

# Development of Homoepitaxial Growth of Ga<sub>2</sub>O<sub>3</sub> by Hydride Vapor Phase Epitaxy

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## Abstract

In this work, we outline our progress toward understanding the promises and limitations of hydride vapor phase epitaxy (HVPE) of homoepitaxial Ga<sub>2</sub>O<sub>3</sub> films in terms of the surface preparation, film nucleation, achievable growth rates, and doping capabilities. We also present evidence that hydrogen acts as a shallow donor in Ga<sub>2</sub>O<sub>3</sub> and show that background hydrogen concentrations can give rise to controlled doping at the 1E16 level and below.

## INTRODUCTION

Monoclinic β-Ga<sub>2</sub>O<sub>3</sub> has recently emerged as a promising material for “ultrawide” bandgap electronics for next-generation high voltage lateral and vertical power switching devices, thanks to its large bandgap (4.9eV), high critical breakdown field (8MV/cm), and its accordingly large high voltage and high frequency figures of merit [1],[2]. Early research in β-Ga<sub>2</sub>O<sub>3</sub> was largely pointed toward its use as a transparent conducting oxide material, especially for UV applications [3], but more recently researchers have demonstrated several devices with promising performance using β-Ga<sub>2</sub>O<sub>3</sub> including MESFETS [4], MOSFETS [5],[6], and SBDs [7].

One major benefit of β-Ga<sub>2</sub>O<sub>3</sub> over the alternative next-generation “ultrawide” bandgap materials (e.g. AlN or diamond) stems from its ability to be grown from the melt. Melt growth techniques are preferable to vapor phase or plasma-based techniques (which must be employed for growth of bulk crystals of GaN, SiC, AlN, and diamond) as melt-based techniques tend to produce much high quality crystals and afford the grower a straightforward path to large crystals. Indeed several melt-based approaches such as Czochralski [8], float-zone [9], and Stepanov (edge-defined, film fed growth or EFG) [10] have all been demonstrated for growth of very high quality β-Ga<sub>2</sub>O<sub>3</sub>, and a commercial grower (Tamura Corporation) has already demonstrated 100mm diameter substrates.

Another benefit afforded β-Ga<sub>2</sub>O<sub>3</sub> lies in its ability to be easily doped n-type. This can be a problem with wide bandgap semiconductors (most egregiously with AlN), but several

shallow donor-type dopants have been identified for β-Ga<sub>2</sub>O<sub>3</sub> including Si [11], Sn [12], and Ge [13]. In fact, nominally undoped crystals typically appear to be conductive and n-type. While oxygen vacancies were once considered the source of the unintentional donors [9] in β-Ga<sub>2</sub>O<sub>3</sub>, Varley et al. showed that oxygen vacancies should in fact behave as deep donors [13]. These authors suggested that the more likely source of conduction in unintentionally doped material was actually due to both interstitial and substitutional H, a prediction which was independently calculated by Li and Robertson [14] and further evidenced experimentally by King et al. [15] and McCluskey et al. [16]. As such, the presence or absence of H is considered to be an important parameter when selecting the technique for growth of epitaxial films of Ga<sub>2</sub>O<sub>3</sub> for devices.

While MBE and MOCVD have both been used to homoepitaxially grow thin films of high structural quality Ga<sub>2</sub>O<sub>3</sub>, each technique has its limitations. MBE is an excellent technique for research purposes, but the ultra-high vacuum levels required and the relatively low growth rates (<1μm/hr) afforded MBE calls into question its ability to be scaled commercially, not to mention its ability to be utilized for thick (tens of microns) drift regions which will be required of the high voltage vertical devices which are well-suited to the β-Ga<sub>2</sub>O<sub>3</sub> material system. MOCVD, on the other hand, can likely be pushed to growth rates as high as perhaps 10μm/hr for β-Ga<sub>2</sub>O<sub>3</sub>, but by nature of the metalorganic precursors for the group-III elements, material grown by MOCVD will always suffer from the potential for inadvertently high H-related donor concentrations. While there have been reports of reasonably low free carrier concentrations in Ga<sub>2</sub>O<sub>3</sub> grown by MOCVD ( $1 \times 10^{17} \text{ cm}^{-3}$ ) [17], the viability of achieving high quality films with significantly lower carrier densities is somewhat questionable, since MOCVD-grown materials are thought to be compensated either by gallium vacancies [18] or from carbon [19] (also unavoidable in the MOCVD technique).

