Chapter 2
Czochralski Method

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Abstract The Czochralski method is one of the leading research and industrial crystal growth technologies that enables to obtain large diameter single crystals of high structural quality at low production costs per volume unit. A possibility of obtaining bulk β-Ga_2O_3 single crystals by the Czochralski method expands the diversity of growth technologies for this compound towards large volumes and high quality suitable for epitaxial growth of layers and device fabrication. Ga_2O_3 is, however, thermally unstable at high temperatures and tends to decompose that has a high impact on the growth process, size, and structural quality of obtained crystals. Additionally, the growth process is also affected by electrical/optical properties of a growing β-Ga_2O_3 crystal. Ga_2O_3 thermodynamics combined with new technical solutions allowed to obtain 2-inch diameter cylindrical single crystals of β-Ga_2O_3 of high structural quality with further scale-up capabilities. Czochralski-grown bulk β-Ga_2O_3 single crystals can be easily doped with a diversity of elements to tune their electrical and optical properties. The bulk β-Ga_2O_3 single crystals can be obtained either as electrical insulators or semiconductors both with a high transparency in the UV and visible spectral regions.

2.1 Introduction

The method was invented in 1916 by Jan Czochralski in Allgemeine Elektricitäts-Gesellschaft (AEG), Berlin, where he worked with metals and alloys. The invention was made during measuring of crystallization velocity of metals (Sn, Zn, Pb) using an apparatus of his design and construction, as described in his paper in 1918 entitled "Ein neues Verfahren zur Messung der Kristallisationsgeschwindigkeit der Metalle" [1]. The apparatus consisted of a support with a crucible containing a molten metal at its base, a pulley, and a silk thread with a glass carrier passing over the pulley and trough two guiding slots. The glass carrier was coated with a metal film for

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better wetting. The carrier was dipped into the slightly overheated melt and pulled upwards once the melt was cooled down to the crystallization temperature. The pulling was aided by a clock mechanism and the velocity was measured with a pointer and scale. The carrier initially pulled up a small amount of the metal melt which crystallized once passing through the liquid–solid interface. Differences in pulling and solidification rates led to an increase or decrease of the crystal diameter being grown.

Following a comprehensive and detailed research study on the Czochralski method by Uecker [2], the method was used for growing crystalline metal fibres in Berlin just after its invention and was subjected to a number of modifications. Gomperz [3] (Germany, 1922) introduced a die and a gas coolant for a growing crystal, Grüneisen and Goens [4] (Germany, 1923) introduced oriented crystal seeds, Hoyem and Tyndall [5] (USA, 1929) introduced a seed necking, and Walther [6] (USA, 1937) introduced a crystal rotation and control of the shape and diameter of the growing crystal, as well as re-designed a furnace for relatively high melting point materials (NaCl) that produced large diameter (2 cm) oriented crystals. These developments combined with the fundamental concept of Jan Czochralski to pull a crystal up from the melt have established key aspects of the method already before World War II.

After World War II, the Czochralski method was used to grow single crystals of elemental semiconductor Ge by Teal and Little [7] (USA, 1950). The invention of a point-contact field-effect transistor by Bardeen, Brattain, and Shockley in 1947 lead to a rapid spread of the Czochralski method for growing large diameter (6 inch) Ge and Si single crystals in 50-ties of the twentieth century and their industrialization, wherein introduction by Dash [8] a neck procedure in 1958 enabled obtaining of high quality, dislocation-free Si crystals. Two decades later Hoshikawa et al. [9] (Japan, 1980) applied a magnetic field to damp the melt convection of conductive melts. Another modification to the Czochralski method was a continuous melt feeding developed by Petrov and Zemskov [10] (Russia, 1957). The Czochralski method also spread on III–V compound semiconductors that were utilized for the first time for growing InSb and AlSb crystals by Gremmelmaier and Madelung [11] (Germany, 1953). To grow volatile compound semiconductors (GaAs, InAs, InP), Gremmelmaier [12] (Germany, 1956) introduced a hot-wall modification, while Metz et al. [13] (USA, 1962) introduced the Liquid-Encapsulated Czochralski technique. The use of the Czochralski method for growing semiconducting crystals proceeded in parallel in USA, Europe, Russia, and Japan.

A discovery of a solid-state laser based on the ruby crystal increased a demand for high structural quality oxide crystals that could be achieved with the use of the Czochralski method. First oxide crystals ($CaWO_4$) by the Czochralski method were obtained in 1960 by Nassau and Van Uitert [14] (USA). Soon after other oxides were grown by the Czochralski method in USA, Europe, and later in Japan. Introducing to the Czochralski method electronic load cells for crystal weighting by Bardsley et al. [15] (UK, 1972) and for crucible weighting by Kyle and Zydzik [16] (USA, 1973) enabled fully an automatic diameter control of the growing crystal. Main events in development of the Czochralski method are listed in Table 2.1.

Table 2.1 Main, chronological events in development of the Czochralski method

Year	Main events in development of the Czochralski method	Inventor	References
1916	Invention of pulling a crystal from the melt	Czochralski	[1]
1922	Die and gas coolant	Gomperz	[3]
1923	Oriented seeds	Grüneisen and Goens	[4]
1929	Seed necking	Hoyem and Tyndall	[5]
1937	Crystal rotation, crystal shape control, high-temperature growth furnace	Walther	[6]
1950	First elemental semiconductors (Ge)	Teal and Little	[7]
1956	Hot wall	Gremmelmaier	[12]
1957	Melt feeding	Petrov and Zemskov	[10]
1959	Neck procedure for Si crystals	Dash	[8]
1960	First oxide crystal ($CaWO_4$)	Nassau and Van Uitert	[14]
1962	Liquid encapsulation Czochralski method	Metz et al.	[13]
1972	Automatic diameter control	Bardsley et al.	[15]
1980	Magnetic field	Hoshikawa et al.	[9]

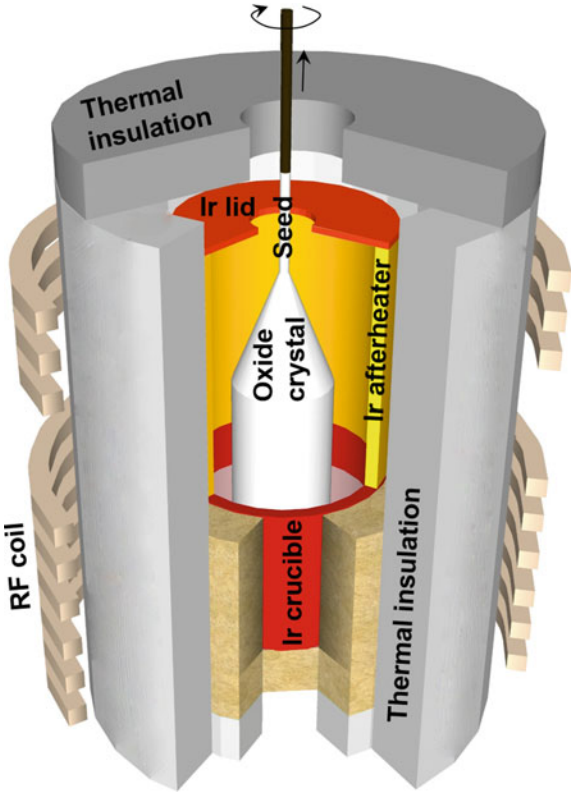
Nowadays, the Czochralski method is used worldwide to grow different type of single crystals: metals, elemental semiconductors, compound semiconductors, halides, and oxides. As large as 450 mm diameter semiconductor and halide crystals, and 200 mm diameter oxide crystals (sapphire, $Bi_4Ge_3O_{12}$) are grown nowadays by the Czochralski method. Large crystal diameter, high structural quality, and low production costs per volume unit make the Czochralski method one of the most frequently used techniques at research and industrial levels.

