

Growth of Single Crystal Beta-Gallium Oxide (β -Ga₂O₃) Semiconductor Material

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Abstract

Gallium oxide has begun to receive attention for its unique properties, including its wide bandgap of about 4.7 - 4.9 eV and estimated electric field breakdown of 8 MV/cm [1]. This is approximately two to three times larger than that of SiC or GaN. These material properties lead to a Baliga Figure of Merit [2] four times that of GaN. Gallium oxide exists in five crystalline polytypes: α , β , γ , δ and ϵ . Beta-gallium oxide (β -Ga₂O₃) is the only stable, single-crystal form of gallium oxide at high temperatures. Gallium oxide is suitable for bulk growth using techniques such as Czochralski, Float Zone, Vertical Bridgman or Edge-defined Film-fed Growth (EFG). Doping with Si or Sn provides n-type conductivity and doping with Mg or Fe provides semi-insulating characteristics. These characteristics enable fabrication of a variety of vertical and lateral device topologies requiring higher power. In this paper we will review on the growth and scale-up of β -Ga₂O₃ from small crystalline grains to 50-mm diameter boules using the Czochralski growth method.

INTRODUCTION

Gallium oxide is an ultra-wide bandgap semiconductor with a bandgap of 4.7–4.9 eV and estimated breakdown electric field of 8 MV/cm [1] offering promise for a variety of high-voltage electronic applications. Originally considered as a substrate for III-nitride epitaxial growth due to its small lattice mismatch with GaN, Ga₂O₃ possesses a Baliga Figure of Merit (BFOM) estimated to be several times higher than those for SiC and GaN providing strong motivation for development of unipolar power devices. Ga₂O₃ has five polymorphic phases of which only the β -phase is thermodynamically stable at melt-based growth temperatures. β -Ga₂O₃ has a base-centric monoclinic crystal structure, as shown in Fig. 1, with a, b, c, and β values of 1.22 nm, 0.3 nm, 0.52 nm and 104-degrees, respectively [3, 4]. β -Ga₂O₃ possesses two strong cleavage planes parallel to the (100) and (001) planes and has strong electrical, optical and thermal anisotropy due to its monoclinic crystal structure. Czochralski growth along [100] and [001] axis is problematic, due to easy cleavage and blistering of the seed. The [010] axis is also subject to cleavage planes inducement of grain boundaries,

twins and cracks even though it is the preferred orientation for epitaxial growth [5].

The Air Force Research Laboratory recently demonstrated Ga₂O₃ MOSFETs achieving record-high 3.8 MV/cm critical field strength [6]. β -Ga₂O₃ power devices are expected to deliver a lower on-resistance limit at a given breakdown voltage and hence higher efficiency than other mainstream power devices despite possessing bulk electron mobilities of 200–300 cm²/V-s. Unintentionally doped (UID) β -Ga₂O₃ typically exhibits n-type conductivity with carrier concentrations in the low 10¹⁷cm⁻³ due to background Si shallow donor impurities. Use of silicon (Si) or tin (Sn) doping over a wide range of $n = 10^{15}\sim 10^{19}$ cm⁻³ has been shown to provide controllable n-type conductivity [7-9]. Self-trapping of holes in the bulk, which prohibits effective p-type conductivity, has been predicted by first-principles calculations of the Ga₂O₃ band structure [10]. Iron (Fe) or magnesium (Mg) dopants are commonly used to obtain high resistivity by acting as a deep acceptor to compensate the residual n-type conduction.

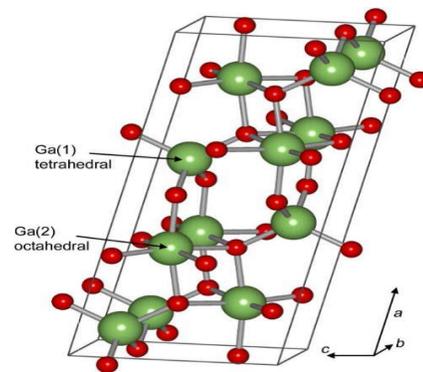


Fig. 1. The monoclinic crystal structure of β -Ga₂O₃.