For thick films required of high voltage vertical switching devices, a growth technique which can achieve both high growth rates as well as high chemical purity (free of C and H) is desired. Hydride vapor phase epitaxy (HVPE) is such a technique and indeed has been validated by Murakami et al.

in their demonstration of a high voltage Schottky diode [7]. Additionally, our preliminary work at Kyma has corroborated this group's claims that high growth rates, high crystal quality, and low background doping are all achievable using HVPE, and we believe, along with these current research leaders in this field that the HVPE technique is the most promising technology for advancing the state of the art in both vertical and lateral device topologies exploiting the excellent material properties of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>.

## RESULTS

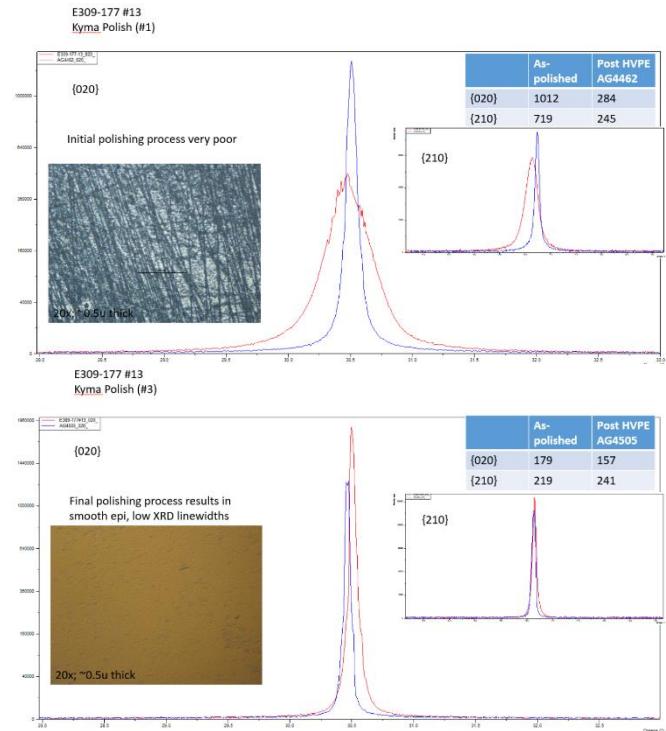
As outlined above, most reported homoepitaxial Ga<sub>2</sub>O<sub>3</sub> structures have been grown using either the MBE or MOCVD technique. We have focused on the application of hydride vapor phase epitaxy (HVPE) for the growth of Ga<sub>2</sub>O<sub>3</sub> on bulk <010> Ga<sub>2</sub>O<sub>3</sub> substrates, which is suitable for producing high quality films which replicate the underlying native substrate's structural quality at growth rates of exceeding 10 microns per hour. Additionally, we have found that it is critical to control subsurface damage and surface miscut prior to homoepitaxial growth of Ga<sub>2</sub>O<sub>3</sub>. Finally, we found that the HVPE technique can produce n-type layers, both lightly as well as heavily doped, to be utilized in various device configurations.

