

Growth of 50mm Beta-Gallium Oxide (β -Ga₂O₃) Substrates

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Abstract

The promise of affordable, large diameter substrates has spawned interest in β -Ga₂O₃ as a disruptive semiconductor for next generation high power electronics. β -Ga₂O₃ is a unique ultra-wide bandgap (~4.9eV) semiconductor in which single crystals can be grown using conventional melt-based techniques such as Czochralski (CZ) or Edge-defined Film-fed Growth (EFG). Use of melt growth technology offers a clear economic advantage over SiC and GaN vapor transport processes even though β -Ga₂O₃ growth requires the use of iridium crucibles. β -Ga₂O₃ possesses an estimated electric field breakdown of 8 MV/cm which is approximately 2-3 times larger than that of SiC or GaN. These intrinsic properties lead to a Baliga Figure of Merit [1] four times that of GaN. Unintentionally doped (UID) β -Ga₂O₃ is slightly conductive with residual Si responsible for n-type conduction. Doping with Mg or Fe act provides acceptors to achieve semi-insulating characteristics. The Air Force Research Laboratory began funding development of bulk β -Ga₂O₃ crystal development with SYNOPTICS in early 2015. SYNOPTICS has successfully scaled the growth of UID, Mg-doped and Fe-doped β -Ga₂O₃ crystals from self-nucleated grains on iridium wire to seeded <010> oriented 50-mm diameter boules. This work has led to the commercial introduction of 25-mm semi-insulating substrates in 2017 and 50-mm semi-insulating substrates targeted for release in late 2018. In this paper, we will review the development of large diameter, semi-insulating β -Ga₂O₃ substrates.

INTRODUCTION

Beta-phase gallium oxide (β -Ga₂O₃) is an emerging ultra-wide bandgap semiconductor poised to impact next generation high voltage power switching and GHz RF power amplification. Unlike GaN and SiC, β -Ga₂O₃ single crystals can be grown using conventional melt-based techniques such as Czochralski (CZ) or Edge-defined Film-fed Growth (EFG). β -Ga₂O₃ possesses a bandgap of ~4.9eV and a theoretical critical field strength (E_c) of 8 MV/cm [1]. This translates into

a Baliga figure of merit (BFOM) estimated to be several times higher than that for SiC or GaN providing strong motivation for development of unipolar power devices. The critical field strength is also a key factor in Johnson's figure of merit (saturation velocity-critical electric field product, $v_{sat} \cdot E_c$) used to describe RF operation. Recent Air Force Research Laboratory fabricated β -Ga₂O₃ MOSFETs achieved record-high 3.8 MV/cm critical field strength exceeding both GaN and SiC bulk values [2]. Additionally, blocking voltages >600V for both enhancement and depletion-mode devices have been demonstrated [3, 4]. 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 mobility's of 200–250 cm²/V-s. β -Ga₂O₃ is one of five crystalline polytypes. It has a base-centric monoclinic crystal structure and is the only stable polymorphic phase at melt-based growth temperatures. The unit cell of β -Ga₂O₃ contains two crystallographically different Ga atoms in the asymmetric unit, one tetrahedral and one octahedral coordination geometry [Fig 1].

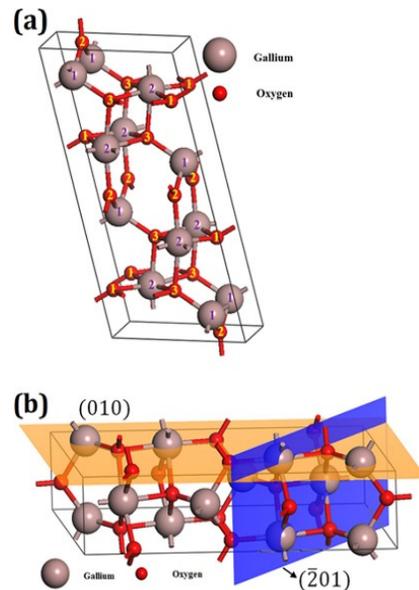


Fig. 1 (a) β -Ga₂O₃ crystal structure and (b) (010) and (201) surfaces [5].

Unintentionally doped (UID) β -Ga₂O₃ typically exhibits n-type conductivity with carrier concentrations in the low 10¹⁷cm⁻³. It can be doped over a wide range to provide controllable n-type conductivity [6-8] using silicon, germanium or tin. Both Fe and Mg dopants are used to obtain high resistivity by acting as a deep acceptors. First-principles calculations of the β -Ga₂O₃ band structure [9] have predicted self-trapping of holes in the bulk, prohibiting p-type conductivity. It is argued that p-type doping is not favorable for many metal-oxides due to the nature of their valance band. In wide-band-gap oxides including ZnO, MgO, In₂O₃, Ga₂O₃, Al₂O₃, SnO₂, SiO₂, and TiO₂, conduction band states originate from metal atoms, whereas the valence-band states are derived mainly from the O 2p orbitals and are characterized by small dispersion, large effective masses, and high density of states [10].

