HVPE growth of α- and ε-Ga₂O₃ on patterned sapphire substrates

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Abstract. Here we report on the growth and characterisation of α- and ε-Ga₂O₃ epitaxial films produced by halide vapour phase epitaxy (HVPE). The films were deposited on two types of substrate: (0001) plain sapphire substrates and (0001) patterned sapphire substrates with regular cone-like features. In order to guarantee the same growth conditions on plain and patterned sapphire, the two substrates were used simultaneously in the same growth run. After the deposition the samples were studied by x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), optical transmission (OT) spectroscopy, and cathodoluminescence (CL). The growth on plain sapphire substrate produced an 11 μm thick continuous α-Ga₂O₃ layer. The full width at half maximum (FWHM) of the (0006) XRD rocking curve is 180 arcsec, which indicates good crystallinity of the layer. In contrast, growth on the patterned sapphire substrate resulted in a layer with regular spaced faceted pyramids at the surface. XRD analysis revealed the presence of both α- and ε-phases in Ga₂O₃ grown on patterned sapphire substrate. The presence of the ε-Ga₂O₃ phase, which has narrower bandgap, was also confirmed by optical transmission measurements. SEM, TEM, and SEM CL observations revealed that α-Ga₂O₃ phase forms columnar structures on top of sapphire cone, and ε-Ga₂O₃ phase fills the valleys between the columns.

1. Introduction

Gallium oxide is a novel ultra-wide bandgap semiconductor material that has attracted rapidly growing interest over the last decade. Owing to its wide bandgap of about 4.8-5.2 eV and high breakdown electric field of 8 MV/cm, this material has potential for applications in high power electronics and UV optoelectronic devices. The current state of research in the area and background information can be found in recent review articles [1–4]. Gallium oxide exhibits several polymorphic modifications each having different crystal structure and physical properties [5]. Among these polymorphs, the monoclinic β-Ga₂O₃ has received the greatest research focus because it is the only thermodynamically stable form under atmospheric pressure [4]. This remarkable advantage allows to produce high-quality β-Ga₂O₃ single crystals by melt growth techniques [6,7]. All other polymorphs are metastable and transform into β-Ga₂O₃ upon heating.
In contrast to β-Ga2O3, other Ga2O3 polymorphs have not been studied to the same extent. However, they can potentially also be of much interest. Among them the most important ones are the metastable rhombohedral α- and hexagonal ε-Ga2O3 phases; both of them have attracted attention because of their higher symmetry and simpler epitaxial relationships with c-plane sapphire, III nitrides, and other hexagonal and pseudo-hexagonal substrates.

Epitaxial films of α-Ga2O3 have been prepared by several techniques including mist chemical vapour deposition (mists-CVD) [8], halide vapour phase epitaxy (HVPE) [9–11], metalorganic vapour phase epitaxy (MOVPE), and pulsed laser deposition (PLD) [11]. Similarly, ε-Ga2O3 films have been grown by MOVPE [12,13], mist-CVD [14,15] and HVPE [10,16]. Phase control in epitaxial growth of Ga2O3 is governed by a number of factors; the main ones being deposition temperature, growth rate, substrate, and precursors. According to previously published results, successful epitaxial growth of α- and ε-polymorphs requires temperature below 800 °C. In contrast, typical growth temperature of β-Ga2O3 epitaxial layers is above 1000 °C.

The HVPE technique has a number of important advantages. Firstly, it enables a much faster growth rate in comparison to other methods. Secondly, it appears that HVPE growth conditions favour the growth of metastable α and ε crystal modifications of Ga2O3.

Yao et al. [17] reported on Ga2O3 growth by MOCVD and HVPE techniques. MOCVD growth consistently yielded β-Ga2O3 films. In contrast, HVPE growth produced α- and ε-phases. One possible explanation why HVPE is favorable for the growth of metastable polymorphs is the significantly faster growth rate that did not allow the adatoms time to rearrange to form the thermodynamically stable β-phase. The second reason is the presence of chlorine in the growth chamber acting as catalyst for the formation of the metastable phases.

