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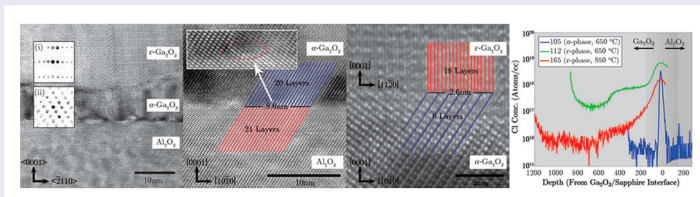
Growth and characterization of α -, β -, and ϵ -phases of Ga_2O_3 using MOCVD and HVPE techniques

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ABSTRACT

Heteroepitaxial films of Ga_2O_3 were grown on *c*-plane sapphire (0001). The stable phase β - Ga_2O_3 was grown using the metalorganic chemical vapor deposition technique, regardless of precursor flow rates, at temperatures between 500°C and 850°C. Metastable α - and ϵ -phases were grown when using the halide vapor phase epitaxy (HVPE) technique, at growth temperatures between 650°C and 850°C, both separately and in combination. XTEM revealed the better lattice-matched α -phase growing semi-coherently on the substrate, followed by ϵ - Ga_2O_3 . The epitaxial relationship was determined to be $[\bar{1}100] \epsilon\text{-Ga}_2\text{O}_3 \parallel [11\bar{2}0] \alpha\text{-Ga}_2\text{O}_3 \parallel [11\bar{2}0] \alpha\text{-Al}_2\text{O}_3$. SIMS revealed that epilayers forming the ϵ -phase contain higher concentrations of Cl introduced during HVPE growth.



IMPACT STATEMENT

This study demonstrates one of the first epitaxial growths of multiple polymorphs of Ga_2O_3 on sapphire (0001) substrates, including its β -, α -, and ϵ -phases. Epitaxial relationship is confirmed through HRTEM.

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KEYWORDS

MOCVD; HVPE; epitaxy; gallium oxide; polymorphs

1. Introduction

The wide band gap material β - Ga_2O_3 has attracted rapidly growing interest in the last decade due to its excellent potential for power [1] and ultraviolet optoelectronic devices [2] and its recent availability as single-crystal substrates [3]. Roy et al. first synthesized and reported five polymorphs of Ga_2O_3 , and designated them α -, β -, γ -, δ -, and ϵ - Ga_2O_3 [4]. δ - Ga_2O_3 has since then been shown to be a nanocrystalline form of ϵ - Ga_2O_3 [5]. Of the four distinct polymorphs, most research has focused on the monoclinic β -phase, which is the only thermodynamically stable phase from room temperature to its melting point at $\sim 1800^\circ\text{C}$; all other polymorphs are metastable and have been reported to transform into the β -phase within the temperature range of 750–950°C [6]. Single-crystal substrates of β - Ga_2O_3 are grown by a variety of melt-based methods, including

floating-zone (FZ) [7–10], edge-defined film-fed growth (EFG) [11], and Czochralski (CZ) [12,13] methods. Epitaxial films of β - Ga_2O_3 have been grown using various vapor phase techniques, including metalorganic chemical vapor deposition (MOCVD) [14], molecular beam epitaxy (MBE) [1,15–19], pulsed-laser deposition (PLD) [20], halide vapor phase epitaxy (HVPE) [21], and MIST epitaxy [22].

However, increasing interest in the other Ga_2O_3 phases has arisen in recent years, particularly the metastable rhombohedral α - and hexagonal ϵ - Ga_2O_3 phases, both of which have been observed to grow epitaxially on oriented substrates. The α - and ϵ -phases are of particular interest because of their higher symmetry and simpler epitaxial relationships with *c*-plane sapphire. Moreover, given their similar structures to other wide bandgap materials such as ZnO and AlN, it should

Table 1. Crystal parameters for α -Ga₂O₃, β -Ga₂O₃, and ε -Ga₂O₃ [5,23,24].

Phase	Crystal System	Point Group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)
α	Trigonal	R $\bar{3}$ c	4.983	–	13.433	–
β	Monoclinic	C2/m	12.214(3)	3.0371(9)	5.7981(9)	103.83(2)
ε	Hexagonal	P6 ₃ mc	2.907	–	9.2559	–

be possible to produce functional heterostructures or tunable bandgaps through alloying. A summary of the crystal parameters of α -, β -, and ε -Ga₂O₃ are provided in Table 1; for more detailed descriptions of the crystal structures, the reader is referred to [5,23]. On *c*-plane sapphire, typical orientations of the α -, β -, and ε -phases are (0001), ($\bar{2}$ 01), and (0001), respectively. These orientations correspond to lattice mismatches of 4.7%, 6.12%, and 5.6% to *c*-plane sapphire, respectively. α -Ga₂O₃ is the best lattice-matched polymorph and has the same corundum structure of sapphire.

