(12) EUROPEAN PATENT SPECIFICATION

(54) **METHOD FOR GROWING BETA PHASE OF GALLIUM OXIDE (BETA-GA2O3) SINGLE CRYSTALS FROM THE MELT CONTAINED WITHIN A METAL CRUCIBLE BY CONTROLLING THE O2 PARTIAL PRESSURE.**

VERFAHREN ZUR HERSTELLUNG DES SS-GA2O3 EINKRISTALLE, DEM IN EINEM METALLTIEGEL ENTHALTENEN IST, DURCH ERSTARRUNGS DES SCHMELZS UND DEM SAUERSTOFFSDRUCK.

MÉTHODE POUR LA CROISSANCE DE MONOCRISTAUX DE BETA-GA2O3 À PARTIR DE SOLIDICATION DE GA2O3 EN FUSION CONTENUE DANS UN CREUSET METALLIQUE, EN CONTROLLANT LA PRESSION PARTIELLE D'OXYGÈNE.

(72) Inventors:
• **GALAZKA, Zbigniew**
12489 Berlin (DE)
• **UECKER, Reinhard**
15345 Eggersdorf (DE)
• **KLIMM, Detlef**
15732 Eichwalde (DE)
• **BICKERMANN, Matthias**
12355 Berlin (DE)

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• **Morteza Asadian: "The Influence of Atmosphere on Oxides Crystal Growth" In: "Modern Aspects of Bulk Crystal and Thin Film Preparation", 13 January 2012 (2012-01-13), InTech, XP055166135, ISBN: 978-9-53-307610-2 DOI: 10.5772/29648, whole document; figures 2-6; compound 3**
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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates in general to a method for growing oxide single crystals from the melt contained within a metal crucible and in particular for growing beta phase of gallium oxide (βGa_2O_3) single crystals from the melt contained within the metal crucible.

BACKGROUND OF THE INVENTION

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[0002] Beta phase of gallium oxide (βGa_2O_3) belongs to the group of transparent semiconducting oxides. It is a semiconductor with a wide optical bandgap of 4.8 eV, what makes it transparent in the visible down to deep ultraviolet spectrum (DUV). Such unique properties offer opportunities for developing a number of applications in the field of electronics (e.g. field effect transistors) and optoelectronics (e.g. light emitting diodes), and environmental monitoring

15 (e.g. gas sensors). For most of such applications bulk single crystals are required, from which electronic or optoelectronic components or substrates for thin film depositions could be prepared.
[0003] For industrial applications large single crystals of high quality are demanded. In the case of oxide single crystals they are typically grown from the melt contained within a metal crucible, e.g. comprising platinum for low and moderate melting points (below 1500°C), iridium for high melting points (roughly between 1500-2200°C) and molybdenum, tungsten

20 or rhenium for very high melting point oxides (above 2200°C). There are several crystal growth techniques operating with the use of the metal crucible, including the Czochralski method, Kyropolous method, Vertical or Horizontal Bridgman method, Vertical Gradient Freeze method, shaped crystal growth methods, such as the Stepanov, Noncapillary Shaping (NCS) and Edge-Defined Film-Fed Growth (EFG) methods and Levitation Assisted Self-Seeding Crystal Growth method (LASSCGM).

25 **[0004]** Gallium oxide is thermodynamically unstable at high temperatures, what in combination with high melting point (about 1820°C) leads to a strong decomposition. To stabilize this compound high oxygen partial pressure (or concentration) is required. However, this creates additional difficulties since iridium or iridium alloy crucible must be used, which has a tendency to a strong oxidation at low and moderate temperatures in particular, although small oxygen concentration can be used (typically maximum 2%). Other metal crucibles cannot withstand even very small oxygen concentrations,

30 while platinum has too low melting point to be used for gallium oxide.
[0005] High oxygen concentration for growing β-Ga_2O_3 single crystals can be applied for those growth methods, which operate on a crucible-free basis. An example of such method applied for β-Ga_2O_3 single crystals is the Optical Floating Zone (OFZ) method, e.g. as described in the publications by Ueda et al., Appl. Phys. Lett. 70 (1997) 3561, Appl. Phys. Lett. 71 (1997) 933, Tomm et al., Sol. Cells 66 (2001) 369, Villora et al., J. Cryst. Growth 270 (2004) 420, Appl. Phys.