2.2 Czochralski Growth Furnace for Oxides

A crystal growth station for growing oxide crystals by the Czochralski method consists of a water-cooled growth chamber accommodating a growth furnace and an inductive heater (RF coil) surrounding the growth furnace that is powered by an RF generator outside the growth chamber, a puller with a pulling shaft that is coupled with a load cell and pulling/rotation motors, and a computer with a PID (proportional, integral, differential) controller for an automatic crystal diameter control, that is coupled with the motors, load cell, and generator.

A heart of the growth station is the growth furnace that defines a growth environment, an example of which is shown in Fig. 2.1. The furnace consists of a metal

Fig. 2.1 Schematic view of a growth furnace of a general purpose for high melting point oxide crystals grown by the Czochralski method



crucible containing the melt, and a thermal insulation surrounding the crucible from all sides with a free space accommodating a growing crystal. The thermal insulation has a central opening at the top part for the pulling shaft, and a viewing window on the side (not shown) for optical observation of melting of the starting material, seeding, and crystal growth. To minimize temperature gradients in the pulling zone above the metal crucible a metal after heater (active or passive) can be utilized, possible with other metal shielding elements, such as lids. For high melting point oxides in the temperature range of about 1500–2200 °C Ir crucibles are most frequently used, at lower temperatures—Pt, while at higher ones—Mo, W, and Rh. Below about 1900 °C also alloys are sometimes utilized, such as Ir–Pt and Pt–Rh.

The thermal insulation in terms of the material type and geometry depends on the melting point of an oxide to be grown and the size of the crystal. It may comprise alumina, zirconia, magnesia, and quartz (outer part of the furnace). For high melting point oxides, to which β-Ga_2O_3 belongs, typically Ir crucibles are used with a typical wall thickness of 1.5–2 mm.

After melting and stabilizing the oxide starting material, an oriented crystal seed attached to the pulling shaft is dipped into the melt, which is then slowly pulled up while rotating. The seed diameter (usually a few mm) is next expanded to a pre-defined cylinder diameter which is typically grown at a constant rate of 1–5 mm/h. The rotation rate depends on the crystal diameter, crystal thermal properties and its transparency to infrared radiation, and on the growth rate. The crystal rotation rate values are usually between 5 and 30 rpm. Once the cylinder length achieves its final length (usually after crystallization of 40–75 wt% of the melt), it is separated from the melt and slowly cooled down to room temperature.

2.3 β-Ga_2O_3—Early Attempts with the Czochralski Method

The first mention of an application of the Czochralski method to grow β-Ga_2O_3 crystals was given in 1983 by Vasil'tsiv and Zakarko [17], which was summarized in one sentence: "*We used single crystals of the β-modification of gallium oxide grown by Czochralski's method from the melt in an iridium crucible*" (from English version published by Plenum Publishing Corporation). This work focuses on luminescence properties of Cr-doped β-Ga_2O_3 with no information about growth experiments and obtained crystals.

The next work on growth of β-Ga_2O_3 crystals by the Czochralski method was published in 2000 by Tomm et al. [18]. Here, a Ga_2O_3 decomposition issue was recognized as a limiting factor and a growth atmosphere consisting of 90 vol% Ar and 10 vol% CO_2 as an oxygen source was proposed. At such growth atmosphere small diameter (1 cm) β-Ga_2O_3 crystals with an irregular shape could be obtained.

An intensive development of the growth of β-Ga_2O_3 single crystals by the Czochralski method was started a decade later by Galazka et al. [19–23]. In-depth experimental and theoretical study of Ga_2O_3 thermodynamics, combined with a diversity of comprehensive growth experiments, led to understanding of the underlying physical phenomena involved in the growth of β-Ga_2O_3 crystals by the Czochralski method and consequently to solutions of the associated problems and limitations. This resulted in 2-inch diameter cylindrical single crystals with the weight up to 1 kg.

2.4 Thermodynamics of Ga_2O_3

Ga_2O_3 is thermally unstable at high temperatures and tends to decompose when grown from the melt (melting point, MP, of Ga_2O_3 is 1793 °C [24]), therefore thermodynamics constitutes a solid background for crystal growth from the melt.

The decomposition of Ga_2O_3 proceeds through a number of reactions (some of them defined by 2.1–2.3) that produce different volatile species: O_2, Ga_2O, GaO, and Ga, with Ga_2O having the highest partial pressure among other Ga-containing species. In addition to volatile species that evaporate, the decomposition of Ga_2O_3 also leads to a formation of metallic Ga in the melt (2.4).

$$Ga_2O_3(s) \rightarrow 2GaO(g) + \frac{1}{2}O_2(g) \tag{2.1}$$

$$2GaO(g) \rightarrow Ga_2O(g) + \frac{1}{2}O_2(g) \tag{2.2}$$

$$GaO(g) \rightarrow Ga(g) + \frac{1}{2}O_2(g) \tag{2.3}$$

$$Ga_2O_3(s,l) \rightarrow 2Ga(l,g) + 1\frac{1}{2}O_2(g) \tag{2.4}$$

where s, g, l refer to solid, gas, and liquid phase, respectively.

Figure 2.2 depicts stability fields of Ga_2O_3 as a function of oxygen partial pressure $p(O_2)$ and temperature. Around MP, the formation of the Ga_2O_3 phase (liquid and solid) would require $p(O_2) > 10^{-4.5}$ atm. At lower $p(O_2)$ values only gas phase will be stable, while at yet lower $p(O_2)$ values Ga_2O_3 will be reduced to metallic Ga. In practice, for obtaining bulk crystals from the melt of high structural quality, $p(O_2)$ should be much higher than the minimum value required for the formation of the Ga_2O_3 phase.

However, the Czochralski method imposes farther restrictions for $p(O_2)$ when growing β-Ga_2O_3 single crystals that arise from contradicting requirements for Ga_2O_3 stability (high $p(O_2)$) and Ir crucibles being used at high temperatures (low $p(O_2)$) that tends to oxidize. In practice, values of $p(O_2)$ should bring the partial

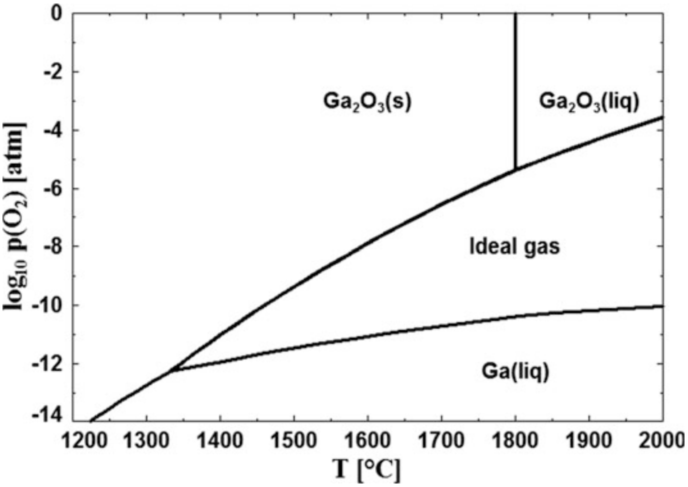


Fig. 2.2 Stability fields of the Ga–O system (s and l stand for solid and liquid, respectively)