Reports of successful epitaxial growths of the metastable α - and ε -Ga₂O₃ phases have recently emerged. Table 2 summarizes the growth methods, growth conditions, and resulting phase(s) described in these reports. With the exception of plasma-assisted MBE [16] growth of β -Ga₂O₃ containing α -Ga₂O₃ inclusions, which was conducted in the range of 500–1000°C, all reported films containing only α - and ε -Ga₂O₃ were grown at temperatures of $\leq 800^\circ\text{C}$. By comparison, typical growth temperatures of β -Ga₂O₃ epitaxial layers by MOCVD are $\sim 1100^\circ\text{C}$, although early MOCVD growth of β -Ga₂O₃

was reported at a growth temperature of 500–600°C [14]. The resulting epitaxial polymorph appears to be determined by a number of conditions, including growth temperature, growth rate, substrate, and source gases; i.e. the stable β -polymorph is favored at higher growth temperatures but can also form at lower growth temperatures, particularly on β -Ga₂O₃ substrates or at slow growth rates.

In the present study, the growth of α -, β - and ε -Ga₂O₃ epitaxial films on *c*-plane sapphire (001) substrates were investigated using different growth conditions, including choice of precursors, flow rates and growth temperatures. Two different growth methods were used: metalorganic chemical vapor deposition (MOCVD) and HVPE. HVPE produced a significantly higher growth rate than MOCVD and is therefore advantageous for growth of the very thick films needed in high voltage power devices. Results from X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (TEM) and secondary ion mass spectrometry (SIMS) are presented in the following sections and discussed in terms of the relationships between the growth conditions and the properties of the films.

2. Method

All samples discussed in this paper were grown in an in-house vertical vapor phase epitaxy reactor at Structured Materials Industries, Inc. (SMI). The reactor consists of a 16-inch diameter stainless steel chamber and

Table 2. Summary of epitaxial growths of α - and ε -Ga₂O₃ reported in the literature.

Method	Substrate	Precursors	Temperature	Pressure	Film Growth
MBE, PLD, MOCVD [25]	<i>c</i> -plane sapphire		575°C (MBE) 650°C (PLD) 800°C (MOCVD)	Low to moderate	3 monolayer pseudo-morphic α -Ga ₂ O ₃ followed by β -Ga ₂ O ₃ (110) α -Ga ₂ O ₃
RF magnetron sputtering [26]	<i>a</i> -plane sapphire	O ₂	> 600°C	N.R.	
Ultrasonic mist CVD [27]	<i>c</i> -plane sapphire	Ga(C ₅ H ₈ O ₃) ₃ , DI water, HCl, N ₂ carrier gas	430–470°C (amorphous at lower <i>T</i> , includes β -Ga ₂ O ₃ at higher <i>T</i>)	Atmospheric pressure	α -Ga ₂ O ₃
HVPE [28]	<i>c</i> -plane sapphire	Gallium chloride (Ga metal + HCl), O ₂ , N ₂ carrier gas	525–650°C	Atmospheric pressure	α -Ga ₂ O ₃
Plasma-assisted MBE [16]	<i>c</i> -plane sapphire	Ga and O ₂ plasma	500–1000°C	Gallium beam equivalent pressure (BEP) = 3×10^{-8} – 1.5×10^{-7}	β -Ga ₂ O ₃ with α -Ga ₂ O ₃ inclusions
MOCVD [29,30]	<i>c</i> -plane sapphire	TMGa and H ₂ O	650°C	100 mbar	ε -Ga ₂ O ₃
ALD [30]	<i>c</i> -plane sapphire	TMGa and H ₂ O	550°C	N.R.	ε -Ga ₂ O ₃
HVPE [31]	GaN (0001), AlN (0001), and β -Ga ₂ O ₃ ($\bar{2}$ 01)	GaCl ₃ and O ₂	550°C	N.R.	ε -Ga ₂ O ₃
Mist CVD [32]	MgO (111), YSZ (111)	Ga(C ₅ H ₈ O ₃) ₃ , DI water, HCl, N ₂ carrier gas	400–700°C	N.R.	ε -Ga ₂ O ₃
HVPE (This work)	<i>c</i> -plane sapphire	GaCl (Ga metal + HCl), O ₂ , Ar carrier gas	650–850°C	500 Torr	α -Ga ₂ O ₃ and ε -Ga ₂ O ₃
HVPE (This work)	<i>c</i> -plane sapphire	GaCl ₃ , O ₂	650–850°C	700 Torr	α -Ga ₂ O ₃ and ε -Ga ₂ O ₃

Note: MBE, molecular beam epitaxy; PLD, pulsed-laser deposition; RF, radio frequency; MOCVD, metal organic chemical vapor deposition; HVPE, hydride vapor phase epitaxy; ALD, atomic layer deposition; N.R., not reported.

a single rotating disc reactor with a 13-inch platter. Gas flows from a showerhead at the top of the chamber. All substrates used in this work were single-side chemo-mechanically polished, 2-inch diameter, *c*-plane (001) unintentionally doped (UID) sapphire (Al_2O_3) wafers obtained commercially.