## SURFACE PREPARATION

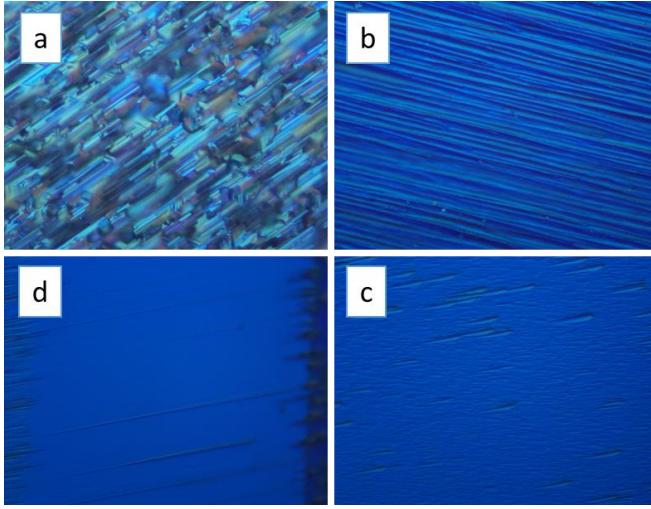
Initial work toward polishing the <010> substrates indicated that a smooth surface was insufficient for realizing high quality homoepitaxial films. Figure 1 (top) shows the result of about 1 micron of Ga<sub>2</sub>O<sub>3</sub> growth on the <010> substrate which was initially polished by Kyma. Clearly, a significant amount of subsurface damage was present in the substrate after this initial polishing, as evidenced by the excessive scratch-like features in the corresponding epi and since the XRD linewidths changed so distinctly after the epi growth. Two additional rounds of polishing followed by epi growth were carried out on the same wafer (the HVPE growth recipes were identical but more material was removed in subsequent polishing steps). Results from the epi growth on the final polishing iteration are shown in Figure 1 (Bottom). Clearly, the improved polishing process had a significant impact on the corresponding epi; the surface morphology is much smoother and does not have the excessive scratch-like features that the initial epi growth exhibited. Additionally, one can see that the XRD linewidths of the substrate itself are significantly improved (post-polishing but prior to regrowth), which implies that one can use the XRD as an assessment of the subsurface damage prior to carrying out epitaxial regrowth.

In addition to the requirement that the all subsurface damage be removed prior to epi (assessed most assuredly through epigrowth but also discernable via XRD or Raman measurements), we found that the magnitude and direction of the surface miscut should be well-controlled in order to

achieve a smooth surface. Figure 2 shows the surface morphology of several epigrowths which were carried out on substrates of differing miscut magnitude in the <001> direction. Growth directly on <010> substrates which are on-axis (top left of Figure 2) results in a very rough morphology of the resultant Ga<sub>2</sub>O<sub>3</sub> film, which likely due to the vast differences in growth rates between the <010> and the <100> or <201> directions, giving rise to columnar growth. As one increases the miscut in the {001} direction, smoother and smoother surfaces are achieved. Note that applying miscuts in the <100> direction gives rise to rough surfaces as well, with exaggerated striations along <100> as exhibited for <001> miscuts due to the low growth rate in the <100> direction.



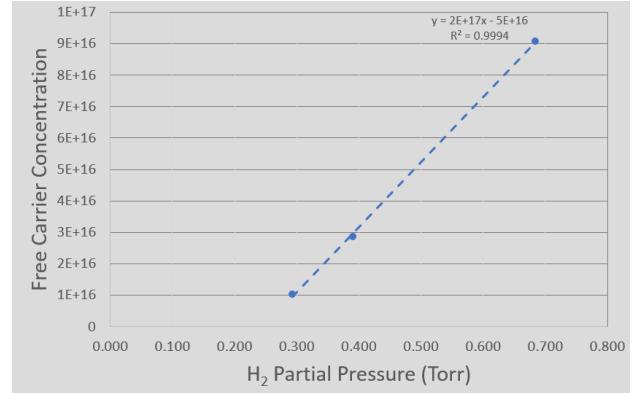
**Fig. 1. Microscope image as well as XRD linewidths for on-axis <020> and off axis <210> reflections. The red curves show XRD reflections post-polish and the blue curves show the same reflections after regrowth of 0.5μm of Ga<sub>2</sub>O<sub>3</sub>. (Top) Despite being smooth after polishing (not shown), the epi shows strong evidence (the scratch-like features which emerged post-epi) for the existence of subsurface damage. (Bottom) The same substrate after the same epi recipe was carried out after a more complete polishing process was performed.**



