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NEWS AND VIEWS

Bulk gallium oxide single crystal growth

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Gallium oxide, as a new type of ultra-wide bandgap semiconductor, is expected to be used in power electronics and solar blind UV photodetectors. The main cause of research and development on β-Ga_2O_3 is inspired by its larger bandgap, higher breakdown field, bigger Baliga figure-of-merit (FOM), shorter absorption edge and lower cost compared to the third-generation semiconductors, such as SiC and GaN.

Gallium oxide is not a new material. The growth history of bulk β-Ga_2O_3 single crystal can be traced back to about 60 years ago with the first study being conducted in 1956[1]. When we industrialize the production of gallium oxide, melt growth methods are the most suitable. Because using these methods we can obtain large-sized crystals with high crystalline quality. But the melting point of β-Ga_2O_3 is approximately 1800 °C, which makes it difficult to grow gallium oxide using the melt methods. The features of melt growth methods used for growing bulk β-Ga_2O_3 crystals are summarized in Table 1. All of the methods can be applied to the growth of cylindrical crystals and the edge defined film-fed growth (EFG) can be used to grow single crystals of other shapes. In addition, both Verneuil and optical floating zone (OFZ) methods are free from the crucible. As for the obtained crystal sizes by different melt growth methods, the crystal diameter is generally below 10 mm by the Verneuil and OFZ methods, although crystals in diameter of 25 mm was reported by using the OFZ method[2]. With vertical bridgman (VB) method, the reported crystal diameter was either 25 or 50 mm with a Pt–Rh (70%–30%) alloy crucible[3]. As for the Czochralski method, the crystal diameter can reach 2 inches at present[4].

Undoubtedly, high quality β-Ga_2O_3 crystal can also serve as a key semiconductor material for future application. The best structural quality of β-Ga_2O_3 single crystal has been obtained by the Czochralski (CZ) and the EFG method, which apply contactless technique and continuous growth direction perpendicular to the crystal cross-section. However, the VB method is a contact technique, where the growing crystal contacts with the crucible. The obtained β-Ga_2O_3 crystal by VB method is considerable, but the contact growth leads to higher dislocation density, cleaving or cracking, which can be a major problem in the growth of large diameter crystals. In addition, the growth of β-Ga_2O_3 single crystal by using Verneuil and OFZ methods can be influenced by high temperature gradients and is often carried out in a small-volume melting zone, which increase the possibility of obtaining relatively low quality crystals. Therefore, considering those determining factors related to bulk β-Ga_2O_3 single crystals such as crystal size, quality, and scalability, the CZ and EFG methods seem to be the most promising techniques up to now.

Nevertheless, there have been noticeable difficulties in growing gallium oxide using the CZ and EFG technique. The schematic of CZ and EFG method is shown in Fig. 1. In the CZ method a rotating seed crystal (approximately at the rate of 5–20 rpm) is slowly pulled up (approximately 1–3 mm/h) directly from a melt surface contained in a metal crucible. In the case of β-Ga_2O_3, an Ir crucible is utilized because of the high melting point of Ga_2O_3. The crucible is heated up inductively by an RF coil arranged around the crucible. However, when the crystal is being growing by CZ method, Ga_2O_3 is thermally unstable at high temperature and tend to decompose. This is a huge challenge for growing gallium oxide single crystal, especially large-sized ones. Subsequently, There are reactions occurring in the liquid phase. The presence of liquid Ga in the melt

Table 1. Features of melt growth methods used for growing bulk β-Ga_2O_3 crystals.

Method	Crystal shape	Crystal size (mm)	Growth direction	Crucible	Structural quality	Scalability
Verneuil	Cylinder	9 × 25	(100) plane	None	Poor	Limited
OFZ	Cylinder	6 × 50 25 × 50	<100> <010> <001>	None	Acceptable	Limited
EFG	Slab	50 × 75 × 3 60 × 55 × 18 110 × 110 × 6	<010>	Ir	Good	High
VGF	Cylinder	50 × 30	<010>	Ir	Acceptable	High
VB	Cylinder	25 × 25	⊥(100)	Pt–Rh	Acceptable	High
CZ	Cylinder	10 × 30 20 × 70 50 × 85	<010>	Ir	Good	High

Abbreviations: OFZ, optical floating zone; EFG, edge defined film-fed growth; VGF, vertical gradient freeze; VB, vertical bridgman; CZ, Czochralski.