For the MOCVD growth runs, the chamber pressure was held at 45 Torr and the temperature was varied from 500°C to 850°C. We established a baseline temperature at 650°C. These conditions were found by SMI in previous studies to maximize growth rate [33]. Trimethylgallium (TMGa) and O_2 were used as precursors, with Ar used as the carrier gas. Typical growth rates were ~ 10 nm/min.

For the HVPE growth runs, two different precursor processes were used. First, 15% HCl in Ar flowing at rates between 138 and 300 sccm over Ga metal was used to form GaCl at 600°C. The substrate temperature was varied between 650°C and 800°C and chamber pressure was kept at 550 Torr. In the second process, Ar carrier gas flowed at 200 sccm into the bubbler held at 700 Torr and 80°C to yield a nominal GaCl₃ flow of ~ 3.3 sccm. The substrate temperature and chamber pressure were kept at 600°C and 550 Torr, respectively. O_2 was used as the oxygen source in both process routes.

SEM images were acquired using an FEI Quanta 600 FEG scanning electron microscope at 15 keV. Secondary electron images were collected using an Everhardt Thornley secondary electron detector. XRD scans were conducted using a Panalytical X'pert Pro MPD X-ray diffractometer with a Cu $K\alpha$ X-ray source. Transmission electron microscopy (TEM) was conducted with an FEI Titan G2 80–300 operating at 300 kV. Images were taken with a 2048 $\times$ 2048 slow-scan CCD camera. SIMS was performed by EAG Analytical on a Physical Electronics ADEPT 1010, Cs was used as the primary beam at 5 keV and the negative ions were collected. Results were calibrated with reference to a standard made by ion implantation of Cl into a single-crystal Ga_2O_3 substrate. Anneals of the implanted samples were performed at 700–1000°C for 1 h in a quartz tube in a resistively heated furnace under an Ar ambient.

3. Results

In concurrence with standard reports of Ga_2O_3 epitaxy, all films grown in this research by MOCVD were observed to be β - Ga_2O_3 . Figure 1(a) shows the XRD spectrum of a representative β - Ga_2O_3 film grown at 650°C, with peaks for the set of $\{\bar{2}01\}$ planes of β - Ga_2O_3 at $2\theta = 18.949^\circ$, 38.420° , 59.184° and 82.375° , corresponding to the $(\bar{2}01)$, $(\bar{4}02)$, $(\bar{6}03)$ and $(\bar{8}04)$ reflections. The peak at $2\theta = 42.269^\circ$ is attributed to the (0006) reflection of the sapphire substrate and is common for

Table 3. Growth conditions for β , α , and ε - Ga_2O_3 films corresponding to the XRD patterns shown in Figure 1(a)–(c), respectively.

Run #	Growth method	Phase	Flow rate (sccm)			Pressure (Torr)	Growth rate (nm/min)
			15% HCl in Ar	TMGa	O_2		
105	HVPE	α	138	–	80	550	9.5
49	MOCVD	β	–	85	2800	45	1
114	HVPE	ε	300	–	800	550	18

Note: The β - Ga_2O_3 films were grown via MOCVD; the α - and ε - Ga_2O_3 were deposited using HVPE. All films were grown at 650°C for an hour.

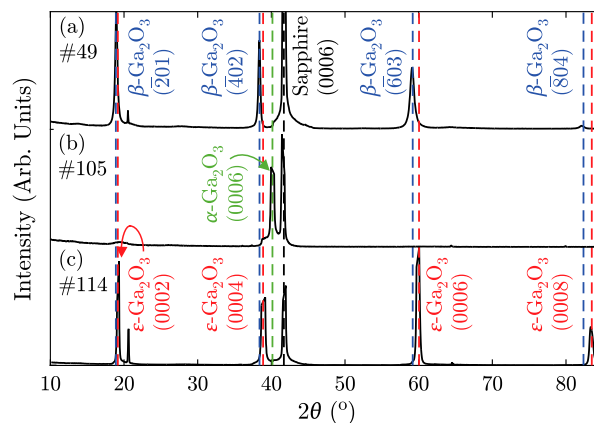


Figure 1. XRD of (a) β , (b) α , and (c) ε -phases. Growth conditions are shown in Table 3.

all the spectra in this figure. Schewski et al. reported the presence of a pseudomorphic layer of α -phase at the Ga_2O_3 /sapphire interface [25]. A shoulder is indeed observed at $2\theta = 40.15^\circ$, which is the location of the α - Ga_2O_3 (0006) peak. However, this shoulder is observed even on a bare sapphire substrate, and our cross-sectional TEM of a β - Ga_2O_3 /sapphire sample did not reveal the presence of an interfacial layer in the local regions observed, as shown in Figure 3(a). The epitaxial relationship was determined to be $(\bar{2}01) \beta\text{-Ga}_2\text{O}_3 \parallel (0001) \alpha\text{-Al}_2\text{O}_3$, which agrees with previous reports [16].