CRYSTAL GROWTH

β -Ga₂O₃ is a unique ultra-wide bandgap material in that single crystals can be grown by a variety of cost-effective melt-based techniques. Growth of β -Ga₂O₃ was first reported by Tomm et al. in 2000 by using a 90% argon and 10% CO₂ atmosphere. The high melting temperature and oxidizing environment of β -Ga₂O₃ requires the use of iridium crucibles. This remains challenging for CZ growth as iridium crucibles will easily oxidize in an atmosphere of only a few percent of oxygen [11, 12]. β -Ga₂O₃ possesses two strong cleavage planes parallel to the (100) and (001) planes which have strong electrical, optical and thermal anisotropy due to its monoclinic crystal structure. The monoclinic phase of β -Ga₂O₃ is stable under normal conditions of temperature and pressure. 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 plane inducement of grain boundaries, twins and cracks. Currently, the <010> oriented material is the preferred orientation for epitaxial growth [11]. EFG β -Ga₂O₃ substrates of differing orientations and doping are commercially available from Tamura Corporation [13]. Crystals can be cut to produce (201) oriented substrates 50 to 100-mm in diameter. Preferred <010> oriented materials are only available in 10x15-mm sizes [Fig 2].

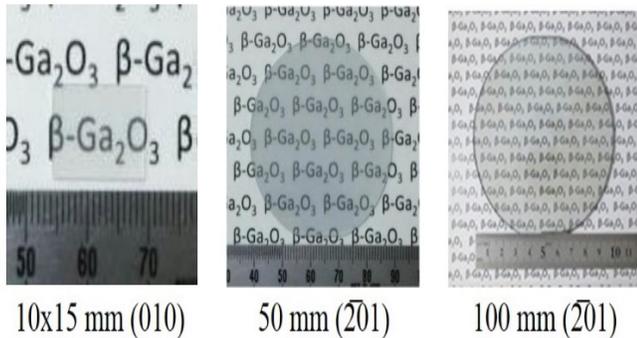


Fig. 2 EFG β -Ga₂O₃ substrates [13].

EXPERIMENTAL

The Czochralski method is the preferred technique for manufacturing a wide variety of bulk semiconductors including silicon, gallium arsenide and sapphire. SYNOPTICS utilizes a water cooled, bell jar type of CZ puller capable of growth temperatures exceeding 2000°C at one atmosphere. It has been used for manufacturing a variety of laser crystals including yttrium aluminum garnet (YAG) and gadolinium gallium garnet (GGG) crystals. Use of atmospheric overpressure or an oxygen rich environment can suppress volatilization of gallium oxide into sub-oxide species. However, growth in a higher oxygen partial pressure atmosphere does expose the iridium crucible to increased oxidation. Since SYNOPTICS pullers 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 iridium crucible degradation. Controlling the O₂ partial pressure can also be used to impact the formation of native point defects such as oxygen and gallium vacancies. Galaska et al. [14] has shown both theoretically and experimentally that scale-up of β -Ga₂O₃ crystal size is strongly affected by the formation of metallic gallium in the melt. Further scale up to 100-mm diameter crystals will require correspondingly higher oxygen concentration in the growth atmosphere, up to 100%. The method of introducing oxygen into the atmosphere is critical to overcoming iridium crucible oxidation.

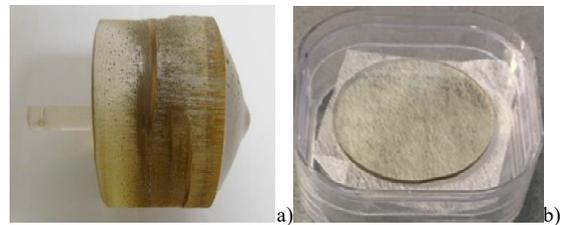


Fig. 3 a) 50-mm Fe-doped boule, b) 25-mm Mg-doped substrate.