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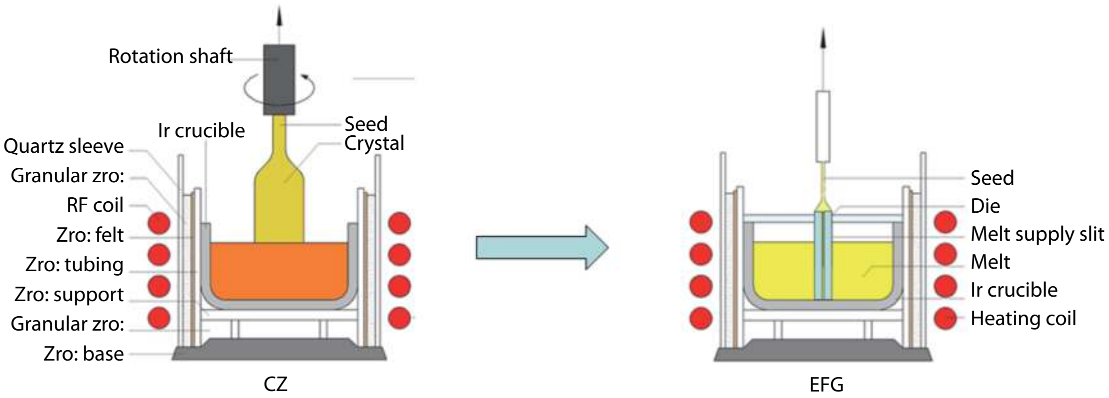

Fig. 1. (Color online) Schematic of CZ and EFG process.

lead to many negative effects, particularly on the formation of Ir–Ga eutectic that can destroy the Ir crucible, and also result in seeding problems and low crystal quality, both due to floating metallic Ga in the melt. In addition, crystal spiral growth turns out to be another challenge caused by the free carrier absorption in the IR spectra. However, the novel approach, by using a low oxygen concentration at low and moderate temperatures, and then high oxygen concentration at high temperatures, allows to obtain crystals of 2″ in diameter. On the other hand, according to the report, when the concentration of free electrons is less than 10^{18} cm^{-3}, the spiral growth tend to be avoided.

The EFG method, evolved from the CZ method, employs a die or a shaper that is placed in a metal crucible and the melt is transported from the crucible to a shaped top surface of the die by a narrow slit or channel due to capillary forces. For growing β-Ga_2O_3 crystals both the crucible and the die are made of iridium. The crucible with a starting material is heated up inductively by an RF coil. The growth direction is always along the [010] crystallographic direction, which is parallel to both cleavage planes (100) and (001). Presently, it is able to fabricate substrate of 2″ (commercialized), 4″ (demonstrated), and possible 6″ (under research & development) by using the EFG method[5].

Furthermore, in view of the available large area, low defect density, fast growth speed, and high crystal quality, the EFG method is predicted to the best technique for mass production of substrates compared to the CZ method. There are some main advantages for using the EFG method to grow β-Ga_2O_3 single crystal.

1) The growth process occurs on the shaped top surface of the die, which avoids the effect of melt convection on crystal growth. Meanwhile, it is also beneficial for improving the doping homogeneity because it is hard for the doping ions to find their ways back to the melt and the segregation coefficient is close to 1.

2) The negative effects, such as floating Ir and Ir–Ga eutectic, on crystal growth are averted due to contactless feature between the growing crystal and the melt.

3) Heavy doping crystals can be realized without the bother of spiral growth.

4) β-Ga_2O_3 single crystal with specified shape and size can be obtained by controlling the shape and size of the die.

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