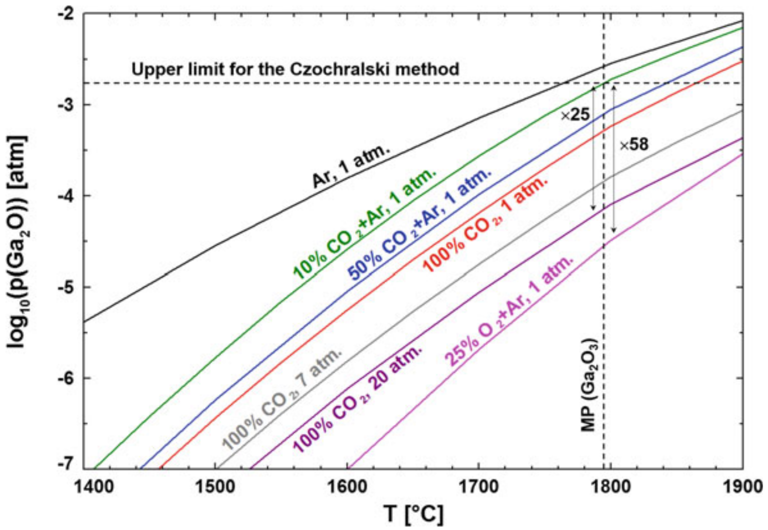


Fig. 2.3 Partial pressure of Ga_2O versus temperature at different oxygen sources and pressures

pressure of Ga_2O, $p(Ga_2O)$ to the level below 2×10^{-3} atm., which seems to be a limit for the Czochralski growth of $\beta\text{-}Ga_2O_3$, as indicated by the horizontal dashed line in Fig. 2.3. It corresponds to a minimum $p(O_2)$ of about 2×10^{-3} atm. Such conditions cannot be met by a neutral atmosphere, such as Ar (Fig. 2.3) or N_2. The minimum level of $p(O_2)$ that brings the $p(Ga_2O)$ just below the upper limit can be achieved by a mixture of Ar +10% CO_2. $p(Ga_2O)$ can further be decreased by increasing the CO_2 concentration in the $(1–x)$Ar (or N_2) + xCO_2 and applying an external overpressure (e.g. 7 or 20 atm. in Fig. 2.3). However, CO_2-based growth atmospheres enable only small diameter (about 1 cm) crystals. To increase the crystal size and structural perfection, higher oxygen concentrations in the growth atmosphere must be used, typically above 10 vol%. Such high oxygen concentrations can be achieved by a direct use of O_2 in a mixture of $(1–y)$Ar (or N_2) + yO_2 (e.g. 75 vol% Ar + 25 vol% O_2 shown in Fig. 2.3).

In particular, CO_2-containing atmospheres provide good results, as CO_2 is an effective oxygen source the concentration of which increases with temperature through the decomposition of CO_2:

$$CO_2(g) \xrightarrow{T} CO(g) + \frac{1}{2}O_2(g) \tag{2.5}$$

and keep Ir crucible intact from oxidation, which proceeds at low and moderate temperatures. Already Ar + 10% CO_2 enabled to obtain small diameter crystals, however, much better results were obtained with CO_2 content up to pure CO_2, which at atmospheric pressure provides $p(O_2) = 7 \times 10^{-3}$ atm. at MP. When using, e.g., directly Ar + 2% O_2 Ir crucibles oxidized to some extent, what was not the

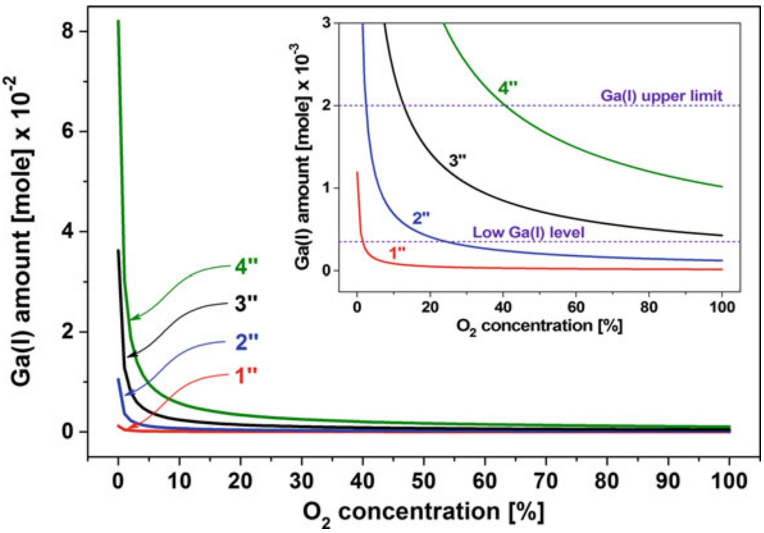


Fig. 2.4 Amount of liquid Ga in the Ga_2O_3 melt versus O_2 concentration during growth of 1, 2, 3, and 4 inch diameter crystals by the Czochralski method. For the calculations, the crucible aspect ratio was set to 1 and the crystal diameter to 0.5 of the crucible diameter. The inset shows a portion of the graph with low concentration range of metallic Ga(l) in the melt Reprinted (with some modifications) from Galazka et al. [22] according to ECS's policy

case for pure CO_2. Yet better results were obtained when using CO_2 under overpressure of 7 atm. that provided $p(O_2) = 2.5 \times 10^{-2}$ atm. at MP with substantially no crucible oxidation. CO_2 under 20 atm. provides $p(O_2) = 2.5 \times 10^{-2}$ atm. at MP and brings $p(Ga_2O)$ down about 25 times as compared with the $p(Ga_2O)$ at the upper limit. In the case of 25 vol% O_2 at atmospheric pressure, $p(Ga_2O)$ will be decreased 58 times.

CO_2-containing atmospheres, preferably under overpressure, were found effective for a decrease of $p(Ga_2O)$ that works well for crystal diameters $\leq$ 1 inch. However, larger diameter (> 1 inch) crystals could hardly be obtained at low oxygen concentrations or low $p(O_2)$. To grow larger crystals larger melt volumes are required that generate higher concentration of metallic Ga(l) (2.4), which is partly in the gas phase and evaporates, but partly remains in the melt in the liquid phase. Metallic Ga floating in the melt and on the melt surface prevents a proper seeding and degradates the crystal quality, if obtained at all. Furthermore, metallic Ga easily forms eutectic with Ir and may damage the crucible even after one growth run. To minimize the formation of metallic Ga much higher oxygen concentrations in the growth atmosphere are required. This is summarized in Fig. 2.4 that shows the amount of metallic Ga(l) in the melt depending on the oxygen concentration in the growth atmosphere during growth of 1, 2, 3, and 4 inch diameter crystals, that require 2.3, 18, 63, and 150 mol of the melt (with the crucible aspect ratio of 1).

Now it is clear that at small-scale growth (crystal diameter $\leq$ 1 inch) the amount of metallic Ga(l) is negligible small even at low oxygen concentrations (< 2 vol%) and will have only a minor impact on the crystal growth stability and crystal quality. Indeed, only small Ga-Ir eutectic signs were occasionally observed which allowed for a long-term usage of the same Ir crucible. However, the growth of 2-inch diameter crystals and larger produce so high metallic Ga(l) concentrations at low oxygen concentrations that make the growth almost impossible. To keep metallic Ga(l) concentration at low and save level (shown in the inset of Fig. 2.4 as a “Low Ga(l) level”), as in the case of 1-inch diameter crystals grown at 1–2 vol% O_2, would require about 20 and 100 vol% O_2 for 2- and 3-inch diameter crystals, respectively. In the case of 4-inch diameter crystals such low level of metallic Ga(l) concentration will never be reached, however, such large crystals still can be obtained, if Ga concentration does not pass the upper limit (inset of Fig. 2.4). Lower melt volumes for the large crystal diameters can be obtained by the use of crucibles with the aspect ratio (height to diameter) below unity.