β -Ga₂O₃ is a unique ultra-wide bandgap material in that single crystals can be grown by a variety of melt-based techniques such as Float Zone, Czochralski, Vertical Bridgman, and EFG methods even though it undergoes reductive decomposition ($\text{Ga}_2\text{O}_3 \rightarrow 2\text{Ga} + 3/2\text{O}_2$) at its melting point of 1820°C. The first reported bulk β -Ga₂O₃ single crystals (1 cm in diameter and 2.5 cm long) grown from

the melt were obtained utilizing the Verneuil method [11-14]. Cylindrical, [010], 50 mm diameter Ga_2O_3 single crystals grown by the Czochralski method, as well as thicker slabs (18 mm) grown by the EFG method have recently been demonstrated [5,15]. EFG $\beta\text{-Ga}_2\text{O}_3$ substrates of differing orientations and doping are presently commercially available from Tamura Corporation.

CZOCHRALSKI GROWTH

The Czochralski (CZ) method is the preferred melt-based approach for manufacturing single crystals of a wide variety of semiconductors including silicon, gallium arsenide and sapphire. The process involves dipping a seed crystal into a melt while pulling upwards and rotating at the same time. Controlling the temperature gradients, rate of pulling and speed of rotation, enables growth of a large, single-crystal, cylindrical boule. Czochralski growth of $\beta\text{-Ga}_2\text{O}_3$ was first reported by Tomm et al. in 2000 by using a 90% argon and 10% CO_2 atmosphere. This amount of oxygen was adequate to decrease the evaporation of the molten Ga_2O_3 to support crystalline growth. The high melting temperature of $\beta\text{-Ga}_2\text{O}_3$ requires the use of iridium (Ir) crucibles. This is problematic for CZ growth as Ir crucibles will easily oxidize in an atmosphere of a few percent of oxygen partial pressure at $\beta\text{-Ga}_2\text{O}_3$ melt temperatures [5,17]. Galaska et al. [18] has shown both theoretically and experimentally that scale-up of $\beta\text{-Ga}_2\text{O}_3$ crystal size is strongly affected by the formation of metallic gallium in the melt. Thus expansion to 100 mm diameter crystals require correspondingly higher oxygen concentration in the growth atmosphere, up to 100%.

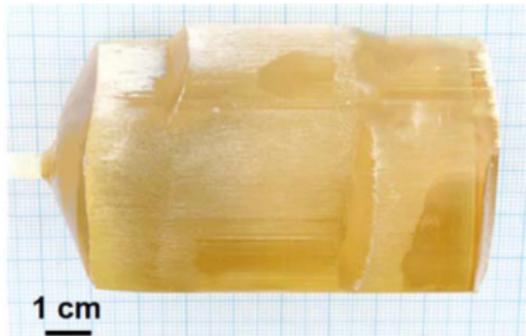


Fig. 2. 50 mm Mg-doped $\beta\text{-Ga}_2\text{O}_3$ crystal grown by Czochralski method [18].

EDGE-DEFINED FILM-FED GROWTH

The EFG growth of $\beta\text{-Ga}_2\text{O}_3$ is similar to Czochralski in that both require atmosphere control due to the use of an iridium crucible. It is most commonly used for growth of large area single crystal ribbons of Al_2O_3 . Shimamura et al. were the first group to demonstrate the growth of 50 mm $\beta\text{-Ga}_2\text{O}_3$ ribbons by pulling from a die fed by capillary action from a

melt. Figure 3 shows (a) 10x15-mm (010) oriented, (b) 50 mm ($\bar{2}01$) oriented, and (c) 100 mm ($\bar{2}01$) oriented $\beta\text{-Ga}_2\text{O}_3$ single crystal substrates [20].

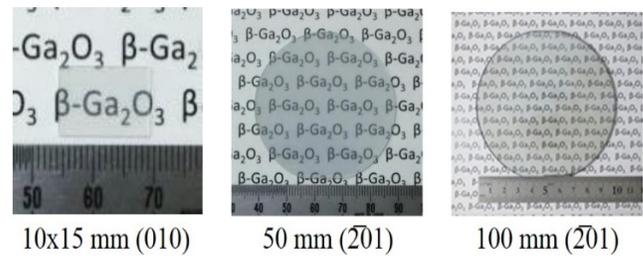


Fig. 3. EFG $\beta\text{-Ga}_2\text{O}_3$ substrates [20].