Recent publication of Sun et al. [18] gives further support to the hypothesis of chlorine’s role in stabilization of metastable Ga2O3 polymorphs. Three different phases of Ga2O3 (α, β, and ε) films on c-plane sapphire were synthesized by only tuning the flow rate of HCl along with other precursors in an MOCVD reactor. Films deposited without HCl flow consisted of pure β-Ga2O3 phase. With continuous increase of the HCl flow, a mixture of β- and ε-Ga2O3 was formed, and later transformed to pure ε-Ga2O3. Further increase of the HCl flow resulted in a mixture of ε- and α-Ga2O3 with a dominant α-phase.

In this work we investigated HVPE growth of Ga2O3 on patterned sapphire substrates (PSSs). Epitaxial growth on PSSs have been widely used in the epitaxy of gallium nitride to increase the output light power of light emitting diodes [19] and decrease defect density [20]. By contrast, epitaxial growth of Ga2O3 on PSS is insufficiently studied, and there are only few publications on this matter [21]. As we show in this work, growth on patterned sapphire substrates offers another approach to control polymorphic composition of epitaxial Ga2O3 layers.

2. Experiment
Ga2O3 epitaxial films were produced by halide vapor phase epitaxy (HVPE) using a hot wall atmospheric pressure reactor. The reactor consisted of a 75 mm quartz tube placed in a multizone horizontal furnace. Gaseous gallium chloride GaCl and oxygen O2 were used as precursors, argon Ar was used as a carrier gas. GaCl vapor was synthesized in situ upstream in the reactor by the reaction of metallic gallium (99.9999%) and gaseous hydrogen chloride (99.999%). Then the GaCl vapor was transported to the deposition zone of the reactor where it was mixed with oxygen to produce Ga2O3. The temperature in the growth zone was 550 °C. HCl flow through the source was varied from 20 sccm to 200 sccm. The oxygen flow was kept constant at 200 sccm. Argon was used as a carrier gas in order to maintain the total gas flow through the reactor at 1 to 2 slm. The input VI/III (2O2/GaCl) ratio was in the range from 2 to 20. Under these conditions the deposition rate was in the range from 1 μm/h

1 According to Fornari et al. [22] ε-Ga2O3 may exhibit both hexagonal (ε) or orthorhombic (k) symmetry, according to the size of the ordered domains and resolution of the used characterization probe. For the purpose of epitaxy and device technology ε-Ga2O3 can however be regarded as a hexagonal semiconductor.
to 2 μm/h. Two types of substrates were used in this study: plain c-face sapphire substrates and cone-shaped patterned c-face sapphire substrates. Both types of substrates were simultaneously loaded into the reactor so the growth conditions were exactly the same. The deposition was conducted for 300 minutes. After the growth, specimens were cooled down to room temperature under a flow of argon. The polymorphic type and structural quality of the produced Ga$_2$O$_3$ layers were characterized by X-ray diffraction (XRD) analysis. The surface morphology and the cross-section of the films were studied by optical and scanning electron microscopy (SEM). Layer thickness was measured by cross-sectional SEM.

3. Results and discussion

Gallium oxide film grown on plain sapphire substrate (Sample A) had a smooth mirror-like surface as observed with the naked eye. SEM analysis (Figure 1) also revealed smooth layer appearance, although some cracking and delamination of the Ga$_2$O$_3$ film from the substrate were observed. The absence of crack decoration indicates that cracking most likely occurred after the growth due to thermal stresses developed during cooling down from the deposition temperature to room temperature.

In contrast, deposition on the patterned sapphire substrate (Sample B) resulted in the replication of the substrate pattern on the surface of the Ga$_2$O$_3$ film. As revealed by SEM and SEM-CL analysis (Figure 2), irregular shaped faceted pyramids of roughly six-fold symmetry were formed exactly above the cone features of the sapphire substrate. The height of the pyramids is approximately 30% of the total layer thickness.