The requirement for very high oxygen concentration to grow large diameter crystals contradicts the abovementioned use of Ir crucibles. Nonetheless, the long-lasting problem of Ir oxidation has successfully been solved and applied by Galazka et al. [21, 22]. For a better understanding of the problem solution, first we need to take a look at Ir oxidation. Ir oxidizes in such a way that at low and moderate temperatures (up to about 1200 °C) IrO_2 is formed, that is in the solid phase and remains on the crucible. This is a very efficient process and IrO_2 may contaminate the starting material (and the melt) in the crucible as well as a growing crystal. However, at higher temperatures IrO_2 is not formed any longer, but instead, IrO_3 forms, which is in the gas phase and evaporates. By a proper furnace design, the gaseous IrO_3 can be evacuated far from the melt and the growing crystal, minimizing in this way the possible contamination of the crystals with Ir. The activities of IrO_2(s) and IrO_3(g) at three different oxygen concentrations in the growth atmosphere (1.5, 25, and 100 vol%) are presented in Fig. 2.5. It can be easily concluded, that using even pure oxygen, the $p(IrO_3)$ at MP is at the level of 2×10^{-3} bar, comparable to the $p(Ga_2O)$ when growing small diameter crystals at low $p(O_2)$, so enabling the use of the Czochralski method. A suitable Ir crucible protection can significantly decrease Ir losses by evaporation.

On the other hand, Ga_2O_3 is substantially stable up to about 1200 °C even at a neutral atmosphere, as concluded from the thermal analysis and annealing experiments. Therefore, combining thermodynamics of Ir–O and Ga_2O_3 systems, we can construct a scheme of an oxygen supply to the growth furnace, which is shown in Fig. 2.6. During heating-up of a growth furnace, at low and moderate temperatures (up to about 1200 °C) solid IrO_2 is efficiently formed, while Ga_2O_3 is stable; therefore, in this temperature range (between room and transition temperatures, RT and TP) only a small O_2 concentration (< 2 vol%) can be used or even no oxygen at all. However, above the TP Ga_2O_3 quickly becomes unstable and higher O_2 concentration is needed. At the same time, IrO_2 is not formed any longer, while the $p(IrO_3)$ increases. Thus, at high temperatures (> TP) we continuously increase the O_2 concentration with increasing temperature up to a pre-defined value at MP

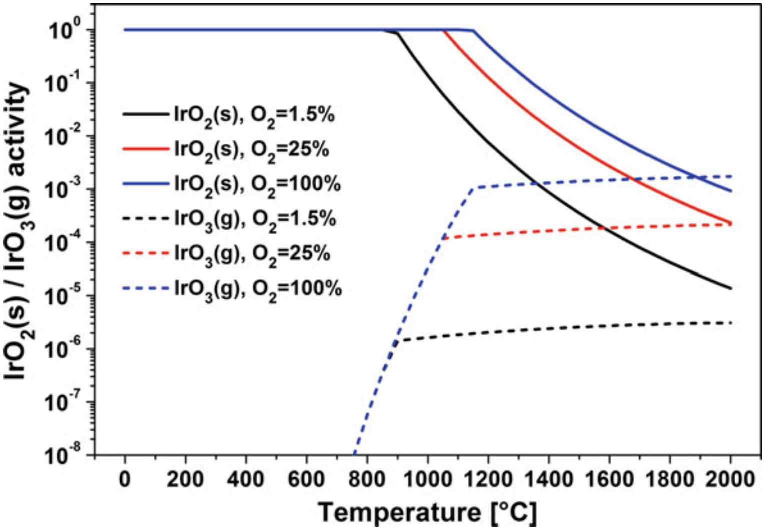


Fig. 2.5 Activities of IrO_2 (solid lines) and IrO_3 (dashed lines) versus temperature at three different oxygen concentrations in the growth atmosphere: 1.5, 25, and 100 vol%. In the case of the gas phase (IrO_3), the activity is equivalent to partial pressure in atm

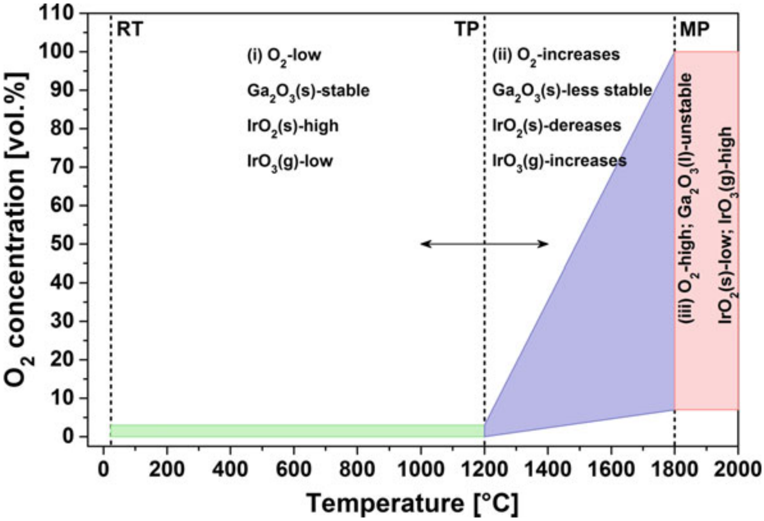


Fig. 2.6 Scheme of oxygen supply to a growth atmosphere allowing for using high oxygen concentration in the growth atmosphere and growing large diameter crystals from the melt. RT, TP, and MP are room temperature, transition point, and melting point, respectively. Reprinted from: Galazka et al. [22], according to ECS's policy

depending on the crystal size to be grown (or melt volume) and evacuate gaseous IrO_3. During crystal growth, we keep the final, high value of the O_2 concentration, which can be further increased or decreased to modify (to some extent) the electrical properties (at very high oxygen concentrations the crystals will be electrically insulating). During cooling down we can apply a reverse scheme of the oxygen supply as compared with the scheme used during heating-up of the growth furnace.

This technique is of a general purpose and can be used for any melt growth method involving a noble metal crucible. It can also be used for other materials that are thermally unstable at high temperatures, what was demonstrated for other transparent semiconducting oxides.

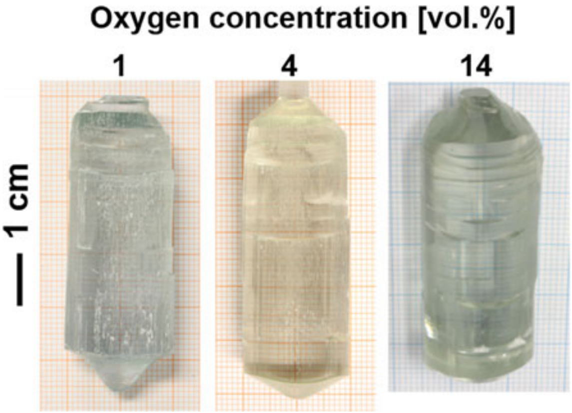
2.5 Crystal Growth

β-Ga_2O_3 single crystals are grown by the Czochralski method with a use of growth stations with an automatic diameter control utilizing the PID controller. The crucibles are made of high purity iridium (3N) of either 40 or 100 mm in diameter for growing 20 mm and 2-inch diameter crystals, respectively, defining the crystal to crucible ratio of about 0.5. Large crucibles had the aspect ratio <1. Above the crucible an active after heater is located that ensures low-temperature gradients in the space accommodating a growing crystal. The growth rate is typically between 1 and 2 mm/h, while the crystal rotation of 8–15 and 4–8 rpm for 20 mm and 2-inch diameter crystals, respectively. The length of the crystals is up to 70 and 100 mm for both crystal diameters, with the crystallization ratio not exceeding 50%. In each case to growth, direction is along <010> that is parallel to both cleavage planes {100} and {001}.