In contrast, the films grown by HVPE were found to consist of α - and/or ε - Ga_2O_3 . Figure 1(b,c) shows the XRD spectra of two samples (#105 and #114) also grown at 650°C containing α - and ε - Ga_2O_3 as the respective dominant phases. For sample #105 (Figure 1(b)), the XRD peak at 40.15° corresponds to the (0006) reflection of α - Ga_2O_3 , while the bump at 19.16° and shoulder at 38.88° suggest that this sample may also contain minor amounts of ε - Ga_2O_3 . For sample #114, peaks for the ε - Ga_2O_3 {0002} set of planes were observed at 19.16° , 38.88° , 60.06° , and 83.50° , corresponding to the (0002), (0004), (0006), and (0008) reflections, respectively. The XRD results shown in Figure 1 are similar to results

we reported previously for samples grown under slightly different growth conditions [34].

In order to understand the growth conditions giving rise to the metastable phases during HVPE, a series of HVPE growth runs with different carrier gas flow rates was investigated. GaCl₃ was used as the Ga precursor and was kept at a constant flow rate of 200 sccm, and at temperature and pressure of 80°C and 700 Torr, respectively. Chamber pressure and growth temperature were 550 Torr and 650°C, respectively. All growth runs were for 1 h.

SEM images of these HVPE films (growth runs #86–#89) are presented in Figure 2(a)–(d), respectively. Distinctive hexagonal islands were observed on the surfaces of films #86 and #87, as shown in Figure 2(a,b), respectively. This observation is consistent with a reported island growth mechanism for ϵ -Ga₂O₃ [30]. Comparison of the SEM images in Figure 2(b,c) shows that the islands grew to a maximum size of ~ 200 nm prior to the onset of coalescence. The surface coverage increases from left to right in general correspondence with a decrease in the O₂ flow rate and increase in the Ar flow rate. For sample #89 (Figure 2(d)), the film achieved complete coverage; according to a spectral reflectometry measurement, the thickness of the film was ~ 300 nm. Accurate thickness measurements of the other films were not obtained due to their non-uniform coverage.

XRD θ -2 θ scans shown in Figure 2(e) indicate that HVPE film #'s 86–89 consist of varying amounts of α - and ϵ -phases. The relative ϵ -to- α -phase peak intensity ratio increased with increasing Ar flow rate, or with increasing film coverage (from left to right, in Figure 2(a–d)).

An increase in the amount of ϵ -Ga₂O₃ relative to α -Ga₂O₃ with increasing thickness can be understood by observing the film/substrate interface in cross-section. A cross-section HRTEM image of sample #89 along the [11 $\bar{2}$ 0] zone axis of sapphire is shown in Figure 3(b). An ~ 10 nm thick interfacial layer on the sapphire substrate was identified as α -Ga₂O₃. The remainder of the film above the α -Ga₂O₃ layer was identified as ϵ -Ga₂O₃. Based on the data shown in Figures 2 and 3, it is possible that the film growth follows a Stranski-Krastanov-like growth mode, beginning with a semi-coherent layer of α -Ga₂O₃ on the sapphire substrate, followed by island growth of ϵ -Ga₂O₃. Further studies are needed to verify the growth mode.

The selected area diffraction pattern of the interfacial layer matches well with the [11 $\bar{2}$ 0] zone axis of α -Ga₂O₃. Furthermore, a closer examination of the sapphire/ α -Ga₂O₃ interface in Figure 3(c) reveals a lattice offset that corresponds to the lattice mismatch between α -Ga₂O₃ and c-plane sapphire. This shows that the α -epilayer grew semi-coherently on the sapphire substrate. Since

