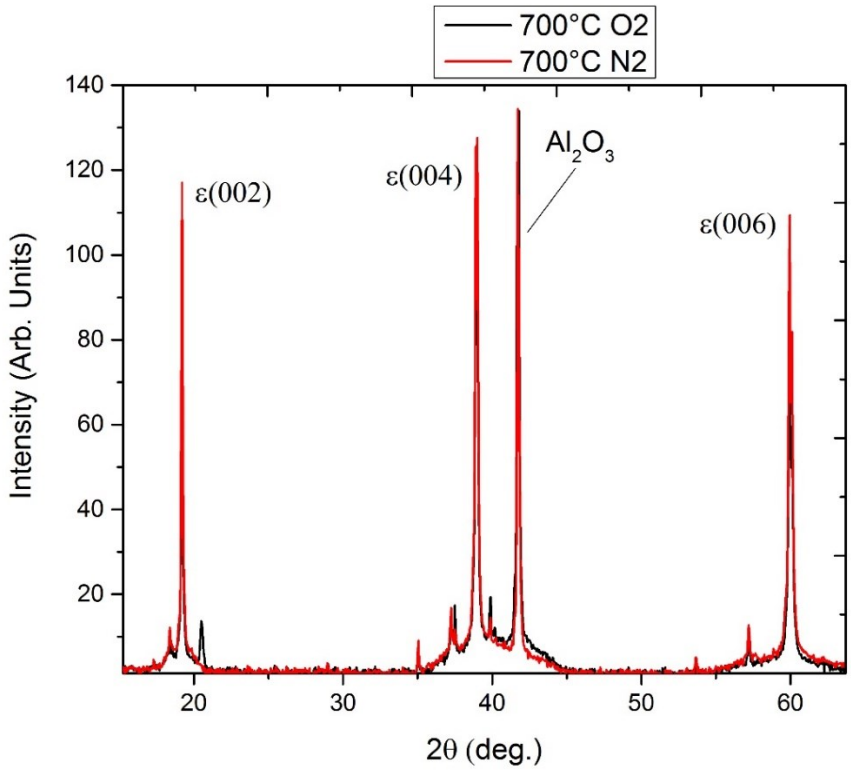


Fig. 2: X-Ray powder diffraction pattern of two Ga_2O_3 thin films annealed at 700 °C under O_2 or N_2 flow.

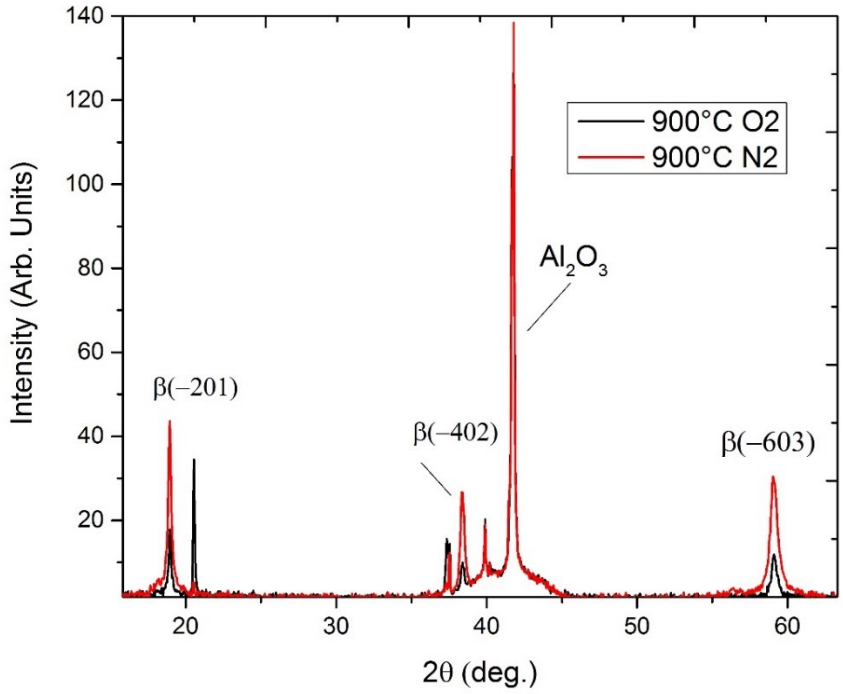
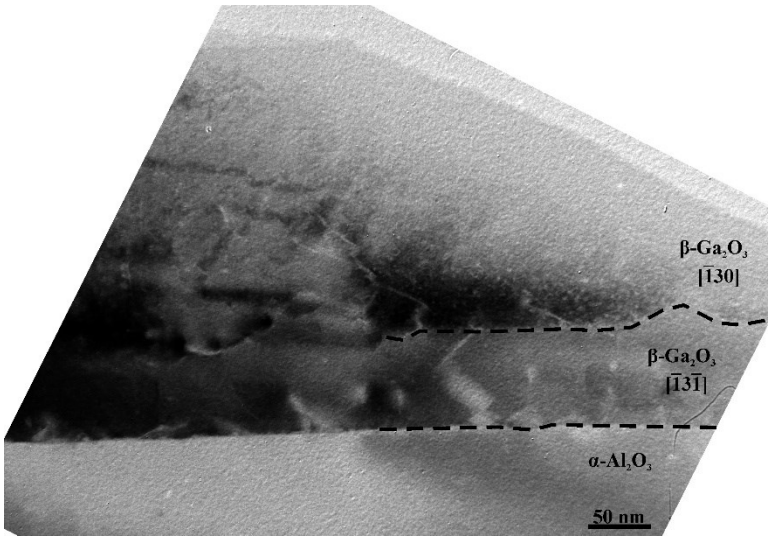
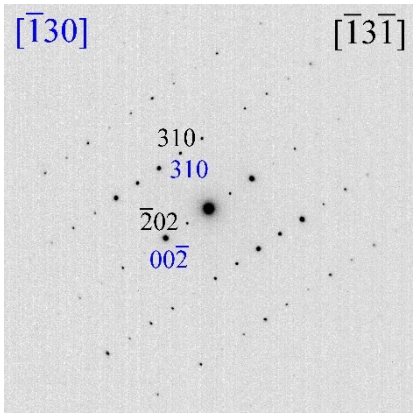