35 Lett. 92 (2008) 202120 and US patent document No. US 8,747,553 B2. In this method a very small portion of the Ga_2O_3 feed rod is molten by a light beam focused on a tip of the feed rod. The molten portion of the feed rod is contacted with a seed, on which a crystal is grown during translation of the seed with respect to the light beam. Due to a very small molten area of the feed rod (very small cross section area of the light beam) the resulted crystal diameter is also small, typically not exceeding 5-6 mm. Although larger crystal (about 25 mm in diameter) was demonstrated, this seems to be

40 a limit for the crystal size, whose quality is highly deteriorated due inhomogeneity of temperature gradients across the liquid-solid growth interface as the result of very small cross section are of the light beam with respect to a cross section of the growth interface. So far, the OFZ method has not found any industrial applications for oxide crystals, due to too small crystal volume.
[0006] Another crucible-less method applied to β-Ga_2O_3 crystals is the Verneuil method described by Chase, J. Am.

45 Ceram. Soc. 47 (1964) 470. Here, the powdered starting material of Ga_2O_3 is molten with H_2-O_2 flames and the liquid drops fall down on a seed and solidify to form a crystal. Due to poor structural quality and small crystal size, this method has not found continuation in the research of β-Ga_2O_3 growth.
[0007] β-Ga_2O_3 single crystals were already grown from melt contained in an iridium crucible with the use of the Czochralski method as described in the publications by Tomm et al., J. Cryst. Growth 220 (2000) 510 and Galazka et

50 al., Cryst. Res. Technol. 45 (2010) 1229 and Galazka et al. J. Cryst. Growth 404 (2014) 184. In the Czochralski method the crystal is pulled out directly from an exposed melt surface contained within the iridium crucible. In both cases a dynamic self-adjusting growth atmosphere containing CO_2 was used. CO_2 decomposes with temperature and releases more oxygen as temperature increases. In this way about 1.2 vol. % of oxygen can be provided at melting point of Ga_2O_3 with no harm to the iridium crucible, because at low and moderate temperatures, where iridium oxidizes the most, oxygen

55 concentration is kept at a very low level. Yet more oxygen (up to 4 %) was provided by applying an overpressure of CO_2 at the level of several bar. The oxygen concentration provided by CO_2 is sufficient to grow cylindrical β-Ga_2O_3 single crystals with diameter of about 20-22 mm from the iridium crucible of 40 mm in diameter.
[0008] Another method applied to grow β-Ga_2O_3 single crystals from the melt contained in an iridium crucible is the

EFG method, as described in the publication to Aida et al., Jpn. J. Appl. Phys. 47 (2008) 8506 and patent application documents JP 2013082587 A, JP 2013103863 A, JP 2013124216 A, JP 2013227160 A, JP 2013237591 A, JP 2013241316 A, WO 2013073497 A1 and WO 2014073314A1. In this method an iridium die is provided in the iridium crucible, which has small openings and a slit on the top that communicates with the openings. The melt is transported through the die by capillary forces to the top slit, from which a crystal sheet is pulled out from the die. The melt surface area and the melt volume in the die slit are typically small, therefore small oxygen concentration is likely sufficient for the stable crystal growth, although these documents do not refer to any oxygen concentration when using iridium components. The crystal sheets may have a relatively large longitudinal cross-section, but typically small thickness (such as a few millimeters) what limits the total crystal volume being a crucial aspect for industrial applications.