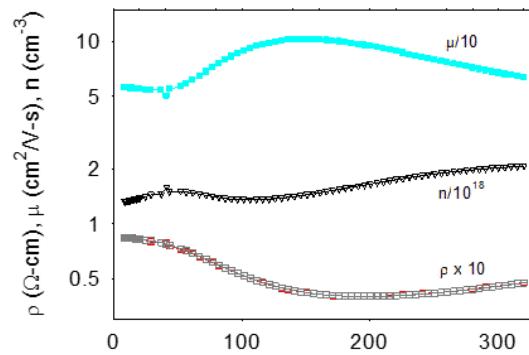
**Fig. 2.** Optical microscope images of homoepitaxial  $\text{Ga}_2\text{O}_3$  films on  $\{010\}$  substrates with surface miscuts towards  $<001>$  direction of a)  $0^\circ$ , b)  $2^\circ$ , c)  $3.5^\circ$ , and d)  $>5^\circ$ . The striations observed in each image are oriented along  $<100>$  directions.

#### DOPING OF $\text{GA}_2\text{O}_3$ BY HVPE

We carried out studies of both nominally undoped layers as well as layers intentionally doped with Si. As discussed above, hydrogen is believed to be an unintentional donor in high quality  $\text{Ga}_2\text{O}_3$ . As such, we grew several layers under different VI/III ratios (which gives rise to different partial pressures of  $\text{H}_2$  from the primary HVPE reaction of  $2\text{HCl} + 2\text{Ga} \rightarrow 2\text{GaCl} + \text{H}_2$ ) between 4 and 8, which gives rise  $\text{H}_2$  partial pressures ranging from 0.2 to 0.4 torr, as well as a layer with intentional  $\text{H}_2$  added to the growth chamber. The resultant apparent free carrier concentration was measured by Hg-probe and is shown in Figure 3. There appears to be a linear trend in free carrier density with the  $\text{H}_2$  partial pressure, with the lowest partial pressure (off the chart) giving rise to a film which is completely depleted and therefore immeasurable. Low  $\text{H}_2$  concentrations are therefore necessary to achieve the lowest possible free carrier densities required of high power devices. Additionally, HVPE layers were grown with  $\text{SiH}_4$  in order to intentionally n-type dope the  $\text{Ga}_2\text{O}_3$ . Figure 4 shows mobility, carrier density, and resistivity from a thin, Si-doped film of  $\beta$ - $\text{Ga}_2\text{O}_3$  on an  $<010>$   $\text{Ga}_2\text{O}_3$ . Notably, the mobility of this film is  $\sim 70\text{cm}^2/\text{V}\cdot\text{sec}$  for a free carrier concentration of  $2 \times 10^{18} \text{ cm}^{-3}$  at room temperature.



**Fig. 3.** Measured free carrier concentration for nominally undoped films as a function of  $\text{H}_2$  partial pressure within the HVPE reactor (intentional and unintentional). Use of higher VI/III ratios which result in lower  $\text{H}_2$  partial pressures gives rise to immeasurably low free carrier concentrations.



**Fig. 4.** Mobility, carrier density, and resistivity vs. T for Si-doped  $\text{Ga}_2\text{O}_3$

#### CONCLUSIONS

We show that HVPE is a viable growth method to produce thick, controllably doped, high quality layers of  $\text{Ga}_2\text{O}_3$ . By controlling the  $\text{H}_2$  concentration in the reactor, one can control the background donor concentration, and it will be critical to manage the  $\text{H}_2$  in order to achieve low carrier densities without compensation, required of power devices.

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