Fig.3: X-Ray powder diffraction pattern of two Ga_2O_3 films annealed at 900 °C in O_2 or N_2 flow.

As it will be discussed later, this observation is also confirmed by the TEM analysis, which additionally proves that the cooling rate applied for reaching room temperature after the treatment has a decisive effect on the microstructure of the converted epilayer. It is also interesting to note that the films annealed in oxygen or in nitrogen atmosphere practically behave in the same way. This proves that Ga_2O_3 is substantially stable, from the point of view of composition and stoichiometry, in the explored temperature range. Something strange happened in samples annealed for three hours at 800 °C, whose X-ray data did not show appreciable peaks of either β or ε type. The films seemed to be opaque to X-ray and to have lost crystallinity. This experimental fact was reproducibly observed in few specimens and strongly supports the idea that the ε-to-β transition takes place via an intermediate fully disordered step around 800°C. The amorphisation is permanent, as it was deduced from the featureless X-ray profiles. Only a baking at higher temperature may enable a recovery of crystalline (β) order, which very well agrees with the results of DSC analysis.



(a)



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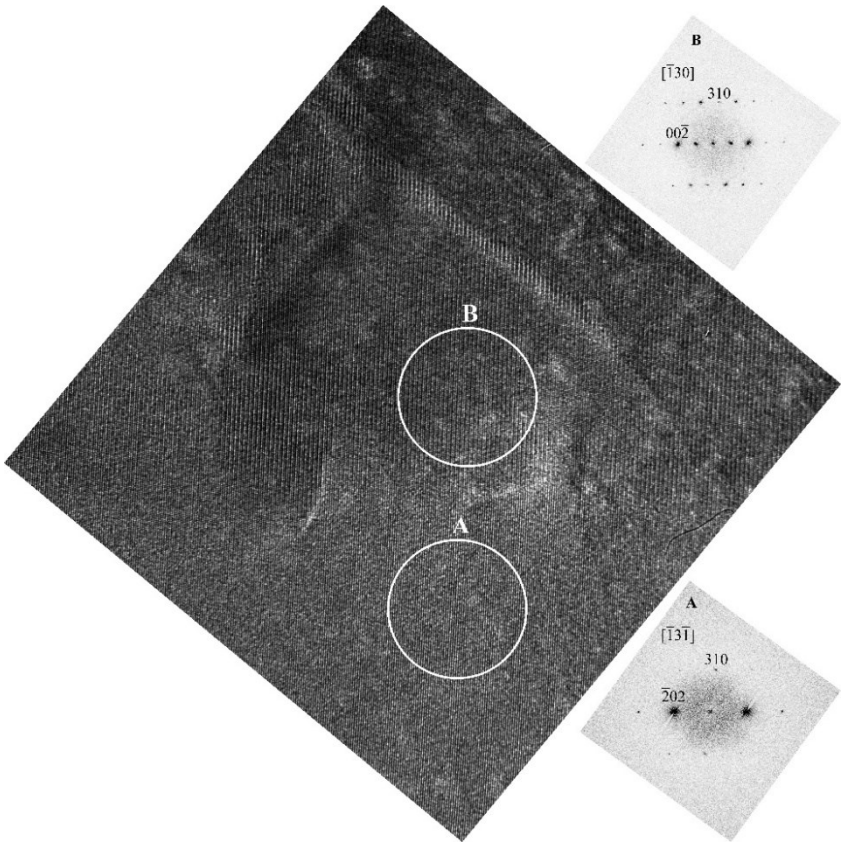
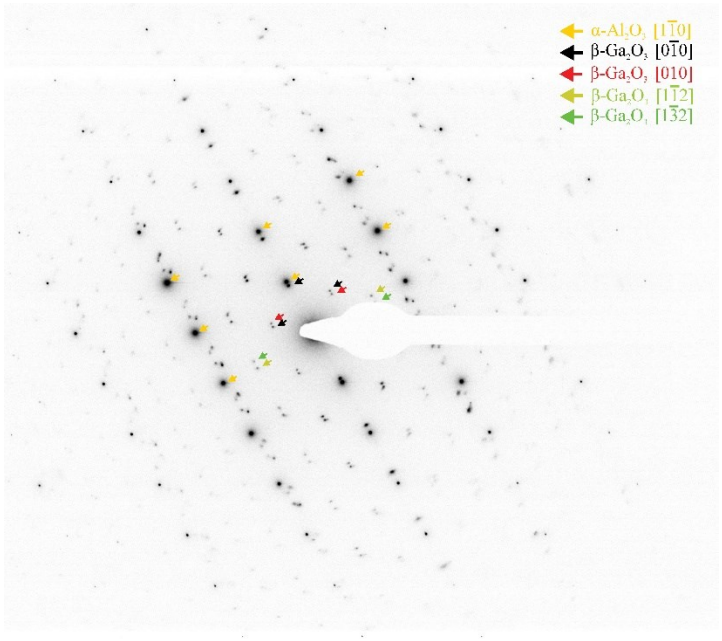


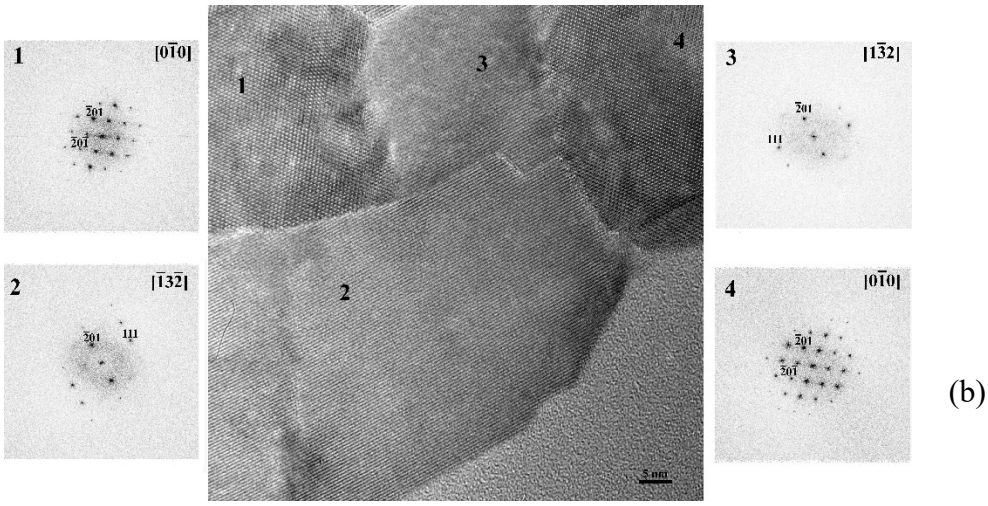
(c)

Fig. 4: TEM analysis of the layer #146c annealed at 1000 °C and cooled rapidly; BF (a), SAED (b) and HRTEM image with the corresponding FFTs (c) show that the layer consists of β-Ga_2O_3 with two dominant orientations.