[0009] To grow larger crystals, such as over 1 kg by weight (e.g. 2 inch in diameter and 4-5 inch long in the case of the Czochralski method), large crucibles must be used. This means much larger exposed melt surface which is in a direct contact with a growth atmosphere providing oxygen, much larger crystal volume in which oxygen from the growth atmosphere must be distributed and much larger contact surface area between the liquid Ga_2O_3 and iridium crucible. Decomposition of Ga_2O_3 produces different species in the gas phase leading to a strong evaporation, but also metallic gallium in the liquid phase (due to oxygen loss). Such liquid metallic gallium is created at the melt surface and in the melt bulk, and changes the melt stoichiometry and temperature, therefore growing a crystal from such affected melt surface is practically impossible. Even if the beginning of the growth is successful, metallic gallium forms a film on the crystal surface, which blocks heat transfer through the growing crystal, what in turn induces growth instabilities decreasing a usable crystal volume. Metallic gallium particles that attach to the crystal surface and built in the crystal lattice significantly deteriorates the crystal quality, which may not be usable for most of the applications. Moreover, metallic gallium transported within the melt via convection flows reacts with solid iridium crucible (and the die in the case of the case of the shaped techniques) and form eutectic leading to a severe crucible damage and consequently high economical losses. Eutectic formation highly increases with increasing the melt volume and crucible size. These negative effects limit the growth of large β-Ga_2O_3 single crystals in terms of a reasonable volume, crystal quality, growth stability and iridium crucible life time, which all define the production yield and costs.

[0010] Zbigniew Galazka et al.: "On the bulk [beta]-Ga2O3 single crystals grown by the Czochralski method", Journal of Crystal Growth, vol. 404, 1 October 2014 (2014-10-01) pages 184-191, discloses the growth of β-Ga_2O_3 single crystals by the Czochralski method with the use of a CO_2 - containing growth atmosphere, which provides at melting point of Ga_2O_3 the oxygen concentration not higher than 4 vol. %.

[0011] Morteza Asadian: "The influence of Atmosphere on Oxides Crystal Growth" in "Modern Aspects of Bulk Crystal and Thin Film Preparation", (2012-01-13), Intech, is a purely theoretical work that incorporates experimental results from the published papers, which are well known to those skilled in the art. The main focus of this document is to minimize the oxidation of iridium at low and moderate temperatures and provide higher oxygen concentration at high temperatures to minimize the evaporation as the result of the decomposition.

SUMMARY OF THE INVENTION

[0012] An object of the present invention is to provide conditions for growing β-Ga_2O_3 single crystals from the melt, which minimize Ga_2O_3 decomposition and eliminate a damage of a metal crucible as the result of metallic gallium formation forming eutectic with iridium.

[0013] Another object of the present invention is to provide conditions for growing β-Ga_2O_3 single crystals from the melt, which ensure a stable crystal growth process.

[0014] Yet another object of the present invention is to provide a method enabling high quality β-Ga_2O_3 single crystals, which would meet requirements for electronic and optoelectronic applications, including substrates for epitaxy.

[0015] Still another object of the present invention is to provide conditions for growing β-Ga_2O_3 single crystals from the melt by different growth techniques utilizing a metal crucible.

[0016] Further object of the present invention is to provide a method for growing β-Ga_2O_3 single crystals from the melt contained within a metal crucible, which would enable for obtaining large crystals of at least 0.5 kg, in particular much over 1 kg.

[0017] According to the first aspect of the invention a method for growing beta phase of gallium oxide (βGa_2O_3) single crystals from the melt contained within a metal crucible is provided, which comprises the steps of:

- providing into a growth chamber a thermal system or growth furnace comprising the metal crucible containing the Ga_2O_3 starting material, a thermal insulation surrounding the metal crucible and a heater disposed around the metal crucible;
- providing or creating a crystal seed within the growth furnace;
- introducing at least into the growth furnace a growth atmosphere containing oxygen;
- heating up the metal crucible by the heater, which in turns heats up the Ga_2O_3 starting material until melting;