20 mm diameter β-Ga_2O_3 crystals obtained at low O_2 concentrations, with the use of the growth atmosphere $(1–x)$Ar + $x$$CO_2$ vol% with $x = 0.1–1$, or Ar + 2 vol % O_2 under atmospheric pressure, are transparent with a bit rough surface as the result of sublimation on the crystal surface of needle-shaped crystals from the gas phase, (decomposition and oxidation of Ga_2O at lower temperatures: $Ga_2O + O_2 \rightarrow \beta\text{-}Ga_2O_3$), by decomposition of the crystal surface itself, as well as by micro-cleaving of the crystal surface due to thermal stress. The degree of the surface roughness is also a function of the temperature gradients and growth time. The crystal surface becomes more smooth and shiny with higher O_2 concentrations obtained from the atmosphere $(1–y)$Ar + $y$$O_2$ vol% with $y = 0.02–0.35$. Relatively high O_2 concentrations (about 2.5–5 vol%) can also be obtained from the CO_2 atmosphere under a total overpressure of 7–20 bar. Examples of 20 mm diameter β-Ga_2O_3 crystals obtained by the Czochralski method at different oxygen concentrations in the growth atmosphere are shown in Fig. 2.7.

The colouration of undoped crystals varies from substantially colourless (low free electron concentration < 10^{17} cm^{-3}), light blue to dark blue (high free electron concentration 10^{17}–10^{18} cm^{-3}), and yellowish (electrical insulators). The crystal colouration may also change depending on intentional doping, e.g. Sn and Si doping

Fig. 2.7 20 mm diameter β-Ga_2O_3 crystals obtained by the Czochralski method at low (~ 1 vol%); high (4 vol%); and very high (14 vol%) oxygen concentration in the growth atmosphere. Different crystal colourations arise from different free electron concentrations



make the crystals dark blue (very high free electron concentration of $>10^{18}$ cm^{-3}), Mg and Ce—yellowish, Al—colourless (when grown at low O_2 concentrations), Cr—green, C (from CO_2 growth atmosphere under overpressure)—grey, but it also may change depending on O_2 concentration in the growth atmosphere.

Low O_2 concentrations (≤ 2 vol%) that produced high-quality 20 mm diameter crystals were not sufficient to obtain 2-inch diameter crystals of high structural quality, due to the formation of an excessive amount of metallic Ga in the melt. Such crystals were either polycrystalline or single crystalline with twins. In such cases, high O_2 concentrations were used during growth, typically in the range of 8–35 vol% with the use of the oxygen supply scheme shown in Fig. 2.6. The total Ir loses of unprotected crucibles is about 5–8 wt% at O_2 concentrations of 20–35% and 50–80 h growth time. Heating-up and cooling-down times for 2-inch diameter crystals were 10–15 and 20–30 h, respectively.

The 2-inch diameter crystals obtained at high O_2 concentrations and low-temperature gradients are transparent with a smooth and shiny surface due to a significant reduction of the Ga_2O_3 decomposition and evaporation. Despite of using high O_2 concentration and Ir parts, there are substantially no Ir particles on the crystal surface. This is the result of the specific scheme of the oxygen supply to the growth furnace, and a furnace design enabling an efficient evacuation of gaseous IrO_3 far from the melt and the growing crystal. Examples of Czochralski-grown 2-inch diameter β-Ga_2O_3 crystals (insulating and semiconducting) are shown in Fig. 2.8a.

The Czochralski-grown bulk crystals enable fabrication of differently oriented wafers for homoepitaxial growth of β-Ga_2O_3 layers. They could be either semiconducting or electrically insulating. The easiest orientations for wafer fabrication are (100) and (001) being parallel to both easy cleavage planes {100} and {001}, respectively, as exemplary shown in Fig. 2.8b, including a misorientation. The most difficult orientation for wafer fabrication is (010) which is perpendicular to both easy cleavage planes, especially when a large wafer diameter (2 inch) and small thickness (0.5 mm) are in quest.

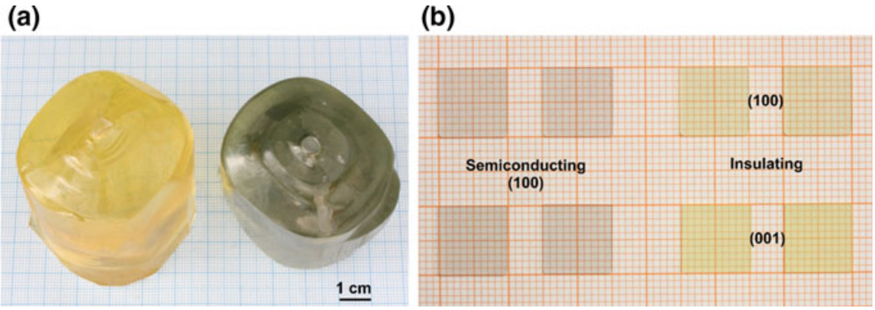


Fig. 2.8 **a** 2-inch diameter β-Ga_2O_3 crystals obtained by the Czochralski method at high oxygen concentration (8–35 vol%). The crystals are electrically insulating by doping with Mg (left) and semiconducting (right); **b** semiconducting and electrically insulating 10 × 10 mm^2 wafers prepared from 2-inch diameter crystals

2.5.1 *Impact of the Free Carrier Absorption on the Growth Stability*

A growing crystal is a medium for heat transfer to remove the latent heat of crystallization from the growth interface. Due to high melting point of Ga_2O_3 radiative heat transport dominates over conduction. The radiative heat transport proceeds in the near infrared (NIR) region with the maximum intensity at about

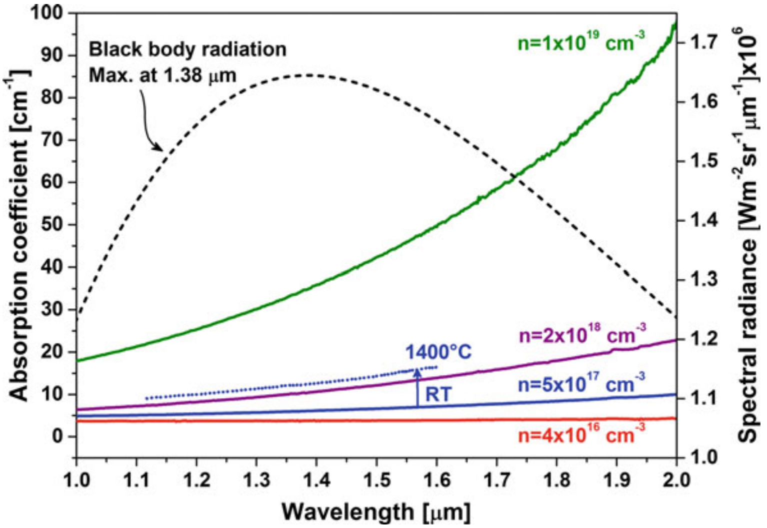


Fig. 2.9 Influence of the free electron concentration on the absorption coefficient of β-Ga_2O_3 single crystals versus wavelength at RT. The dotted line represents the absorption coefficient measured at 1400 °C for the same sample having free electron concentration at the level of 5×10^{17} cm^{-3} at RT. The dashed line represents the radiation spectrum of a black body at the melting point of Ga_2O_3. Reprinted from: Galazka et al. [20], Copyright (2014) with permission from Elsevier

