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

J.D. Blevins¹, D. Thomson¹, K. Stevens², G. Foundos², A. Lindsey², J.H. Leach³, J. Rumsey³

¹Air Force Research Laboratory (AFRL), Wright-Patterson AFB, OH
²Northrop-Grumman SYNOPTICS, Charlotte, NC
³Kyma Technologies, Raleigh NC

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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 provides deep 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 [Fig 1a]. This work has led to the commercial introduction of 25-mm [Fig 1b] 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 · 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 mobilities of 200–300 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 with tetrahedral and the other with octahedral coordination geometry [Fig 2]. It is composed of two types of gallium ions and three types of oxygen ions [5]. Unintentionally doped (UID) β-Ga₂O₃ typically exhibits n-type conductivity with carrier concentrations in the range of low 10¹⁷ cm⁻³. It can be doped over a wide range to provide controllable n-type conductivity [6-8] using silicon or tin. Both Fe and Mg dopants are used to obtain high resistivity by acting as 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 valance-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].

![Fig. 1 a) 50-mm Fe-doped boule, b) 25-mm Mg-doped substrate](image)

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*Fig. 1 a) 50-mm Fe-doped boule, b) 25-mm Mg-doped substrate*
**CRYSTAL GROWTH**

β-Ga$_2$O$_3$ 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-Ga$_2$O$_3$ was first reported by Tomm et al. in 2000 by using a 90% argon and 10% CO$_2$ atmosphere. The high melting temperature and oxidizing environment of β-Ga$_2$O$_3$ 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-Ga$_2$O$_3$ 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-Ga$_2$O$_3$ 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 induction of grain boundaries, twins and cracks. The <010> oriented material is the preferred orientation for epitaxial growth [11]. Presently, EFG β-Ga$_2$O$_3$ 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.

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. Growth of β-Ga$_2$O$_3$ single crystals has been demonstrated with a variety of melt-based techniques. 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 O$_2$ 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-Ga$_2$O$_3$ 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.

UID, Fe and Mg-doped β-Ga$_2$O$_3$ single crystals were grown by the Czochralski method with an inductively heated iridium crucible in 91% CO$_2$ and 9% O$_2$ atmosphere. 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 β-Ga2O3 slicing and polishing. These crystal planes are highly susceptible to mechanical stress and can easily cleave during processing as shown in Figure 7. 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 10-20µ and a slicing pitch of 750µ was utilized [Fig 5]. 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% SiO2 slurry in NaOH.

The substrates were further characterized with atomic force microscopy (AFM), Wyko and x-ray diffraction (XRD). Figure 5 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 5x5mm region sampled. AFM indicated that the β-Ga2O3 surfaces were pristine and free of scratches and exhibited a value of Ra of 0.1nm. 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. These substrates exhibited linewidths for the <020> reflection ranging from ~50-250 arc-sec, with an average linewidth of 165 arc-sec for the entire boule (41 substrates) [Fig 6].

**THERMAL CONDUCTIVITY**
The room temperature thermal conductivity of UID and Fe-doped <010> β-Ga2O3 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 β-Ga2O3 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 <010> has the highest thermal conductivity of 27.0 ±2.0 W/mK [Fig 9].

Fig. 9 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 <010> 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 near-term availability of larger diameter substrates will accelerate the development of this novel ultra-wide bandgap semiconductor technology.