- contacting the crystal seed with the molten Ga_2O_3 starting material contained within the metal crucible;
- growing a β-Ga_2O_3 single crystal on the crystal seed by temperature gradients between the crystal seed and the melt;
- cooling down the grown β-Ga_2O_3 single crystal to room temperature once the crystal growth step has been completed;

wherein the method further comprises the step of

i) providing into the growth furnace the growth atmosphere with a variable oxygen concentration or partial pressure in such a way that the oxygen concentration reaches a growth oxygen concentration value in the concentration range of 5 - 100 vol. % below the melting temperature of Ga_2O_3 or at the melting temperature or after complete melting of the Ga_2O_3 starting material adapted to minimize creation of metallic gallium amount and thus eutectic formation with the metal crucible and to improve stoichiometry of the Ga_2O_3 starting material and crystal growth stability; and
ii) maintaining the growth oxygen concentration value within the oxygen concentration range during the crystal growth step of the β-Ga_2O_3 single crystal from the melt at the growth temperature and the oxygen concentration:
iii) does not exceed an intermediate oxygen concentration value in the range of 0 - 5 vol. % during the heating up step from room temperature to an intermediate temperature value, intermediate temperature value being located within the temperature range between 1000 °C and the melting temperature of Ga_2O_3 and
iv) increases from the intermediate oxygen concentration value to the growth oxygen concentration value in the concentration range of 5 - 100 vol. % during the heating up step from the intermediate temperature value to the melting temperature of Ga_2O_3 or at the melting temperature or after complete melting of the Ga_2O_3 starting material if the intermediate temperature value substantially equals to the melting temperature.
According to one preferred embodiment, the oxygen concentration:
v) decreases from the growth oxygen concentration value to a final oxygen concentration value being lower than the growth oxygen concentration value during the cooling down step from the growth temperature to room temperature.

[0018] Preferably the growth oxygen concentration value is substantially constant within the oxygen concentration range at the growth temperature during the entire crystal growth step. Alternatively, the growth oxygen concentration value decreases to a second oxygen growth concentration value within the oxygen concentration range at the growth temperature after an early stage of the crystal growth step. In further alternative embodiment, the growth oxygen concentration value increases to a third growth oxygen concentration value within the oxygen concentration range at the growth temperature at the later stage of the crystal growth step. In still alternative embodiment, the growth oxygen concentration value first decreases to a second growth oxygen concentration value within the oxygen concentration range at the growth temperature after an early stage of the crystal growth step, and increases to a third growth oxygen concentration value within the oxygen concentration range at the growth temperature at the later stage of the crystal growth step.

[0019] In addition to oxygen the growth atmosphere may contains at least one of the gases selected from the group consisting of Ar, N_2, He, Ne, CO_2, CO, H_2 and H_2O, or any combination thereof.

[0020] Advantageously, the growth atmosphere can be applied to the Czochralski method, Kyropolous method, Vertical Bridgman method, Vertical Gradient Freeze method, Horizontal Bridgman method, to shaped crystal growth techniques, such as Stepanov, Noncapillary Shaping and Edge-Defined Film-Fed Growth methods, Levitation Assisted Self-Seeding Crystal Growth method and Micro-Pulling Down method.

[0021] According to the second aspect of the invention a bulk β-Ga_2O_3 single crystal is provided, which is obtained by the above-describe method.

[0022] According to the third aspect of the present invention a use of bulk β-Ga_2O_3 single crystal is provided, which is in the form of fabricated wafers or substrates for epitaxial films or layers.

[0023] The inventors have unexpectedly found out through a series of comprehensive experiments that a very high oxygen concentration can be used in connection with an iridium crucible or its alloys at high temperatures. This discovery is in a high contrast to a common, long-lasting believe being reflected in the literature and experiments, that oxygen concentration should not exceed about 2-5 vol. % in connection with iridium. An essential feature of the present method is to maintain a very high oxygen concentration during crystal growth (5 - 100 vol. %) from the melt contained within an iridium (or its alloy) crucible, while keeping lower oxygen concentration at lower temperatures during heating up / cooling down steps, when iridium oxidation rate is much higher as compared with high temperatures. Furthermore, partial pressure of iridium oxide at high temperatures is very high so that it simply evaporates and does not contaminate the melt inside the crucible, again, in contrast to high oxygen concentration provided at low and moderate temperatures during heating up, when iridium oxide typically contaminates the melt. Moreover, with high oxygen concentration less oxygen vacancies, twins and grain boundaries are formed in a growing oxide crystal, therefore the crystal quality significantly improves. Most importantly, such growth conditions enable for obtaining large crystals (over 1 kg by weight)

what is important from industrial point of view, and also extend life-time of iridium crucibles by elimination of eutectic formation between iridium and metallic gallium typically formed during decomposition process. Additionally, the teaching of the present invention has a general meaning and can be successfully applied to any high-melting point oxides requiring high oxygen partial pressure, including those thermo-chemically unstable ones.