1.38 µm. This is the spectral region, where the free carriers present in Ga_2O_3 (as it is a semiconductor) absorb the radiation, wherein the absorption increases with the free carrier concentration [20]. Figure 2.9 presents the black body radiation at MP of Ga_2O_3 and absorption coefficients of Czochralski-grown β-Ga_2O_3 crystals having different free electron concentration ranging from 4×10^{16} to 10^{19} cm^{-3}. These absorption coefficients were measured at RT, and the absorption increases with temperature, for example, at 1400 °C (dot line in Fig. 2.9), which is still far below the MP, the absorption coefficient increases with respect to that at RT by factor of about 2.

Problems with heat removal from the growth interface and its accumulation in the crystal due to free carrier absorption causes flattening and consequently convex-to-concave interface inversion once a crystal achieves a certain length, which decreases with the free carrier concentration. The concave interface is highly unstable and the most heat tries to dissipate through a triple point (solid crystal-melt-gas atmosphere) at the crystal periphery (meniscus). Such situation promotes a lateral growth over the melt surface (foot formation) that continuous to a certain point as it approaches the crucible wall (the hottest part of the growth furnace) and then changes the direction towards the central part of the crucible. Because the growing crystal is pulled up and rotates, this phenomenon will lead to a corkscrew (or spiral) formation. Such spiral structure enables a better heat dissipation as the crystal has a larger surface area exposed vertically to lower temperatures. The structural quality of the spiral part is at least as good as the cylindrical part of the crystal or even better; however, it provides less usable volume.

When considering 2 cm diameter crystals, the spiral substantially does not occur in electrically insulating crystals or at low free electron concentration, below 10^{17} cm^{-3}, as the interface is convex towards the melt (Fig. 2.10). The cylinder length may reach even 7 cm, corresponding to the crystallization fraction of about 50%. At higher free carrier concentration ($1–5 \times 10^{17}$ cm^{-3}) still a long cylinder can be grown, but the interface is only slightly convex towards the melt. At high free electron concentration (at the level of 10^{18} cm^{-3}), the cylinder length is of about 4–5 cm, while at very high free electron concentration of about 2–3 cm maximum. To obtain larger volume of highly conductive Ga_2O_3 the Vertical Gradient Freeze (VGF)/Bridgman methods were successfully utilized by Galazka et al. [21, 22].

In the case of 2-inch diameter crystals, the situation is more critical due to a larger optical thickness of the growing crystal. The cylinder length of 2-inch diameter crystals with the free carrier concentration of mid-10^{17} cm^{-3} approaches 2 inch, while in the case of electrically insulating crystals the cylinder length approaches 4 inch. However, it also depends on the temperature gradients. Larger temperature gradients enable longer cylinders; however, the crystal quality deteriorates due to twin formation. Electrically insulating crystals can be obtained in a different way: (i) by doping with Mg acting as a compensating acceptor, (ii) by doping with Al expanding the band gap, (iii) by using a very high oxygen concentration in the growth atmosphere that creates compensating gallium vacancies, and (iv) by a combination of any of (i)–(iii).

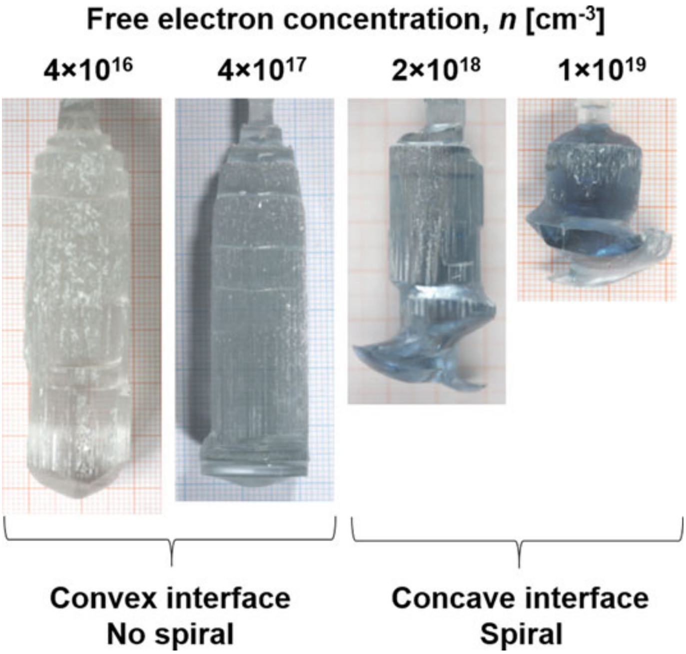


Fig. 2.10 β-Ga_2O_3 single crystals (2 cm diameter) showing an impact of the free carrier absorption on the growth stability: semiconducting with $n = 10^{16}$ cm^{-3} (undoped); semiconducting with $n = 10^{18}$ cm^{-3} (undoped); and semiconducting with $n = 10^{19}$ cm^{-3} (doped with Si)

2.6 Structural Quality

Structural quality of the obtained β-Ga_2O_3 crystals depends on many factors, in particular on (i) O_2 concentration in the growth atmosphere; (ii) temperature gradients in the growth furnace, (iii) seed quality, (iv) operating parameters; and (v) purity of the materials (starting material, crucible, insulation). Too low O_2 concentration in the growth atmosphere in relation to the melt volume may produce a polycrystal or a single crystal with a high density of twins. High-temperature gradients enable to obtain a single crystal with an extended length (better heat removal from the interface), but this is accompanied by a higher density of twins and also low angle grain boundaries, so the usable volume might be limited. High-temperature gradients during growth and cooling down may lead to an excessive thermal stress in the crystal that may result in crack formation, in particular along the {100} cleavage plane. If there are any twins in the seed, they can easily extend into the growing crystal, while propagating dislocations can be limited by a seed necking. High growth and crystal rotation rates may induce the spiral formation at early stage of growth (higher amount of the latent heat to be dissipated and enlarged forced convection promoting the interface inversion). Also, high

