

# Progress in atomic layer deposited $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> materials and solar-blind detectors

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## ABSTRACT

Atomic layer deposition (ALD) offers a low thermal budget method for producing  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> films on sapphire substrate. In this paper we review the recent progress on plasma-enhanced ALD growth of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and present the optical and photoconductive properties of the deposited films. We show that the deposited material exhibits an epitaxial relationship with the sapphire substrate, and with an atomically sharp film-substrate interface. The  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> films had an optical bandgap energy measured at 5.11 eV, and exhibited a broad luminescence spectrum dominated by ultraviolet, blue and green bands, in line with current literature. We finally demonstrate the suitability of the material for solar-blind photodetection.

**Keywords:** Gallium oxide, Corundum phase, Atomic layer deposition, Solar-blind detection

## 1. INTRODUCTION

Gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) has recently emerged as a wide bandgap semiconductor with promising applications for high power and high frequency electronics, as well as ultraviolet optoelectronics.<sup>1</sup> This compound is a polymorphic sesquioxide, with reported phases labelled  $\alpha$ ,  $\beta$ ,  $\epsilon$ ,  $\kappa$ , and  $\gamma$ <sup>2,3</sup> – with the  $\epsilon$  and  $\kappa$  phases being ordered and disordered variants.<sup>4</sup> The monoclinic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is the only thermodynamically stable polymorph, and has therefore attracted most research interest to date. The rhombohedral  $\alpha$ -phase is metastable, but presents several assets for device applications. For example  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> exhibits the widest bandgap energy (*ca.* 5-5.3 eV<sup>5-8</sup>) amongst all phases of Ga<sub>2</sub>O<sub>3</sub>, making it interesting for power electronic applications. Moreover, it is isostructural with several other semiconducting sesquioxides, therefore exhibiting much promise for bandgap and functionality engineering through alloying with *e.g.* Al<sub>2</sub>O<sub>3</sub>,<sup>9</sup> In<sub>2</sub>O<sub>3</sub>,<sup>9</sup> Cr<sub>2</sub>O<sub>3</sub>,<sup>10</sup> Fe<sub>2</sub>O<sub>3</sub>,<sup>11</sup> Ti<sub>2</sub>O<sub>3</sub>,<sup>12</sup> or Rh<sub>2</sub>O<sub>3</sub>.<sup>13</sup>

Due to its metastability, progress in  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> synthesis only arose recently. In recent years, films of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> have successfully been deposited at temperatures in the range of 550-700 °C using mist chemical vapour deposition (mist-CVD),<sup>5,9</sup> halide vapour phase epitaxy (HVPE),<sup>14-16</sup> metalorganic chemical vapour deposition (MOCVD),<sup>6,17</sup> or molecular beam epitaxy (MBE).<sup>18,19</sup> In comparison, plasma-enhanced atomic layer deposition (PEALD)<sup>7,8,20-22</sup> allows the deposition of crystalline  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> material at much lower temperatures, nearing 250-300 °C. In this paper we review the conditions for growing  $\alpha$ -phase Ga<sub>2</sub>O<sub>3</sub> by PEALD and present the optical and photoelectric properties of the films.

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## 2. METHODS

Undoped Ga<sub>2</sub>O<sub>3</sub> films were deposited on *c*-plane sapphire substrates with a  $0.25 \pm 0.10^\circ$  miscut towards (11 $\bar{2}$ 0) using an Oxford Instruments OpAL PEALD reactor. Adduct grade triethylgallium (TEGa) and dry O<sub>2</sub> were used as the gallium and oxygen sources, respectively, while argon was used for chamber purges and as the precursor carrier gas. Several sets of samples were grown, to investigate the impact of substrate temperature, O<sub>2</sub> flow rate and plasma power on the crystallinity of the Ga<sub>2</sub>O<sub>3</sub> films. Table 1 lists the experimental conditions used in each set.