[0024] More advantages and other features of the inventive method to growth bulk β-Ga$_2$O$_3$ single crystals or other thermally unstable oxide crystals will be apparent from the detailed description of the embodiments in reference to the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025]

Fig. 1A and 1B are plots of amount of liquid metallic gallium and gaseous gallium suboxide (Ga$_2$O), respectively, produced during decomposition of Ga$_2$O$_3$ at its melting temperature;
Figs. 2A and 2B are plots of oxygen concentration in a growth atmosphere vs. temperature during heating up / growth and growth / cooling down steps, which demonstrate the principle of the present invention;
Fig. 3 schematically shows the principle of the Czochralski method to which the present invention can be applied;
Fig. 4 schematically shows the principle of the Kyropolous method to which the present invention can be applied;
Figs. 5A and 5B schematically show the principle of the Vertical and Horizontal Bridgman method or Vertical Gradient Freeze method to which the present invention can be applied;
Fig. 6 schematically shows the principle of the shaped crystal growth methods to which the present invention can be applied; and
Fig. 7 schematically shows the principle of the Levitation Assisted Self-Seeding Crystal Growth method to which the present invention can be applied.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0026] Fig. 1A shows amount changes of liquid metallic gallium (Ga) in the Ga$_2$O$_3$ melt (that is at melting point of Ga$_2$O$_3$ which is 1820°C) as the result of Ga$_2$O$_3$ decomposition versus oxygen concentration interacting with the Ga$_2$O$_3$ melt. The metallic Ga amount **CR1** is formed within 2.3 mole of the Ga$_2$O$_3$ starting material contained within an iridium crucible of 50 mm in diameter and height to grow 1 inch diameter single crystal; the metallic Ga amount **CR2** is formed within 18 mole of the Ga$_2$O$_3$ starting material contained within an iridium crucible of 100 mm in diameter and height to grow 2 inch diameter single crystal, while the metallic Ga amount **CR3** is formed within 63 mole of the Ga$_2$O$_3$ starting material contained within an iridium crucible of 150 mm in diameter and height to grow 3 inch diameter single crystal. Metallic Ga forms with iridium (Ir) eutectic that destroys the crucible containing the Ga$_2$O$_3$ melt. In addition to liquid metallic Ga also gaseous metallic Ga is formed in the melt, which in areas adjacent to the crucible wall also forms Ga-Ir eutectic. Further, the presence of metallic Ga in the Ga$_2$O$_3$ melt creates difficulties in growing a β-Ga$_2$O$_3$ single crystal and/or obtaining good structural quality thereof, due to changes in melt chemistry and melting temperature. These negative effects, arising from metallic Ga, increases with a melt volume, as higher concentration of metallic Ga is produced. For example, in the case of a growth atmosphere containing 1 vol. % of oxygen the metallic Ga amount **CR2** increases with respect to **CR1** by factor of about 23, while the metallic Ga amount **CR3** increases with respect to **CR1** by factor of about 79. Other words, using 1 vol. % of oxygen growing 2 or 3 inch diameter single crystal will result in Ir crucible damage with no possibility to obtain a single crystal. The amount of metallic Ga can be significantly decreased, at least by several times, by increasing the oxygen concentration **OC** at the level of at least 5 vol. %. In the case of that lowermost value (5 vol. %) the metallic Ga amount **CR2** increases with respect to **CR1** by factor of only 8, while in the case of metallic Ga amount **CR3** - by factor of about 27. When considering a decrease of metallic Ga amount when using 5 vol. % of oxygen with respect to 1 vol. % of oxygen, it decreases by factor of 3 and 9 for **CR1** and **CR2, CR3**, respectively. As clearly shown in Fig. 1A, for higher oxygen concentrations in the range 5 - 100 vol. % the decrease of metallic Ga amount will be more pronounced. Plots **CR1, CR2** and **CR3** indicate that to minimize the metallic Ga amount a much higher oxygen concentration should be used with an increase of the crystal size to be grown.