UID, Fe and Mg-doped β -Ga₂O₃ single crystals were grown by the Czochralski method with an inductively heated iridium crucible in 91% CO₂ and 9% O₂ atmosphere [Fig 3]. This amount of oxygen was adequate to decrease the evaporation of the molten gallium oxide to support crystalline growth as well as minimize the oxidation rate of the iridium crucible. Crystals were 50-mm in diameter and nominally 50-mm long. The growth rate was approximately 2.25 mm/h at a crystal rotation of 2.0 rpm. In each case the crystals were grown along the <010> crystallographic direction, parallel to both (100) and (001) cleavage planes. Formation of twins along the cleavage planes was problematic requiring the boules to be cored to smaller, single-grain diameter. Twins can form with domain boundaries parallel to the (100) cleavage plane during the cone portion of growth, and will propagate throughout the run. There is an increased likelihood of twin formation when diameter growth progresses as a series of steps, rather than a smooth transition from seed

diameter, to full crystal diameter. At each of these steps, there is an increased probability for twinning to occur. The orientation of twin domains are related by 180° rotation about the a-axis and can be easily distinguished when viewed under cross polarizers.

FABRICATION AND POLISHING

The presence of two strong cleavage planes parallel to the (100) and (001) planes complicate $\beta\text{-Ga}_2\text{O}_3$ slicing and polishing. These crystal planes are highly susceptible to mechanical stress and can easily cleave during processing as shown in Figure 5. Crystals up to 40-mm in diameter were sliced and polished using a combination of mechanical and chemical mechanical polishing processes. A multi-wire saw with a 150μ diameter wire with a fixed diamond abrasive of $10\text{-}20\mu$ and a slicing pitch of 750μ was utilized [Fig 4a]. Crystal orientation is critical to avoid chipping associated with wire motion in the cleavage direction. Approximately 150μ of material was removed in a series of lapping processes using progressively smaller diamond grit slurries. Due to cleaving and flaking at the edges, several different grinding slurries and platen surfaces were considered. Several microns of material was removed in the final chemical-mechanical-polishing (CMP) step of 50% SiO_2 slurry in NaOH.

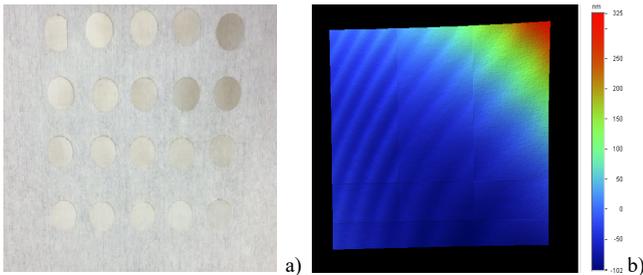


Fig. 4 a) As-sliced $\langle 010 \rangle$ Fe-doped $\beta\text{-Ga}_2\text{O}_3$ substrates, b) Wyko image of a Fe-doped $\langle 010 \rangle$ $\beta\text{-Ga}_2\text{O}_3$ surface after CMP.

The substrates were further characterized with atomic force microscopy (AFM), Wyko and x-ray diffraction (XRD). Figure 4b shows an image of a set of white light interferometer measurements. The surface was observed to be free of any scratching or other defects over the $5 \times 5 \text{mm}$ region sampled. AFM indicated that the $\beta\text{-Ga}_2\text{O}_3$ surfaces were pristine and free of scratches and exhibited a value of R_a of 0.1nm [Fig 5]. The substrates were measured using XRD to assess their crystalline quality. Existence of broad XRD linewidths can indicate the presence of subsurface damage, even for substrates which exhibit an otherwise smooth surface [16]. These substrates exhibited linewidths for the $\langle 020 \rangle$ reflection ranging from $\sim 50\text{-}250$ arc-sec, with an average linewidth of 165 arc-sec for the entire boule (41 substrates) [Fig 6].

A twin-free 40-mm diameter $\langle 010 \rangle$ substrate [Fig. 7] was produced from a 52-mm diameter crystal. The 40-mm diameter slug was cored from the as-grown boule and then

sliced into 1.2mm thick wafers using a Takatori wire saw with boron carbide slurry (~ 9 micron grit size). Post-slice grinding used a 40 micron aluminum oxide/water mixture with removal rates of 0.001 inches per 1.5 hours. After grinding the wafers were pre-polished on a lead lap using 9 micron diamond paste with a removal rate of 0.001 inches per 2 hours. A final polish is performed with a felt pad with 500S colloidal silica and water mixture. Total removal of ~ 0.0006 inches.