The following conditions were kept constant between growth sets: 0.1 s TEGa dose, 5 s TEGa purge, 5 s O<sub>2</sub> plasma duration, 5 s O<sub>2</sub> plasma purge. 100 sccm Ar was used as a carrier gas during the TEGa dose and to remove unreacted precursors from the chamber during the purge steps. The base pressure in the chamber (with no process gases flowing) was *ca.* 10 mTorr. During the deposition processes the chamber pressure varied between *ca.* 80 mTorr (during the plasma steps) and 160 mTorr (during the TEGa dose). The TEGa source was maintained at 30°C, with line temperatures into the reactor chamber held at 80°C and 90°C. For the lowest temperature deposition (120°C substrate) the chamber walls were held at 125°C, while the chamber walls were set at 150°C for all other growths. 500 cycles were used for the growth of each film, resulting in a film thickness of approximately 25 nm. Finally, a thicker sample (4700 cycles, *ca.* 250 nm thick) was deposited using the optimal conditions listed in Table 1.

The structure of the samples was investigated by X-ray diffraction (XRD) using a PANalytical Empyrean diffractometer with a Cu K $\alpha_1$  X-ray source. A two-bounce Ge analyser was used for  $2\theta$ - $\omega$  scans, and a PIXcel detector was used to acquire reciprocal space maps. The atomic structure of the samples was observed using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) in an aberration-corrected FEI Titan operated at 200 kV.<sup>23</sup> The optical bandgap of the material was obtained using a Shimadzu UV-2600 UV-vis transmittance spectrophotometer equipped with an integrating sphere. The luminescence properties were obtained using room temperature cathodoluminescence (CL) in a JEOL JXA-8530F field-emission electron probe microanalyser (EPMA) operated at 5 kV. Finally, photoelectric characterisation was performed using a Signatone probe station equipped with a Thorlabs Deuterium light source coupled to a SolarLS ML44 monochromator to illuminate the sample with a monochromatic light.

## 3. RESULTS AND DISCUSSION

### 3.1 Growth

The impact of the substrate temperature, O<sub>2</sub> flow and plasma power on the resulting phase of the thin films was investigated by means of XRD. The results are summarised in Figure 1. The intense peak at  $2\theta = 41.68^\circ$  visible in all the diffractograms corresponds to the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 0006 reflection from the substrate. The  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> 0006 reflection occurs near  $2\theta = 40.25^\circ$ , which is the value for relaxed  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>.<sup>24</sup> Small deviations in peak

Table 1. Summary of samples sets and growth conditions investigated.

Sample set	Approx. thickness (nm)	Substrate temperature (°C)	O <sub>2</sub> flow (sccm)	O <sub>2</sub> plasma power (W)
Temperature	25	120, 150, 200, 250, 300, 350, 400, 450	20	300
O <sub>2</sub> flow	25	250	10, 20, 40, 60, 100	300
Plasma power	25	250	20	25, 50, 100, 200, 300
Optimal	250	250	20	300