[0027] Another essential finding of the present invention is that iridium oxide from oxidation of iridium at high temperatures does not contaminate the Ga$_2$O$_3$ melt and the growing crystal. This is due to a very high partial pressure of iridium oxide at high temperatures, which simply evaporate to the environment immediately after creation at the crucible wall.

[0028] In addition to metallic Ga, decomposition of the Ga$_2$O$_3$ melt produces a number of volatile species in the gas phase, including oxygen, Ga$_2$O, GaO and Ga, which evaporate to the environment. The most volatile species in addition to oxygen is Ga$_2$O, the amount versus oxygen concentration of which is shown in Fig. 1B. Applying oxygen concentration **OC** of at least 5 vol. % decreases amount (and fugacity) of Ga$_2$O by more than one order of magnitude, thus decreases the evaporation of Ga$_2$O$_3$ during the growth process. Minimizing of Ga$_2$O evaporation in addition to metallic Ga is crucial

to keep the melt more stoichiometric and to stabilize the crystal growth process.

[0029] Therefore, by applying the oxygen concentration **OC** in the range between 5 - 100 vol. %, the Ga_2O_3 melt can be significantly stabilized by minimizing formation of metallic Ga in the Ga_2O_3 melt and Ga_2O vapor that evaporates from the melt surface. Thus it is sufficient for both crystal growth stability and iridium (or its alloy) crucible durability. It is to be stressed that such high oxygen concentrations (5 - 100 vol. %) in connection with the iridium crucible, which is suitable for growing Ga_2O_3 single crystals from the melt, has never been reported, mentioned or suggested in the prior art, despite of utilizing iridium crucibles for growing various oxide single crystals for decades.

[0030] The essence of the present invention is to apply a very high oxygen concentration (5 - 100 vol. %) for growing β-Ga_2O_3 single crystals from the melt contained within an iridium (or its alloy) crucible around the melting point of Ga_2O_3 which is 1820°C, while keeping a relatively low oxygen concentration at low and moderate temperatures, where iridium oxidizes the most and Ga_2O_3 decomposition is minor. This strategy is described in Fig. 2A during heating a crystal growth furnace up and growing a β-Ga_2O_3 single crystal, and in Fig. 2B during growing the β-Ga_2O_3 single crystal and cooling the crystal growth furnace down after the crystal growth process has been completed.