FLOAT ZONE

Float zone (FZ) is presently the preferred method for manufacturing high resistivity silicon boules. This technique utilizes a RF heating coil to create a traveling melt zone that converts polycrystalline feedstock into single crystal material. $\beta\text{-Ga}_2\text{O}_3$ crystal diameters of about 25 mm were grown by Villora et al along the [100], [010] and [001] crystallographic directions [19].

VERTICAL BRIDGEMAN

The Vertical Bridgeman method combines attributes of the Czochralski and FZ techniques through introduction of a controlled temperature gradient. Crystallization occurs at the boundary of the higher temperature melt zone and lower temperature crystallized solid. The requirement to minimize the oxygen partial pressure of the growth atmosphere is avoided through use of a platinum-rhodium crucible rather than an iridium crucible used for the CZ method.

EXPERIMENTAL RESULTS

In this work Czochralski growth of $\beta\text{-Ga}_2\text{O}_3$ was conducted using a water cooled, bell jar type of puller with RF heating, iridium crucible and computerized diameter control. This type of puller is capable of growth temperatures exceeding 2000°C at one atmosphere and has been used for manufacturing a variety of laser crystals including yttrium aluminum garnet (YAG) and gadolinium gallium garnet (GGG) crystals. The growth atmosphere as well as the vertical and radial temperature gradients are readily changeable. The growth atmosphere can easily be modified as the system consists of a flowing-gas atmosphere. The vertical and radial temperature gradients are readily changeable via refractory ceramic spacing and crucible position in the RF-coils. Modifying the temperature gradients was critical to achieving seeded growth of $\beta\text{-Ga}_2\text{O}_3$ single crystals.

High quality $\beta\text{-Ga}_2\text{O}_3$ single crystal seeds with the desired crystallographic orientation are not commercially available.

An iridium wire loop was used to nucleate large β -Ga₂O₃ grains. Growth was initiated at 1820°C in a 98%CO₂/2%O₂ atmosphere to suppress highly volatile gallium oxide melt as well as minimizing crucible weight loss. The first as-grown, unseeded gallium oxide crystal is shown in Fig. 4. The largest single grain regions were extracted for subsequent seed fabrication. These grain regions were not large enough to orient seeds along the desired [010] crystallographic direction but did support the fabrication of randomly oriented seeds.



Fig. 4. First growth attempt using Ir wire as a seed.

Several growth attempts were required utilizing differing puller designs aimed at establishing the appropriate temperature gradients and atmosphere conditions. Attempts at using seeds of random crystallographic orientation were largely unsuccessful. In particular, seed burn off or melt back occurred on multiple occasions. Upon further investigation, it was discovered the crucible was leaking. Due to the volatility of the gallium oxide melt, gallium metal was likely interacting with the iridium crucible causing weakened areas. The growth puller design was further refined to reduce the volatility of the gallium oxide by improving control of the growth atmosphere. A rigid iridium wire was used to successfully initiate growth of large, single grain crystalline sections (Fig. 5). Results of this experiment indicate that growth environment modifications clearly improved the growth and control of volatile gallium sub-oxides.



Fig. 5. Ir wire nucleated crystal and first seeded growth.

Crystalline grains from the use of a rigid iridium wire were suitable for fabrication of seeds up to 30 mm in length. While the seed was not completely single crystal the majority of it was. Use of these seeds led to the first successful boule growth

(Fig. 5). The longer seed could accommodate some melting the seed while keeping the iridium seed rod holder away from the melt. Subsequent attempts demonstrated a controllable and reproducible seeded growth process although the large color non-uniformity and twining limited their use. Further improvement of crystalline quality and color uniformity was necessary. A series of 9 growth experiments were conducted to understand the color variation impact of differing cool-down conditions. The growth conditions remained constant with a 98% CO₂ / 2% O₂ atmosphere. Following the growth cycle, crystal cooling occurred in a variety of 98% CO₂/2% O₂, Argon (Ar) and Nitrogen (N) containing atmospheres. The use of a two stage cool down process consisted of the as-grown crystal being “soaked” for approximately 35 minutes above the melt in an Argon atmosphere followed by cooling down in a 98% CO₂/2% O₂ environment. Figure 6 highlights the color uniformity achieved with this process.