High-resolution (HR) TEM investigations carried out on films annealed at 1000 °C confirmed the complete transformation of the ε-phase into the monoclinic β-phase (a = 12.21 Å; b = 3.03 Å; c =



(a)



(b)

(c)

Fig. 5: TEM analysis of the layer #146e annealed at 1000 °C and cooled in 12 hours. (a) SAED pattern shows that four different orientations of epitaxial β-Ga_2O_3 co-exist in the annealed layer (two pairs of (-201)-type twins). (b) and (c) HRTEM images of the layer with the corresponding FFTs showing the epitaxial β-Ga_2O_3.

5.75 Å; β = 103.6°; C2/m sg. [16]). A remarkable difference in lattice orientation between samples cooled slowly or rapidly was however observed. Figure 4 shows the cross-section of the epilayer cooled-down rapidly (#146c in Table 1). It is entirely consisting of monoclinic β-Ga_2O_3 and exhibits two large sub-layers, with perfect epitaxial match, (310)-oriented respect to the sapphire substrate (see the high-resolution image and the corresponding FFTs and SAED patterns in Fig. 4).

When the cooling rate is very low (down to room temperature in twelve hours), we instead found a pure-phase β-film, oriented with the (-201) plane of β-Ga_2O_3 || to Al_2O_3 (0001), which is typical for all epitaxial technologies on *c*-oriented sapphire [17] [18] [19]. As clearly visible in Figure 5, the annealed layer (sample #146e, about 180 nm thick) is composed of polycrystalline β-Ga_2O_3. Four different orientations of epitaxial β-Ga_2O_3 exist in the layer, forming two pairs of (-201)-type twins. However, all grains share the same [-201]* direction parallel to the [00l]* direction of the substrate.

In order to understand the kinetic of phase transformation, a very thick ε-Ga_2O_3 layer (about 9 μm) was grown on *c*-oriented sapphire. Some fragments were cut and utilized for DSC analysis. The results are summarized in Figure 6, where we reported two curves corresponding to different heating rates of 5 and 10 K/min, respectively. Each of the DSC heating curves shown in Fig. 6 was obtained from a virgin, thick ε-Ga_2O_3 specimen. Thermal effects are small but similar for both measurements, which is very satisfactory considering the very little sample mass (around 1.5 mg). As expected, thermal effects are less pronounced for the lower heating rate, because transformation heats have the possibility to thermalize with the measurement system over a longer time period. Also the heating run at 20 K/min of a third virgin specimen (not shown in figure to avoid a confusing overlap) showed very comparable results.

A first, weak temperature effect is observed in the 10 K/min curve at 620-650 °C. Here the DSC curve bends down to the endothermal direction, which indicates a slightly increased heat capacity. One can try to define the onset of this phenomenon by the 1st derivative (dashed line in figure), which provides a value of 622 °C. Two additional exothermal peaks, whose inflection points are located at 824 °C

and 891°C, respectively, are also observed in 10 K/min heating curve. As said before, all thermodynamic effects are more pronounced in the 10 K/min curve, yet very clear also for the 5 K/min rate. If one scales the area of the larger exothermal effect (about 550 mJ, see Figure 6) to the mass of the specimen, a heat of phase transformation around 70 kJ/mol is estimated from the larger peak.