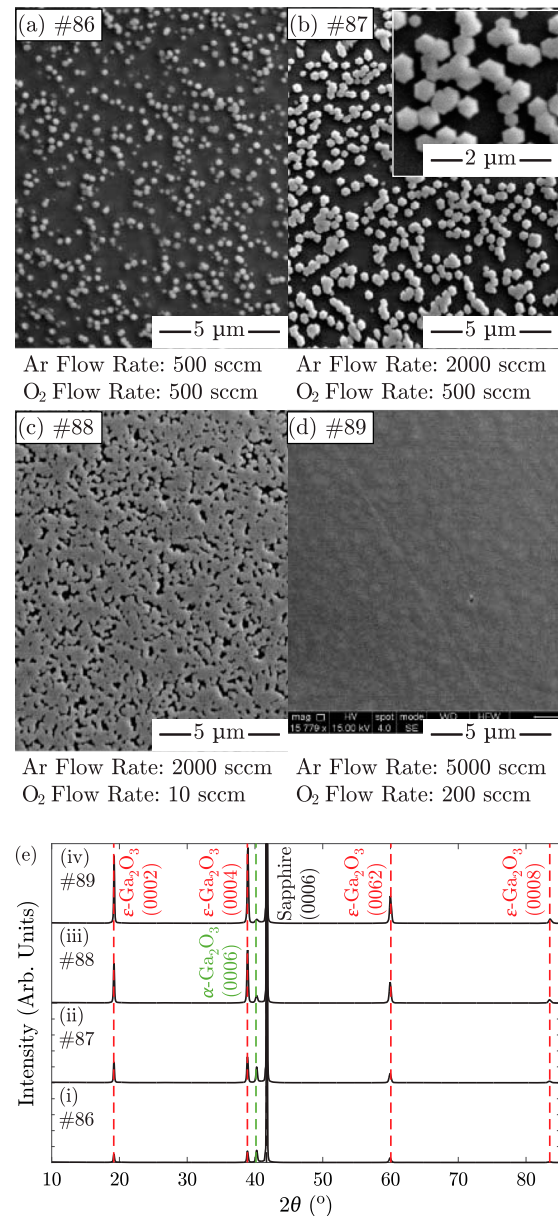


Figure 2. SEM images showing a series of heteroepitaxial Ga₂O₃ films having respective sample #'s 86–89 and grown by HVPE on c-plane sapphire. The Ar and O₂ flow rates are indicated. The inset of (b) shows a magnified image of the hexagonal islands achieved under these particular conditions; they were also present in the film shown in (a). (e) XRD of samples shown in (a)–(d), respectively.

the (2 $\bar{1}\bar{1}$ 0) lattice spacings of α -Ga₂O₃ and sapphire projected along the [10 $\bar{1}$ 0] are 4.3 and 4.1 Å, respectively, in a relaxed film every 20 layers of α -Ga₂O₃ should correspond to 21 layers of sapphire. A misfit dislocation is generated every 8.6 nm.

As shown in Figure 3(b), after ~ 10 nm the α -phase transitioned to the ϵ -phase. Twinning is observed in the ϵ -phase due to the hexagonal sixfold symmetry of ϵ -Ga₂O₃ and its island nucleation growth mode. The selected area diffraction pattern for one grain of the