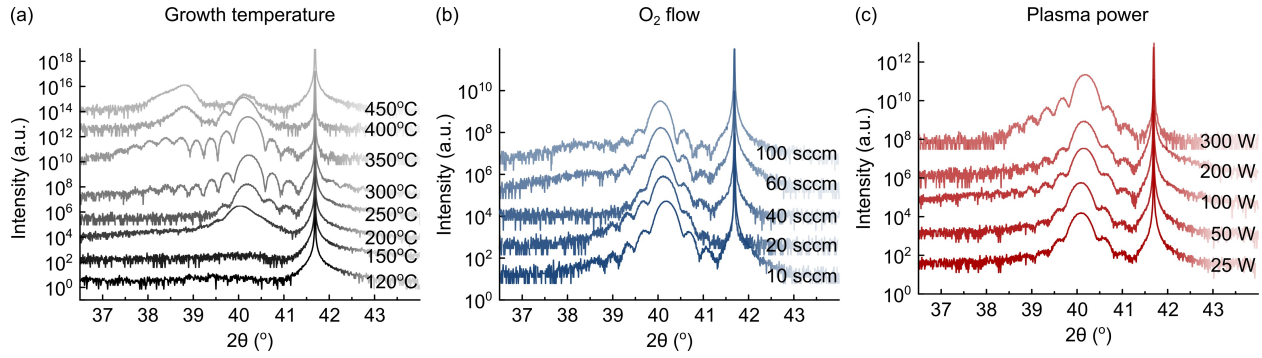


Figure 1. XRD  $2\theta$ - $\omega$  scans of the samples grown under various (a) temperature, (b)  $O_2$  flow, and (c) plasma power.

position can be ascribed to strain in the film. Peaks occurring at lower angles ( $2\theta = 38 - 39^\circ$ ) correspond to reflections from other phases of  $Ga_2O_3$  – in particular  $\beta$ - and  $\epsilon$ - $Ga_2O_3$  exhibit several reflections in that range.

We note that the substrate temperature seems to have the dominant impact on the crystallinity of the deposited film – as illustrated in Figure 1(a). For temperatures below  $200^\circ C$ , no film reflection could be observed, indicating that the films are amorphous. This is in line with previous work which also reported amorphous materials at such low temperatures,<sup>21,25</sup> in particular Borujeny *et al.* identified  $190^\circ C$  as the onset temperature for deposition of crystalline  $Ga_2O_3$  on sapphire by PEALD.<sup>21</sup> For substrate temperatures in the range of  $200$ - $350^\circ C$ , the diffractograms exhibit an  $\alpha$ - $Ga_2O_3$  0006 reflection. Fringes on either side of the peak are indicative of the film thickness and warrant a uniform thickness and good crystalline quality of the deposited material. We find that  $250$ - $300^\circ C$  seems to be the optimal temperature for  $\alpha$ - $Ga_2O_3$  deposition by PEALD. Other studies have also reported  $\alpha$ - $Ga_2O_3$  growth by ALD on sapphire in that temperature window.<sup>8,20-22</sup> For substrate temperatures above  $400^\circ C$ , we observe a noticeable quenching of the intensity of the  $\alpha$ - $Ga_2O_3$  0006 reflection and the appearance of reflections near  $2\theta = 38 - 39^\circ$  – in agreement with other studies.<sup>8,21</sup> This is indicative that growth at such temperatures favours the  $\beta$ - and  $\epsilon$ -phases which are more stable than  $\alpha$ - $Ga_2O_3$ .<sup>26</sup>

When grown at  $250^\circ C$  we find that, over the range of values investigated, the  $O_2$  flow and plasma power seem to have a negligible effect on the resulting phase of the film. As seen in Figure 1(b-c) all the films were  $\alpha$ - $Ga_2O_3$ . Minor variations in peak position could be ascribed to variations in the strain state of the films. It should be pointed out that this result is in contrast with Wheeler *et al.* who found that the plasma conditions offer wide scope for tuning the phase of the film.<sup>8</sup> We point out, however, that Wheeler *et al.*'s study used different precursors and different pressure during plasma than our present work. The use of PEALD offers even greater possibilities as a study from Ilhom *et al.* recently reported that *in situ* Ar plasma annealing at the end