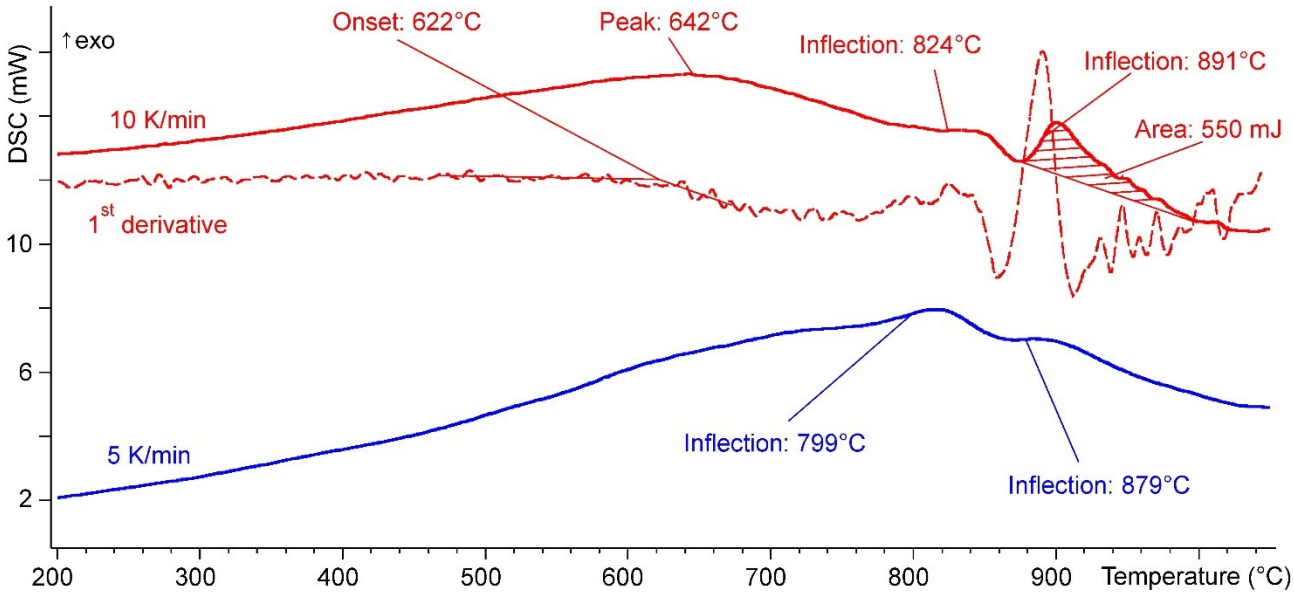


Figure 6: DSC curves of two ε-Ga_2O_3 layers on sapphire recorded at 10 and 5 K/min. The first derivative (DDSC) of the 10 K/min is also shown as a dashed line.

For the rate of 5 K/min, both effects (defined by their inflection points) are shifted to lower temperatures by 25 and 12 K, respectively, which is partly related to the thermal inertia of the measuring system. However, it must be noted that the area of the band around 799 °C becomes somewhat larger now, compared to the band at 879 °C. Such modifications of peak position and area are typical for kinetically driven reactions. Unfortunately, given the very small sample mass, the experimental data are too noisy to allow a detailed kinetic analysis and to find the process activation energy.

To reconcile all experimental observations, we propose that some kind of re-organization of the ε lattice already occurs at about 620 °C, as proved by the endothermic band of the DSC characteristics. However, as demonstrated by the X-ray diffraction profile in Figure 2, the ε-Ga_2O_3 film remains essentially crystalline up to 700 °C. Above this temperature, it would seem that a kind of slow amorphisation occurs, up to the "glass transition" at 800 °C. This is again consistent with the endothermic drop following the first inflection point of both DSC curves as well as with the absence of clear diffraction peaks in the X-ray spectra of samples annealed at 800 °C. Finally, at 880-890 °C the sample acquires enough energy for the crystallisation of the thermodynamically stable β lattice, as demonstrated by the corresponding DSC exothermic peak and the X-ray and TEM measurements. In view of determining the effective usability of ε-Ga_2O_3, one should therefore consider that a drastic loss of crystallinity is seen only when the treatment temperature approaches 800 °C, but that some minor structural modification initiates already below 700 °C. When planning applications for this nice polymorph of gallium oxide it is therefore necessary to include only technological steps (metallisation, thermal diffusion, etc.) at relatively low temperature.

4. Conclusions

In summary, undoped single-phase ε-Ga_2O_3 epitaxial films prepared by MOCVD were submitted to thermal treatments…..

Acknowledgements

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Table I: Summary of annealing experiments of ε-Ga_2O_3 epilayers

Sample #	Annealing T (°C)	Dwell Time (h)	Cooling Rate (°C/min)	Flowing gas	Film Thickness (nm)	Final phase	Notes
146 b2	700	3		O_2	500	ε	+Unknown peaks
146 g1	700	3		N_2	500	ε	+Unknown peaks
146 g5	900	3		O_2	500	β	+Two extra-peaks
146 g6	900	3		N_2	500	β	+Two extra-peaks
146 c	1000	6	fast	O_2	500	β	Mostly (310) oriented
146 e	1000	2	slow	O_2	500	β	Mostly (-201) oriented
224 c	500	3	slow	O_2	600	ε	
224 b	750	3	slow	O_2	700	ε + β	
224 d	1000	3	slow	O_2	450	β	

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