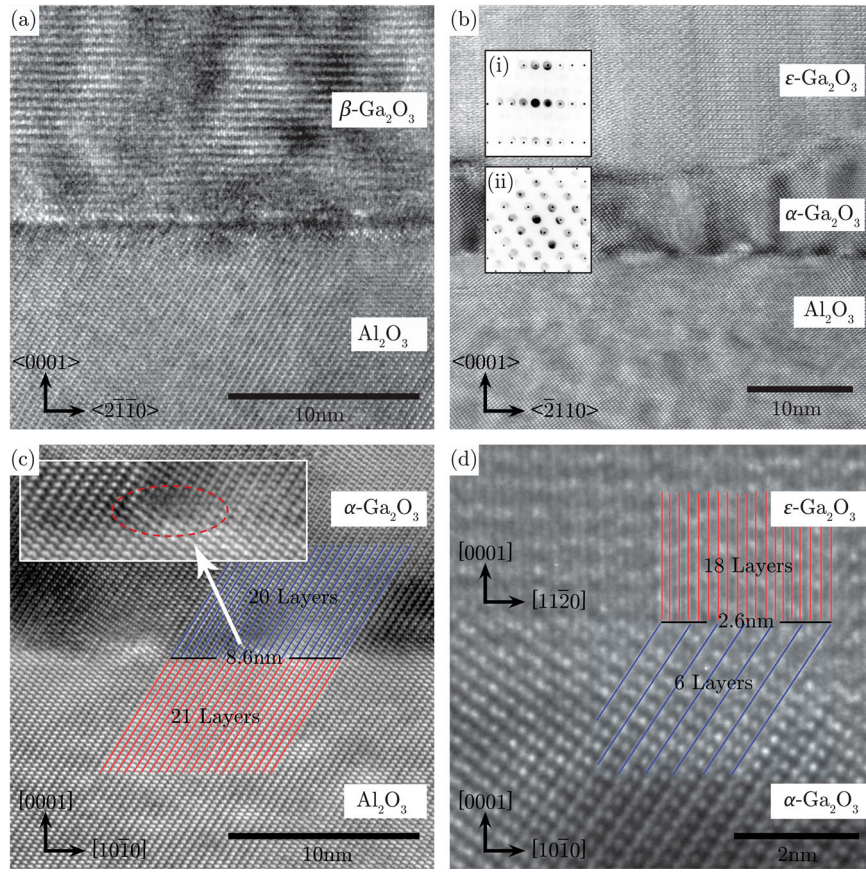


Figure 3. (a) Cross-section TEM of β - Ga_2O_3 epitaxial layer grown by MOCVD on sapphire (0001) at 650°C . The epitaxial relationship is $[201] \beta\text{-Ga}_2\text{O}_3 \parallel [0001] \alpha\text{-Al}_2\text{O}_3$. (b) Cross-section HRTEM of Ga_2O_3 on c -plane sapphire along the Al_2O_3 $[11\bar{2}0]$ zone axis (sample #89). An $\sim 10\text{nm}$ thick interfacial layer of α - Ga_2O_3 grew directly on the substrate, followed by a thicker layer of ϵ - Ga_2O_3 . Insets show selected area diffraction corresponding to (i) ϵ - Ga_2O_3 $[\bar{1}100]$ and (ii) α - Ga_2O_3 $[11\bar{2}0]$. The epitaxial relationship was found to be $[\bar{1}100] \epsilon\text{-Ga}_2\text{O}_3 \parallel [11\bar{2}0] \alpha\text{-Ga}_2\text{O}_3 \parallel [11\bar{2}0] \alpha\text{-Al}_2\text{O}_3$. (c) Cross-section HRTEM of α - Ga_2O_3 on c -plane sapphire along the α - Al_2O_3 $[11\bar{2}0]$ zone axis. Inset is magnified image of misfit dislocation. (d) Cross-section HRTEM of ϵ - Ga_2O_3 on α - Ga_2O_3 along the α - Ga_2O_3 $[11\bar{2}0]$ zone axis.

top layer matches closely with the $[\bar{1}100]$ zone axis of ϵ - Ga_2O_3 . This shows that ϵ - Ga_2O_3 $[11\bar{2}0]$ is oriented parallel to α - Ga_2O_3 $[10\bar{1}0]$ as shown in Figure 3(d), which corresponds to a rotation of 30° relative to

each other. The other grains are 60° rotations in the xy -plane. Since the lattice spacing in the $[11\bar{2}0]$ directions of ϵ - Ga_2O_3 is $1.45 \text{ \AA}$, 18 layers of ϵ - Ga_2O_3 is about 2.6 nm ; this agrees with our TEM observations.

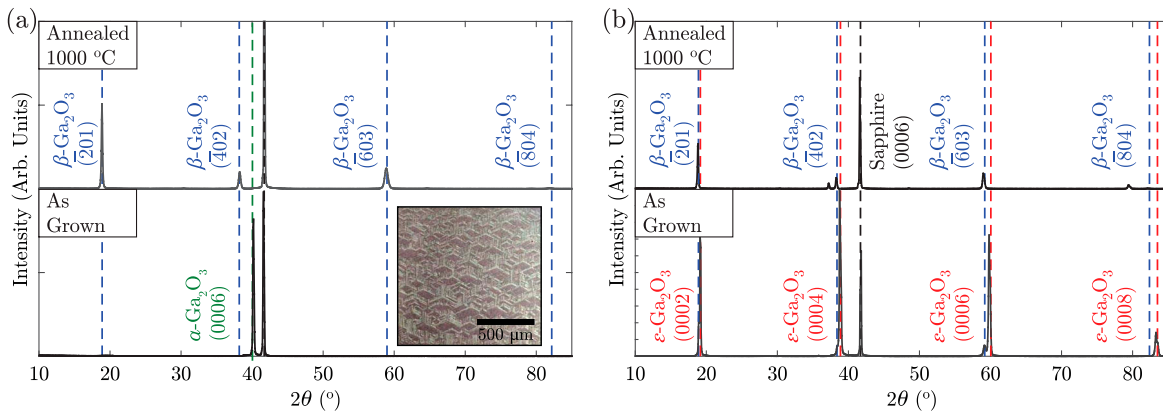


Figure 4. (a) XRD of α - Ga_2O_3 grown on c -plane sapphire before and after annealing at 700°C for 1 h. Inset shows an optical image of the surface microstructure of the β - Ga_2O_3 that transformed from the α - Ga_2O_3 after annealing at 700°C for 1 h. (b) XRD of ϵ - Ga_2O_3 grown on c -plane sapphire before and after annealing at 1000°C for 1 h.

Since α - and ε -Ga₂O₃ are metastable phases, we annealed them to determine at what temperature they would transform to β -Ga₂O₃. The results of XRD characterization are shown in Figure 4. Figure 4(a) shows that α -Ga₂O₃ transformed into β -Ga₂O₃ after annealing at 700°C in air for 1 h. Crystalline facets were observed and were visible to the naked eye (Figure 4(inset)). ε -Ga₂O₃ was also annealed in air for 1 h between 700°C and 1000°C in 100°C increments. The transformation from ε -Ga₂O₃ to β -Ga₂O₃ was detected only after annealing at 1000°C, as shown in Figure 4(b). There were no visible changes in the surface microstructure as a function of annealing temperature for the ε -to- β -Ga₂O₃ samples. In comparison, a previous study [35] reported complete transformation from ε -to- β -Ga₂O₃ after a 3-hr anneal at 900°C, whereas analysis by differential scanning calorimetry indicated the transformation actually begins somewhere between 700°C and 800°C.