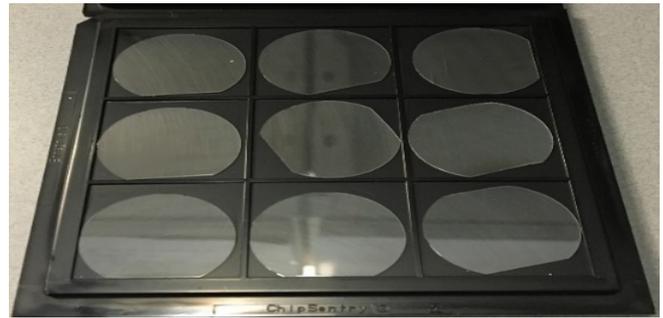


Fig. 5 25-mm epi-ready $\langle 010 \rangle$ $\beta\text{-Ga}_2\text{O}_3$ substrates.

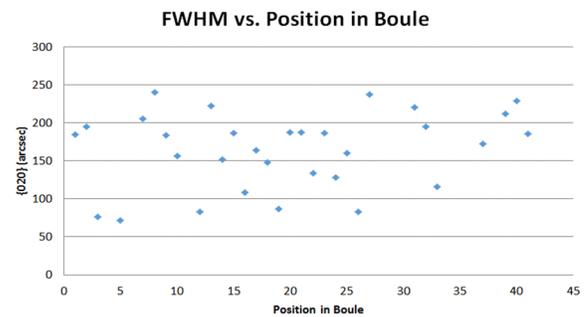


Fig. 6 XRD linewidths of $\langle 010 \rangle$ $\beta\text{-Ga}_2\text{O}_3$ substrates.

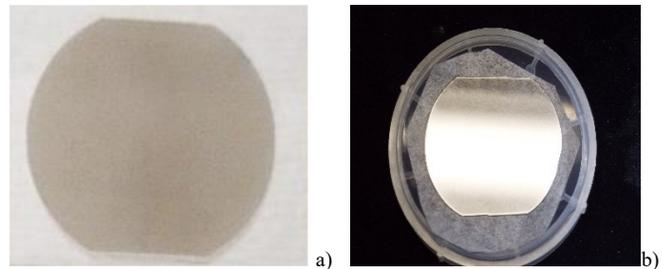


Fig. 7 a) As-cut 40-mm $\langle 010 \rangle$ $\beta\text{-Ga}_2\text{O}_3$ substrate, b) Polished 40-mm $\langle 010 \rangle$ $\beta\text{-Ga}_2\text{O}_3$ substrate.

THERMAL CONDUCTIVITY

The room temperature thermal conductivity of UID and Fe-doped $\langle 010 \rangle$ $\beta\text{-Ga}_2\text{O}_3$ samples was investigated using time-domain thermo-reflectance (TDTR). This technique is well-established for measuring cross-plane and in-plane thermal conductivities. The thermal conductivity of $\beta\text{-Ga}_2\text{O}_3$ is highly anisotropic and rather poor compared to other wide bandgap semiconductors. For these measurements, pump beam modulation frequencies of 2.2, 3.6 and 6.3 MHz were

utilized for two different laser spot sizes. Thermal conductivity values of 24.23 ± 1.66 W/mK and 24.88 ± 1.80 W/mK were obtained for UID and Fe-doped samples respectively indicating almost no doping dependence. Guo et al reported $\langle 010 \rangle$ has the highest thermal conductivity of 27.0 ± 2.0 W/mK [Fig 8].

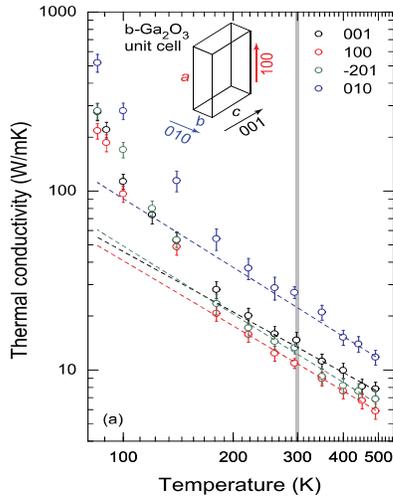


Fig. 8 Temperature-dependent thermal conductivity of β -Ga₂O₃ measured along different crystal directions [15].

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CONCLUSIONS

Czochralski growth of 50-mm diameter UID, Mg-doped and Fe-doped $\langle 010 \rangle$ β -Ga₂O₃ crystals was demonstrated. Growth was conducted in an atmosphere 91% CO₂ and 9% O₂ to minimize melt decomposition. The presence of twinning limited single crystal diameter to ~ 40 -mm. XRD results indicate further improvement in crystalline quality is necessary. Fabrication and polishing processes were demonstrated to achieve epi-ready surfaces. The ability to grow crystals via a melt-based process offers a clear cost and manufacturability advantage compared to SiC and GaN. The commercial availability of larger diameter substrates will accelerate the development of this novel ultra-wide bandgap semiconductor technology.