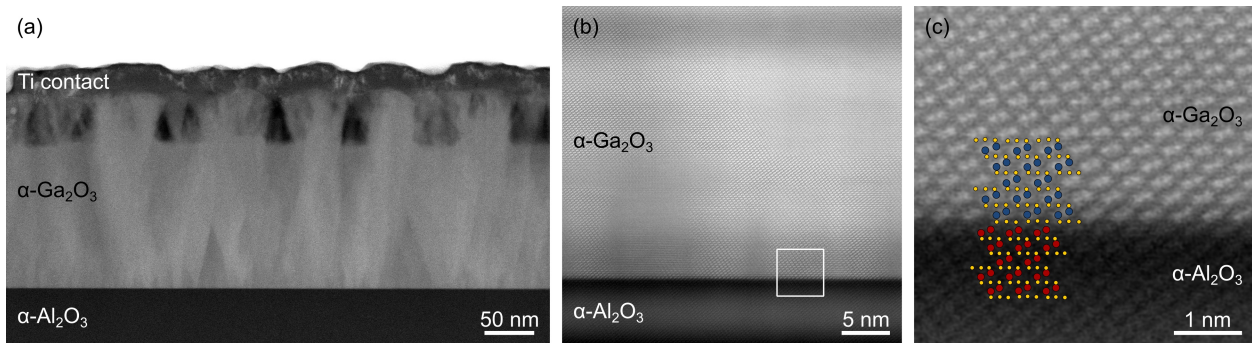


Figure 2. (a) HAADF-STEM image of the film, and (b) film-substrate interface. (c) Zoomed-in image of the region marked by a square in (b), with crystal model overlay (blue: Ga; red: Al; yellow: O). All images were observed along the  $\langle 11\bar{2}0 \rangle$  zone axis.

of every PEALD cycle could be used to produce  $\beta$ -phase  $\text{Ga}_2\text{O}_3$  on sapphire as well as other substrates (Si, glass).<sup>27</sup>

Lastly, we note that the growth of the aforementioned samples was also conducted on silicon substrates, and that all these films deposited on silicon were amorphous. This is in line with earlier literature on  $\text{Ga}_2\text{O}_3$  deposition by ALD<sup>28–30</sup> (with the exception of Ilhom *et al.* who used an extra plasma step to crystallise the films<sup>27</sup>). This highlights that the sapphire substrate plays a critical role in stabilising the corundum phase – as expected owing to its similar crystal structure and relatively low lattice mismatch of about 4.8% with  $\alpha$ - $\text{Ga}_2\text{O}_3$ . We illustrate the importance of the sapphire substrate in Figure 2, which depicts cross-sectional aberration-corrected HAADF-STEM images of the thick  $\text{Ga}_2\text{O}_3$  film. We note the columnar structure of the film, with all columns starting at the film-substrate interface, and propagating through the whole layer (Figure 2(a)). The several columns illustrate the mosaicity of the film, which has also been reported in  $\alpha$ - $\text{Ga}_2\text{O}_3$  films grown using other methods.<sup>14,31</sup> Regions of different contrast have been identified as amorphous and  $\epsilon$ - $\text{Ga}_2\text{O}_3$  inclusions.<sup>20</sup> Figure 2(b-c) provide high resolution images of the film-substrate interface, where the sharpness of the interface and epitaxial growth of the film on the sapphire substrate can be clearly observed.

### 3.2 Optical properties

UV-vis transmittance spectroscopy was used to measure the optical bandgap of the thick film. The transmittance of the film in the 200–700 nm wavelength range is presented in Figure 3(a), where a sharp increase in transmittance can be observed in the 230–280 nm region. Using the Tauc plot  $(\alpha h\nu)^2$  vs  $h\nu$  (inset of Figure 3(a)) to estimate the direct bandgap energy of the film, as is conventionally used with this material,<sup>6–8,14,19</sup> we obtain an optical bandgap of 5.11 eV, which is well within the 5–5.3 eV range of values reported in the literature.<sup>5–8,12,14,19</sup>