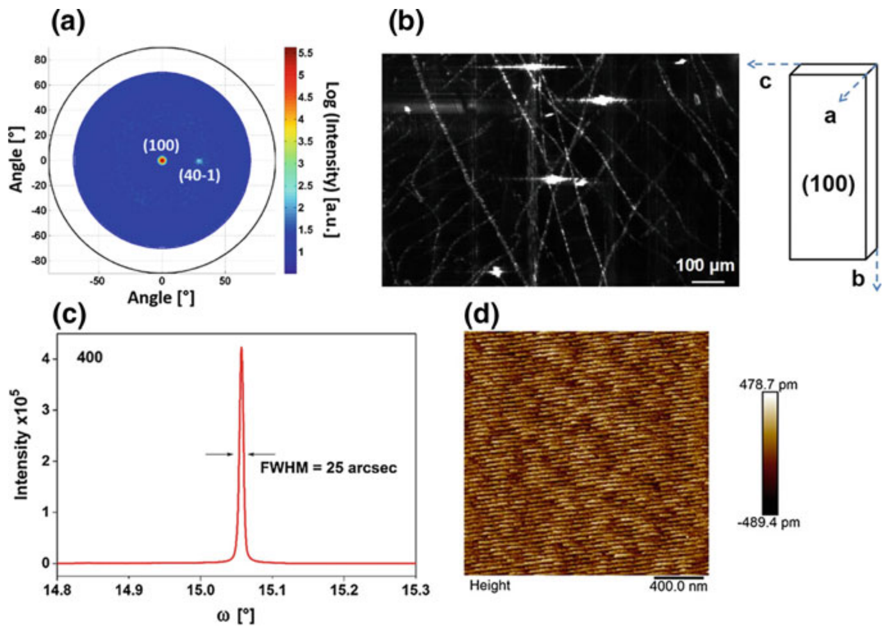


Fig. 2.11 Structural quality of Czochralski-grown β-Ga_2O_3 single crystals: **a** X-ray stereographic projection of an (100) oriented wafer, reprinted from: Baldini et al. [25], Copyright (2018) with permission from Elsevier; **b** dislocations revealed in the crystal volume by the laser scattering tomography, reprinted from: Galazka et al. [20], Copyright (2014) with permission from Elsevier; **c** FWHM of the rocking curve of an (100)-oriented wafer; and **d** roughness of an (100) wafer revealed by the atomic force microscopy, figure courtesy of Raimund Grüneberg and Günter Wagner, IKZ, Berlin, Germany

growth rates may induce higher dislocation density and other structural defects. Impurities may introduce point defects and induce growth instabilities and/or growth kinetics, and consequently decrease the crystal quality. Additionally, impurities at very low segregation coefficient may lead to a constitutional supercooling when high concentrations and/or high growth rates are used. Moreover, some of the impurities may affect heat transfer through the growing crystal (e.g. through enhancement of the free electron concentration or when they have absorption bands themselves in the NIR region) leading to growth instabilities. However, some of the impurities may have a positive, thermodynamically stabilizing effect (decrease decomposition rate of Ga_2O_3) that improves the crystal quality by lower density of point defect and more stable growth process.

Typically, β-Ga_2O_3 single crystals of 2 cm and 2 inch diameter obtained by the Czochralski method at optimized growth conditions and operating parameters are crack-free (Figs. 2.7 and 2.8) and twin-free, that is well visible in the X-ray texture shown in Fig. 2.11a. The dislocation density, as revealed by the laser scattering tomography, is below $5 \times 10^3\ \mathrm{cm}^{-2}$ (Fig. 2.11b) [20]. A projection of the dislocations in the crystal volume revealed their propagation substantially parallel to the cleavage plane {100}. The full width at half maximum (FWHM) of the rocking curve is typically below 50, often below 30 arcsec [20, 22, 25], as shown in Fig. 2.11c. Chemo-mechanical polishing (CMP) of (100)- and (001)-oriented wafers prepared from the Czochralski-grown crystals produced a very smooth surface with the RMS roughness well below 0.5 nm, such as 0.15 nm shown in Fig. 2.11d. High structural quality of the β-Ga_2O_3 single crystals and fabricated wafers enable epitaxial growth of high-quality layer, as well as a preparation of a diversity of electronic and optoelectronic devices.

2.6.1 *Intentional Doping and Residual Impurities*

β-Ga_2O_3 single crystals grown by the Czochralski method can be easily doped with a number of elements to tune electrical and optical properties as well as to minimize the thermal decomposition and stabilize the growth process. The following elements were used for intentional doping of β-Ga_2O_3 crystals grown by the Czochralski method [20, 22, 23, 26]: Cu^{1+}, Mg^{2+}, Cr^{3+}, Al^{3+}, Ce^{3+}, Sn^{4+}, and Si^{4+}, which are added to a Ga_2O_3 starting material in the form of a corresponding dopant oxide powder. Examples of β-Ga_2O_3 single crystals doped with Mg, Ce, Al, Cr, and Si are shown in Fig. 2.12. Also other dopants, such as Li^{1+}, Ni^{2+}, Co^{2+}, and Ge^{4+},

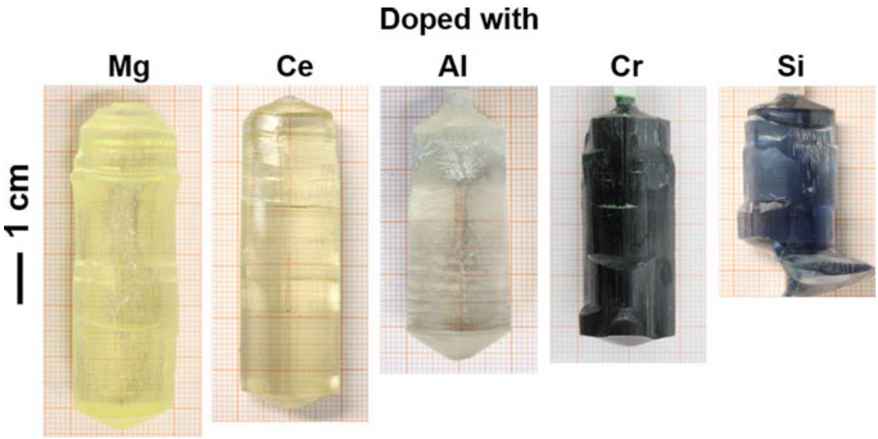


Fig. 2.12 Czochralski-grown β-Ga_2O_3 crystals doped with Mg, Ce, Al, Cr, and Si

as well as double and triple doping were studied in Czochralski growth experiments of Ga_2O_3 single crystals by Galazka et al. [27, 28].

Divalent ions aimed to compensate the electrical conductivity and, indeed, Mg fulfil this expectancy very well, while Cu has too high vapour pressure at MP of Ga_2O_3, therefore it is impractical. Tetravalent ions Sn and Si are shallow donors in β-Ga_2O_3 and increase its electrical conductivity. Cr showed electroluminescence and could potentially constitute an active element in the β-Ga_2O_3 host for solid-state lasers. Al expands the bandgap down to the UVC band, while Ce enhances scintillation properties under gamma radiation.

The incorporation of a dopant into the β-Ga_2O_3 crystal lattice strongly depends on the ionic radii of the dopant, valency, its thermal stability, coordination number, solubility in β-Ga_2O_3, $p(O_2)$ in the growth atmosphere, and on operating parameters (growth and rotation rates). The dopant concentration that is incorporated into a growing crystal depends on initial dopant concentration in the melt, solidified melt fraction, and the effective segregation coefficient of the dopant, and it is generally expressed by the Scheil-Gulliver relation:

$$C_S = C_0 k_{\mathrm{eff}} (1 - g)^{k_{\mathrm{eff}} - 1} \tag{2.6}$$

where C_S is the dopant concentration in the crystal, C_0 is the initial dopant concentration in the melt, k_{eff} is the effective segregation coefficient, and g is the crystallization fraction of the melt.

By measuring the dopant concentration at different locations of an obtained crystal and fitting the measured values with the Scheil-Gulliver relation, it is possible to determine the effective segregation coefficient for given growth conditions and operating parameters. The effective segregation coefficients of elements used for doping Czochralski-grown β-Ga_2O_3 crystals, along with their ionic radii in tetrahedral (IV) and octahedral (VI) sites in the β-Ga_2O_3 crystal lattice, are collected in Table 2.2. Depending on a dopant type there is some deviation from the segregation equation due to a high vapour pressures of Ga_2O, SnO and Cr-, and Cu-containing species (evaporation), which are $p(O_2)$ dependent, as well as due to oxidation states of Cr and Ce, or incorporation in structural defects (e.g. Ce).