Figure 3 shows the XRD spectra of two samples A and B. Sample A grown on plain sapphire exhibits two peaks which were identified as (0006) reflections of sapphire and α-Ga$_2$O$_3$ therefore the film deposited on plain sapphire substrate have rhombohedral α-Ga$_2$O$_3$ structure. In contrast, sample B grown on PSS exhibits also a peak corresponding to (004) reflection of ε-Ga$_2$O$_3$. Thus, we may conclude that this sample also contains some amount of ε-Ga$_2$O$_3$. The narrowest ω-scan of α-Ga$_2$O$_3$ on plain sapphire substrate has FWHM of 184 arcsec. In contrast, ε-Ga$_2$O$_3$ formed on patterned sapphire substrate in between of α-Ga$_2$O$_3$ columns was of poorer crystalline quality with FWHM of about 1500 arcsec.

![Figure 1. SEM bird’s eye view image of α-Ga$_2$O$_3$ layer grown on c-plane sapphire.](image-url)
Figure 2. Top view SEM image (a) and cross-sectional SEM CL image (b) of the Ga$_2$O$_3$ layer grown on patterned sapphire substrate. The observed contrast in the CL image suggests the presence of both $\alpha$ and $\varepsilon$ phases.

Figure 3. XRD $\omega$-2$\theta$ scan profiles of Ga$_2$O$_3$ layers grown on (0001) plain and patterned sapphire substrates.

Optical transmission spectra for Ga$_2$O$_3$ films grown under the same conditions on different substrates are shown in Figure 4. The transmission spectrum for the Ga$_2$O$_3$ grown on plain sapphire exhibits an absorption edge at about 245 nm (5.06 eV). The film grown on patterned sapphire substrate has an absorption edge at about 257 nm (4.82 eV). Absorption edge positions are in good agreement with reported values of bandgap energies of $\alpha$-Ga$_2$O$_3$ and $\varepsilon$-Ga$_2$O$_3$. 
Figure 4. Optical transmission spectra for Ga$_2$O$_3$ films grown on plain (curve 1) and patterned (curve 2) sapphire substrates under the same conditions. The difference in the absorption edge positions clearly indicates that the films have different polymorphic composition.

Figure 5. Cross-section TEM of Ga$_2$O$_3$ epitaxial layer grown on patterned sapphire substrate; SAED patterns show that the columns are composed of α-Ga$_2$O$_3$ and the material between the columns is ε-Ga$_2$O$_3$.

XRD and OT measurements provide sufficient evidence to confirm that the Sample B grown on patterned sapphire substrate contains a considerable amount of ε-phase. However, these methods do not give any insight on the spatial arrangement of α-Ga$_2$O$_3$ and ε-Ga$_2$O$_3$ domains within the layer. CL images and spectra acquired from the columns and the material between them are very different both in terms of intensity and spectral distribution. Therefore, we may conclude that the columns and the surrounding material are composed of different polymorphs.

Further evidence for this hypothesis was obtained by TEM analysis. Figure 5a shows a cross-section TEM image of the sample B. Selective area electron diffraction (SAED) patterns (Figures 5c
and 5d) were recorded from the columnar structures and material in the valleys between the columns. We identified the material above and between the sapphire cones as $\alpha$-Ga$_2$O$_3$ and $\varepsilon$-Ga$_2$O$_3$, respectively.

4. Conclusions
We have demonstrated the successful growth of $\alpha$-Ga$_2$O$_3$ and $\varepsilon$-Ga$_2$O$_3$ by HVPE technique. It was found that with all other conditions being the same, the type of crystal polymorph of the epitaxial layer is strongly influenced by the substrate. Growth on c-plane sapphire substrates resulted in $\alpha$-Ga$_2$O$_3$ films. The X-ray rocking scans of the (0006) peak confirmed relatively high crystallinity of $\alpha$-Ga$_2$O$_3$ films with the FWHM of 184 arcsec. In contrast, deposition on patterned sapphire substrates templates produced a mixed structure containing both $\alpha$-Ga$_2$O$_3$ and $\varepsilon$-Ga$_2$O$_3$. The $\alpha$-phase formed vertical columns each originating from the cone on sapphire substrate, protruding up to the surface and capped with an irregular shaped faceted pyramid on top. The $\varepsilon$-phase was located between these columns. The $\varepsilon$-Ga$_2$O$_3$ phase had poorer crystallinity with the narrowest FWHM of XRD rocking curve of 20-25 arcmin.

The present results show that growth on patterned substrates offers a new approach to control polymorphic composition of Ga$_2$O$_3$.

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