Room temperature CL was conducted to assess the luminescence properties of the thick film. The resulting CL spectrum is shown in Figure 3(b). In agreement with the literature, no band edge emission could be observed. Instead, the CL spectrum exhibits a broad emission spectrum from which four main components can be distinguished. We observed bands at 340 nm (*ca.* 3.6 eV), 394 nm (*ca.* 3.1 eV), 465 nm (*ca.* 2.7 eV), 550 nm (*ca.* 2.3 eV), as well as a tail that extends to even longer wavelengths. The CL spectrum present some similarities with the CL data obtained by Polyakov *et al.* on HVPE-grown Sn-doped  $\alpha$ - $\text{Ga}_2\text{O}_3$ .<sup>32</sup> However in our study, the samples are nominally undoped so we would not expect to see strong Sn-related luminescence as any Sn in the film (if any) should be in trace amount. Literature on luminescence of  $\alpha$ - $\text{Ga}_2\text{O}_3$  is scarce,<sup>32,33</sup> we therefore turn our attention to the literature on  $\beta$ - $\text{Ga}_2\text{O}_3$  to try to assess the origin of the luminescence in our sample. Luminescence of  $\beta$ - $\text{Ga}_2\text{O}_3$  generally exhibits mainly UV (3.2–3.6 eV), blue (2.8–3.0 eV) and green (2.5 eV) lines,<sup>34–36</sup> but a red (1.7–1.9 eV) line has also been reported.<sup>37–39</sup> The UV line as been ascribed to recombination between free electrons and self-trapped holes (STHs), while the other lines relate to donor acceptor

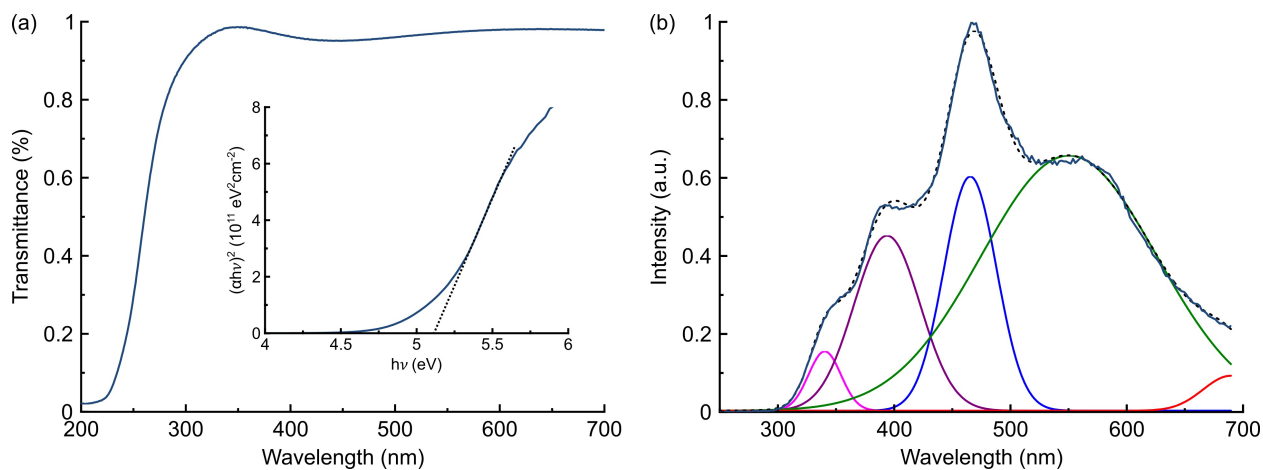


Figure 3. (a) UV-vis transmittance spectrum of the thick  $\alpha$ - $\text{Ga}_2\text{O}_3$  film, with Tauc plot in inset. (b) Room temperature CL spectrum of the thick  $\alpha$ - $\text{Ga}_2\text{O}_3$  film.

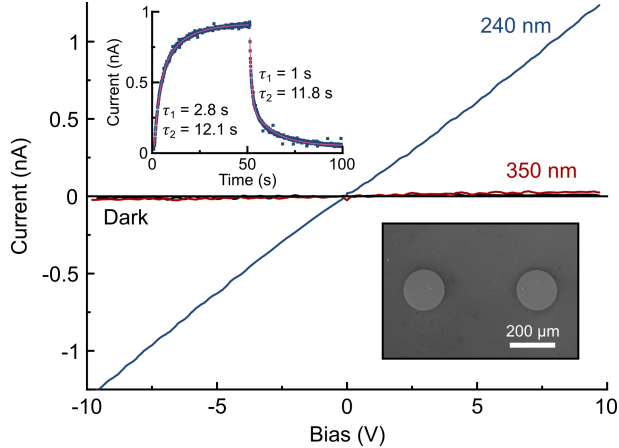


Figure 4. I-V characteristic of the thick  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> film tested under 240 nm, 350 nm and dark illumination. In insets, 240 nm photoconduction transient, and scanning electron microscope image of the contact structure used.