Fig. 6. 35 mm UID crystals with improved cool down cycle.

Mg and/or Fe doping are both viable approaches for obtaining semi-insulating β -Ga₂O₃ crystals. Both Mg and Fe have been shown to be efficient compensating acceptors. A series of crystals doped with 0.10 to 0.40 mol% MgO were grown in 2 to 10 vol.% O₂ containing atmospheres to minimize melt decomposition. Galaska et al. has reported Czochralski single crystal growth of β -Ga₂O₃ using overpressure and/or higher O₂ partial pressure can improve control of the gallium oxide melt volatilization. Since the CZ pullers at Northrop Grumman SYNOPTICS are not designed to employ an overpressure, oxygen is introduced to the growth environment in such a way to minimize sub-oxide species volatilization without significant Ir crucible degradation. Fig. 7 highlights two Mg-doped crystals grown with increasing Mg concentration. Initial Hall Effect measurements indicate that samples from both boules are likely highly resistive, ie. >10¹⁰ Ohm-cm at room temperature (Fig 9).



Fig. 7. 50 mm crystals doped with (a) 0.20 mol% MgO and (b) 0.30 mol% MgO.

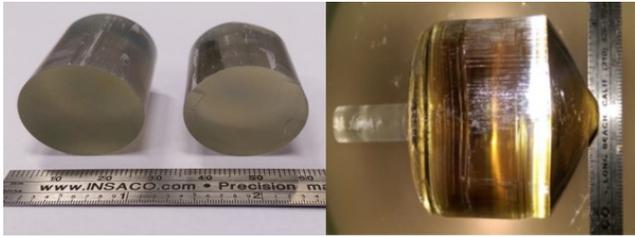


Fig. 8. (a) 25-mm Mg-doped boules and (b) 50-mm Fe-doped crystal.

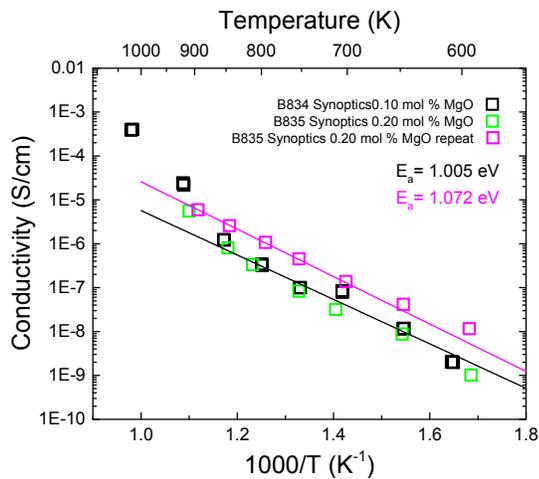


Fig. 9. Hall Effect measurements.

The crystallinity of both UID and doped crystals grown to date has been impacted by the formation of twins. The highest quality grain-free regions of boules have been used as seeds to minimize multi-grain formation. Greater care is taken to properly orient the seeds along the [010] axis. Potential solutions include use of higher oxygen partials, improved seed quality and size optimization, modified growth rates, improved temperature gradients and potentially varying seed orientation.

CONCLUSIONS

Czochralski growth of UID, Mg-doped and Fe-doped [010] β -Ga₂O₃ crystals was demonstrated. Growth process was scaled from self-nucleated grains on iridium wire to seeded [010] oriented 50 mm diameter β -Ga₂O₃ boules. Growth was investigated in 100% CO₂/10%O₂ atmosphere to minimize melt decomposition. The primary technical challenge going forward is to improve the boule crystallinity. The near term availability of 50-mm diameter substrates will accelerate the development of this novel ultra-wide bandgap semiconductor technology.

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