4. Discussion

Films grown via MOCVD on (001) sapphire substrates in the temperature range of 500–850°C consistently yielded the stable β -Ga₂O₃ phase. In contrast, deposition using HVPE within approximately the same temperature range of 650–850°C consistently resulted in the growth of metastable α - and ε -Ga₂O₃ phases. The fact that both the α - and ε -Ga₂O₃ are better lattice matched with the substrate surface crystallography alone does not explain why these phases were not observed when grown using the MOCVD technique. One reason for the non-equilibrium growth during HVPE that is common for all these samples is the significantly faster growth rate, that did not allow the adatoms time to rearrange to form the thermodynamically stable β -phase. I.e. the diffusing adatoms initially bonded to the oxygen and aluminum sites of the (0001) surface, mimicked the surface crystallography (α -Ga₂O₃ also possesses the corundum structure) and were unable to undergo rearrangement to the β -Ga₂O₃ phase before the next layer of adatoms had deposited on the surface. Each layer of α -Ga₂O₃ was constrained or buried by the rapidly depositing subsequent layers. Moreover, the period after the cessation of growth was too brief and the cooling rate too fast to allow the transformation to the β -Ga₂O₃ that was achieved during longer term annealing at 700°C, the center of the deposition range.

A second reason for the sequential occurrence of both the α - and ε -Ga₂O₃ phases in the HVPE grown samples is believed to be associated with the presence of Cl, as revealed in SIMS investigations of three additional samples grown under the conditions noted in Table 4 and resulting from incorporation from GaCl/GaCl₃ used during growth. The Cl detection limit on the tool is $\sim 1 \times 10^{15}$ atoms/cc. The depth profiles acquired from these studies are shown in Figure 5(a)–(c). A comparison plot of the Cl concentrations in the three films in Figure 5(d) and the associated data presented in Table 4 reveal the average Cl concentration in samples #112 and #165 to be 1–2 orders of magnitude higher than in sample #105. All profiles show a very high Cl concentration at the Ga₂O₃/Al₂O₃ interface that ranges from $\sim 1 \times 10^{18}$ atoms/cc (#165) to $\sim 5 \times 10^{19}$ atoms/cc (#105 and #112). The presence of Cl at the outset of growth would result in the formation of very stable Al–Cl bonds at the Al₂O₃(0001) surface having a bond dissociation energy, $\Delta H_{f,298} = 495$ kJ/mole, and changes in both the surface energy of the sapphire and the interfacial energy between the two oxides. The overriding factor (rapid growth rate, similarity in crystal structure and favorable lattice matching, high concentrations of Cl) that controls the formation of the α -Ga₂O₃ cannot be determined unequivocally; however, it surmounts all other phenomena that would initiate the formation of either the β or the ε phases.

However, the presence of Cl apparently affects the onset of formation and continued growth of the ε phase atop the α phase. The SIMS profile and the phase result in Table 4 for sample #105 shows that the Cl is solely concentrated at the Ga₂O₃/Al₂O₃ interface and that α -Ga₂O₃ is the only deposited phase, respectively. By contrast, the analogous profiles and phase results for samples #112 and #165 reveal the presence of Cl either throughout the entire film (#112) or primarily contained in approximately half the film (#165) and the formation of the ε -Ga₂O₃ phase, respectively. The reason for the latter set of results may be associated with incorporation of the Cl to relieve stress in the growing film. Consider that Cl[−] has an ionic radius of 167 pm, compared to 126 pm for O^{2−}. If Cl substitutes for O in the crystal lattice, it would introduce compressive stresses in the lattice. Note that the ε -phase has a larger lattice spacing than the α -phase and should therefore accommodate Cl impurities more easily. Further investigations are

Table 4. Growth conditions for three growth runs of heteroepitaxial Ga₂O₃ on c-plane sapphire using HVPE.