pair recombination involving a range of intrinsic (e.g.  $V_O$ ,  $V_{Ga}$ ,  $Ga_i$ ) or extrinsic (e.g.  $Si_{Ga}$ ,  $N_O$ ) defects. While we here expect limited contribution from extrinsic defects, the luminescence we observe in Figure 3(b) is aligned with the main luminescence lines reported in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, which we therefore tentatively ascribe to electron-STH recombination (340 nm line) and donor acceptor pair recombinations (394 nm, 465 nm, 550 nm lines). Further work would nevertheless be necessary to ascertain the exact defects involved.

### 3.3 Solar-blind photodetectors

To test the suitability of the material for solar-blind detection, circular Ti/Au electrodes *ca.* 180  $\mu$ m in diameter and spaced *ca.* 500  $\mu$ m apart (as shown in the scanning electron microscopy image in inset of Figure 4) were deposited onto the thick  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> film using UV photolithography and thermal evaporation. Figure 4 shows the photocurrent and transient characteristics when the device is illuminated under light at 240 nm, 350 nm, and in the dark. A clear increase in photocurrent can be observed when the film is illuminated by above bandgap light (*i.e.* 240 nm), as opposed to below bandgap illumination (*i.e.* 350 nm) or dark conditions. At 10 V bias, the photocurrent under 240 nm illumination is measured at 1.2 nA for a dark current of *ca.* 6 pA resulting in a photo-to-dark-current-ratio (PDCR) of about 220. It should be noted that the dark current has a low accuracy because it is limited by the source meter's detection limit and noise, moreover the photocurrent could be increased if the electrode structure were optimised (*i.e.* interdigitated electrodes). This result nevertheless demonstrates the suitability of ALD-grown  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> for solar-blind sensing. Previous studies on ALD-grown  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> photodetectors<sup>22,40</sup> reported responsivities nearing 1 A.W<sup>-1</sup> that are well within the range of responsivities reported for detectors obtained using different growth methods, and based on other more mature phases of Ga<sub>2</sub>O<sub>3</sub>.<sup>41</sup>

With regards to time response, our data show a relatively slow rise and decay, but still in agreement with literature values for Ga<sub>2</sub>O<sub>3</sub> detectors (all phases included).<sup>41</sup> Using a bi-exponential fit for the rise and decay response (shown in inset of Figure 4) we obtained time constants of 2.8 s and 12.1 s for the fast and slow rise components, respectively, and 1.0 s and 11.8 s for the fast and slow decay components, respectively. The particularly slow response of Ga<sub>2</sub>O<sub>3</sub> photodetector devices has been ascribed to an accumulation of STHs at the semiconductor/metal interface.<sup>42,43</sup> It should be noted that Lee *et al.* reported ultrafast, sub-microsecond response time for ALD-grown  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>-based photodetectors<sup>22</sup> which is amongst the fastest performance obtained so far in the field.

## 4. CONCLUSION

In this paper we have reviewed the recent progress on the use of PEALD for the growth of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> with a very low thermal budget in comparison to other growth methods. We reported that the temperature, plasma conditions,

and substrate play a determining role in the resulting phase of the film. We went on to present the optical and photoelectric properties of thick  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> film grown under the optimal conditions. The optical bandgap energy was measured at 5.11 eV, and CL measurement showed a broad luminescence spectrum consisting of ultraviolet, blue and green bands, in line with current literature. We finally demonstrated that ALD-grown  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> films are suitable for solar-blind photodetection and exhibit performances in par with other more mature phases of Ga<sub>2</sub>O<sub>3</sub>.

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