Table 2.2 Ionic radii of dopants at tetrahedral (IV) and octahedral (VI) sites (Ga^{3+} sites in the crystal lattice), and segregation coefficients (k_{eff}) at corresponding oxygen concentrations in the growth atmosphere

		Ga^{3+}	Mg^{2+}	Cr^{3+}	Al^{3+}	Ce^{3+}	Si^{4+}	Sn^{4+}
Ionic radii (Å)	IV	0.47	0.57	–	0.53	–	0.26	0.69
	VI	0.62	0.72	0.62	0.68	0.87	0.40	0.83
O_2 (vol%)		–	1–35	4–24	1.5–21	1.5–35	1–2	2–17
k_{eff}		–	0.4	3.1–1.5	1.1	< 0.1	≈0.1	< 0.1[a]

[a] Affected by a strong dopant evaporation

Among dopants shown in Table 2.2 Cr incorporates into the growing crystal most easy and its concentration in the crystal decreases from its top to the bottom part ($k_{\mathrm{eff}} > 1$), while Al incorporates substantially uniformly ($k_{\mathrm{eff}} \cong 1$). Modifiers of the electrical conductivity (Mg, Sn, and Si) are built-in into the crystal structure with the fraction below about 40% ($k_{\mathrm{eff}} < 1$); therefore, their concentrations increase from the top to the bottom part thereof. This is not a problem for Mg, which compensates the electrical conductivity even at small amount (>6 wt. ppm); however, Sn and Si create a dopant gradient and consequently inhomogeneous free carrier concentration along the crystal if their concentrations are small. An increasing dopant concentration with the crystal length ($k_{\mathrm{eff}} < 1$) may lead to a constitutional supercooling that deteriorates the crystal quality. However, this happens at high dopant concentration in the melt (usually > 1 mol%) and large crystallization fraction (>0.7), what is not the case during growth of β-Ga_2O_3 crystals by the Czochralski method. To compensate the electrical conductivity 0.1–0.2 mol% of MgO in the melt was found to be sufficient. The same relates to SiO_2, which already in the amount of 0.1–0.2 mol% in the melt induce the free electron concentration at the level of 10^{19} cm^{-3}, that is about the maximum value that can be obtained in bulk crystals grown from the melt. Higher doping levels of SiO_2 up to 2 mol% do not increase the free electron concentration, but instead, they deteriorate the crystal quality by forming twins and grains. However, initial doping level of SnO_2 in the starting material must be higher, 1–2 mol% due to high fugacity and consequently losses of SnO at MP of Ga_2O_3.

The obtained crystals always contain some residual impurities coming mainly from a Ga_2O_3 starting material, an Ir crucible, and a thermal insulation. Their concentrations vary between crystals depending on material supplier, insulation type, and a re-use number. The main impurities are Al and Zr typically below 10 wt. ppm. Also other impurities, such as Mg, Ni, Co, Fe, Ti, Si, and Mo at concentration below 3–5 wt. ppm, are occasionally found in different bulk crystals.

2.7 Effect of Annealing

The Czochralski-grown β-Ga_2O_3 crystals can be obtained either as electrical insulators or as *n*-type semiconductors, both normal and degenerate. The electrical properties can be controlled by growth conditions, in particular by O_2 concentration in the growth atmosphere, and/or by intentional doping (e.g. Mg, Sn, Si). In this way, the free electron concentration can be controlled within three orders of magnitude (10^{16}–10^{19} cm^{-3}) with the Hall electron mobility up to 152 $\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$ [20]. Electrically insulating state is obtained at high O_2 concentration conditions and/or by doping with Mg. All crystals show a very steep absorption edge at about 260 nm and a good transparency in the visible/NIR spectral regions at low free electron concentrations.

Further modification of the electrical properties could be achieved by post-growth heat treatments at different atmospheres, temperatures, and times.

Annealing of the undoped crystals in the O_2-containing atmospheres at or above about 1000 °C for at least several hours results in lowering the free electron concentration to the level of about 1–2 $\times$ 10^{17} cm^{-3}, with a slight improvement of the Hall mobility. After such annealing, a thin, electrically insulating surface layer is formed [20]. Annealing in a hydrogen-containing atmosphere up to 900 °C for 10 h does not affect the free electron concentration (if at the level of about 10^{18} cm^{-3}) but significantly lowers the Hall mobility. However, annealing in the presence of hydrogen crystal samples previously annealed in the presence of O_2 ($\geq$ 1000 °C) increases the free electron concentration and improves the Hall mobility [26]. Annealing in the oxygen- and hydrogen-containing atmospheres is reversible. On the other hand, annealing Sn-doped crystals in the O_2-containing atmosphere at or above about 1000 °C for at least several hours fully or almost fully (depending on sample thickness) converts highly conducting crystals into electrical insulators [26], in contrast to undoped crystals. Modification of the electrical properties by annealing is also reflected in optical properties of the crystals, such as transmittance (e.g. through free carrier absorption) and cathodoluminescence.

In terms of thermal stability of the Czochralski-grown β-Ga_2O_3 single crystals, understood as a noticeable decomposition (i.e. detectable mass loss), they are stable up to about 1200–1300 and 600 °C in atmospheres containing O_2 and H_2, respectively, and 10 h annealing time [26]. However, a surface deterioration may start already at lower temperatures.

2.8 Summary

The Czochralski method was found to be a very efficient growth technique to obtain bulk β-Ga_2O_3 single crystals from the melt. Thermal instability of Ga_2O_3 required understanding its thermodynamics both in the gas and liquid phase. Although stabilization of the Ga_2O_3 decomposition from the point of view of evaporation can be achieved at relatively low O_2 concentration in the growth atmosphere (<2 vol%), the formation of metallic Ga in the liquid phase requires much higher O_2 concentrations with an increase of melt volumes (to obtain larger crystals). This contradicts the requirement for Ir crucibles that tend to oxidize. A combination of Ga_2O_3 and Ir thermodynamics led to a design of a new O_2 supply scheme to a growth furnace that allows to use a high O_2 concentration along with Ir crucibles, including pure O_2. Such technique enabled to obtain 2-inch diameter β-Ga_2O_3 single crystals with the weight up to 1 kg. Additionally to problems arising from Ga_2O_3 thermodynamics, the growth of bulk β-Ga_2O_3 single crystals by the Czochralski method is also affected by the free carrier absorption that results in shorter crystals with high free electron concentrations. The Czochralski method enables intentional doping to tune electrical, optical, and scintillation properties of bulk β-Ga_2O_3 crystals. Sn and Si are used to increase the electrical conductivity, Mg to compensate the electrical conductivity, Cr to introduce absorption bands in the visible spectrum, Al to expand the bandgap, and Ce to enhance the scintillation properties. Al and Ce were also found to have a thermodynamically stabilizing effect on Ga_2O_3 decomposition. In addition to intentional doping, the material's properties can also be tuned by $p(O_2)$ in the growth atmosphere and post-growth heat treatment. The obtained crystals can be either semiconductors or electrical insulators both with a very good transparency in the UV and visible spectral regions. High structural quality of the obtained bulk β-Ga_2O_3 single crystals enables to prepare differently oriented wafers for homoepitaxial growth of β-Ga_2O_3 layers and device fabrication.

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