Run #	Phase	Temp. (°C)	HCl % of total flow	HCl to O ₂ ratio	Thickness (nm)	Growth rate (nm/min)	SIMS Aver. Cl Conc. (atoms/cc)
105	α	650	0.37%	0.25875	350	11.7	3×10^{15}
112	ε	650	0.69%	0.05625	900	30	5×10^{17}
165	ε	850	0.71%	0.075	1250	41.7	2×10^{16}

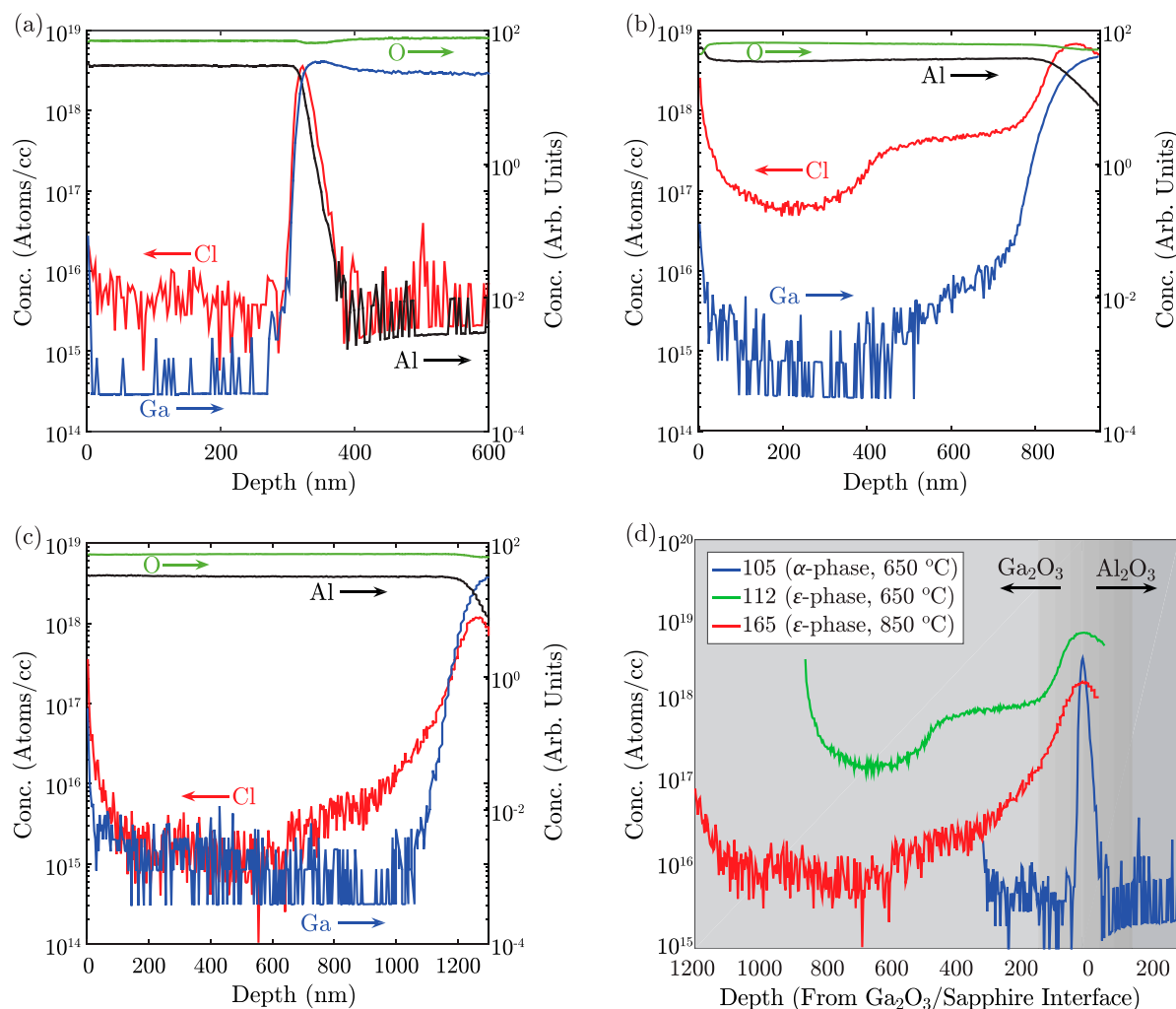


Figure 5. Cl^- concentration in atoms/cc and Ga, Al and O concentration in arbitrary units, measured by SIMS for samples (a) #105, (b) #112, and (c) #165, respectively. (d) Cl^- concentration in three samples measured by SIMS. Sample #105 shows α -phase and was grown at 650°C , sample #112 shows ε -phase and was grown at 650°C . Sample #165 shows ε -phase and was grown at 850°C .

necessary to confirm or provide other explanations for these results.

5. Summary

Growth of the stable phase $\beta\text{-Ga}_2\text{O}_3$ was achieved on (0001) sapphire substrates using MOCVD within the temperature range of $650\text{--}850^\circ\text{C}$. The metastable phases α - and $\varepsilon\text{-Ga}_2\text{O}_3$ were observed when grown at the same temperature range using HVPE. The growth of these latter phases is likely due to a combination of high growth rates and low growth temperature. Although Cl was detected in the HVPE grown films – and was highest in the $\varepsilon\text{-Ga}_2\text{O}_3$ layers – the possible role of Cl in the growth mechanism requires further investigation.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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