REFERENCES

[1] M. Higashiwaki et al., *Appl. Phys. Lett.*, vol. 100, p. 013504, (2012).
 [2] A. J. Green, K. D. Chabak, E. R. Heller, R. C. Fitch, M. Baldini, A. Fiedler, K. Irmscher, G. Wagner, Z. Galazka, S. E. Tetlak, A. Crespo, K. Leedy, and G. H. Jessen, *IEEE Electron Device Letters* **37** (7), 902 (2016).
 [3] K. Chabak, N. Moser, A. Green, D. Walker, S. Tetlak, E. Heller, A. Crespo, R. Fitch, J. McCandless, K. Leedy, X. Li, and G. Jessen, "Enhancement-mode Ga₂O₃ wrap-gate fin field-effect-transistors on native (100) β -Ga₂O₃ substrate with high breakdown voltage," *Appl. Phys. Lett.*, vol. 109, p. 213501, Nov. 2016.
 [4] M. H. Wong, K. Sasaki, A. Kuramata, S. Tamakoshi, and M. Higashiwaki, "Field-plated Ga₂O₃ MOSFETs with a breakdown

voltage of over 750 V," *IEEE Electron Device Lett.*, vol. 37, no. 2, pp. 212–215, Feb. 2016.
 [5] S. J. Pearton et al, A review of Ga₂O₃ materials, processing, and devices *Appl. Phys. Rev.* **5**, 011301 (2018).
 [6] N. Ueda, H. Hosono, R. Waseda, H. Kawazoe, *Applied physics letters* 1997, **70**, 3561-3563.
 [7] E. G. Villora, K. Shimamura, Y. Yoshikawa, T. Ujiie, K. Aoki, *Applied Physics Letters* 2008, **92**, 202120.
 [8] K. Sasaki, A. Kuramata, T. Masui, E. G. Villora, K. Shimamura, S. Yamakoshi, *Applied Physics Express* 2012, **5**, 035502.
 [9] A. Denisenko and E. Kohn, "Diamond power devices. Concepts and limits," *Diamond and Related Materials*, vol. 14, pp. 491–498, 3// 2005.
 [10] J. B. Varley, A. Janotti, C. Franchini, and C. G. Van de Walle, "Role of self-trapping in luminescence and p-type conductivity of wide-band-gap oxides," *Physical Review B*, vol. 85, p. 081109, 02/27/ 2012.
 [11] Z. Galazka, K. Irmscher, R. Uecker, R. Bertram, M. Pietsch, A. Kwasniewski, M. Naumann, T. Schulz, R. Schewski, D. Klimm, and M. Bickermann, On the bulk β -Ga₂O₃ single crystals grown by the Czochralski method, *J. Cryst. Growth* **404** (2014) 184–191.
 [12] D. Klimm, S. Ganschow, D. Schulz, R. Bertram, R. Uecker, P. Reiche, and R. Fornari, Growth of oxide compounds under dynamic atmosphere composition, *J. Cryst. Growth* **311** (2009) 534–536.
 [13] Akito Kuramata, Takekazu Masui, Kimiyoshi Koshi, Shinya Watanabe, Yu Yamaoka, and Shigenobu Yamakoshi, Properties of Gallium Oxide Single-crystal Substrates Made by Edge-defined Film-fed Growth, 1st International Workshop on Gallium Oxide and Related Materials 2015.
 [14] Scaling-Up of Bulk β -Ga₂O₃ Single Crystals by the Czochralski Method, Zbigniew Galazka, Reinhard Uecker, Detlef Klimm, Klaus Irmscher, Martin Naumann, Mike Pietsch, Albert Kwasniewski, Rainer Bertram, Steffen Ganschow, and Matthias Bickermann, *ECS Journal of Solid State Science and Technology*, **6** (2) Q3007-Q3011 (2017)
 [15] Z. Guo, A. Verma, X. Wu, F. Sun, A. Hickman, T. Masui, et al., "Anisotropic thermal conductivity in single crystal β -gallium oxide," *Applied Physics Letters*, vol. 106, p. 111909, 2015.
 [16] J.H. Leach, K. Udary, T. Schneider, J.D. Blevins, K.R. Evans, G. Foundos, and K.T. Stevens, "Development of homoepitaxial growth of Ga₂O₃ by hydride vapor phase epitaxy," Paper 14.3, CS Mantech 25 May 2017, Indian Wells, CA USA.