[0031] As shown in Fig. 2A, an initial oxygen concentration value **C0** is typically small at room temperature **RT**, usually in the range of 0 to about 3 vol. %. The oxygen concentration **OC** increases from the initial oxygen concentration value **C0** to an intermediate oxygen concentration value **C1** in the temperature range between room temperature **RT** and an intermediate temperature value **T1** in any way, e.g. linearly (profile **1**), exponentially (profile **2**), asymptotically, in a step-wise manner or in any combination thereof. Although the intermediate temperature value **T1** is 1400 °C in this example it may have any value in the temperature range **ST** between 1000 °C and the melting temperature **MT** of a Ga_2O_3 starting material. This exemplary value of 1400°C is a compromise between minimizing of the iridium crucible oxidation (which may contaminate a Ga_2O_3 starting material) and avoiding Ga_2O_3 decomposition during the heating up step. Alternatively, in the temperature range between room temperature **RT** and the intermediate temperature value **T1** the oxygen concentration **OC** may be constant (i.e. **C0** = **C1**) as shown by profiles **3** and **4**. Although **C0** has typically a small value, in some applications it may have a very high value, such as 35 % (profile **4**). This is applicable to growth runs with fast heating rates (e.g. 300-500 K/h), when passing through temperatures critical for iridium is very fast. At higher temperatures, i.e. above **T1**, the Ga_2O_3 starting material is more susceptible to decomposition, while iridium oxidation decreases. Therefore the oxygen concentration can be increased to a higher value, i.e. a growth oxygen concentration value **C2** around the melting temperature **MT** of the Ga_2O_3 starting material, which is then maintained within an oxygen concentration range **SC** during the crystal growth step. In this transition region, the oxygen concentration **OC** can be increased in any way, as shown by different profiles **5** to **9** or any combination thereof. E.g. the oxygen concentration **OC** can be maintained at substantially low value of **C1** to the temperature near or at or just above the melting temperature **MT** and then it can be abruptly increased to the value **C2**, as shown by the profile **5**. Alternatively, the oxygen concentration **OC** can be maintained at a high constant value of **C1** in the temperature range **ST**, at the melting temperature **MT** and during the crystal growth step (**C2** = **C1**), as shown by the profile **8**. The oxygen concentration **OC** can be increased in the temperature range **ST** linearly (profile **6**), exponentially (profile **7**), in a step-wise manner (profile **9**), asymptotically or in any other manner. The way how the oxygen concentration increases or maintains constant is not essential and any profile can be used to achieve the growth oxygen concentration value **C2** between 5 and 100 vol. %. The profiles **1-9** are only exemplary and in practice they might be different, due to diffusion processes, relatively large volume of a crystal growth chamber (hundreds of liters), gas flow rates and gas convection (e.g. due to temperature gradients). Also heating time from room temperature **RT** to the melting temperature **MT** can be appropriately adapted for the crystal growth method and size of a growth furnace. It can be for example between 5 and 30 h.

[0032] According to the present invention it is essential that before melting, during melting or just after melting of the Ga_2O_3 starting material the oxygen concentration approaches the growth oxygen concentration value **C2** in the oxygen concentration range **SC** between 5 and 100 vol. % for the reasons explained in connection to Figs. 1A and 1B. Once all the Ga_2O_3 starting material is molten (i.e. at liquid phase), a β-Ga_2O_3 single crystal can be grown from the melt at the growth oxygen concentration value **C2**. The value **C2** can be substantially constant at the growth temperature **GT** during the whole crystal growth step, as shown by profiles **10** in Figs. 2A and 2B. Alternatively, the growth oxygen concentration value **C2** may decrease to a second growth oxygen concentration value **C2'** at the growth temperature **GT** as shown by the profile **10'** in Fig. 2A. This change always takes place within the oxygen concentration range **SC**. There are several reasons to decrease oxygen concentration during the crystal growth stage: a) upon melting, during seeding and during early stage of the crystal growth step there is a higher decomposition rate of the exposed melt surface as compared with a later stage of the crystal growth step with much smaller exposed melt surface and lower temperature gradients, where smaller oxygen concentration can be used; b) high oxygen concentration (approximately above 25 vol. %) may lead to a high electrical resistivity of the obtained crystals (this is not a problem when semi-insulating or insulating crystals are required); c) lower oxygen concentration will decrease iridium losses. On the other hand, the oxygen concentration may increase at later stage of the crystal growth step from the growth oxygen concentration value **C2** to a third growth oxygen concentration value **C2''** (as shown by the profile **10''** in Fig. 2B) in order to improve the heat transfer through a growing crystal, by lowering the free electron concentration and thus lowering the free carrier absorption in

the near infrared spectrum, which becomes more critical with a crystal length. During the crystal growth step both changes can be applied as well. In such case the oxygen concentration **OC** is decreased from the value **C2** to **C2'** at early stage of the crystal growth step and next increased from the value **C2'** to **C2"** at the later stage of the crystal growth step.

[0033] It is to be noted that at the liquid-solid interface the melting temperature **MT** and the growth temperature **GT** are the same. However, the **MT** and **GT** are understood in this description in a broader scope. Due to radial temperature gradients within a metal crucible (e.g. the temperature typically decreases from the crucible wall towards the centre), the melt in the crucible is hotter near the crucible wall than in the centre (e.g. by 50 - 100 K). Therefore the **MT** covers all temperatures within the crucible leading to complete melting of the Ga_2O_3 starting material. On the other hand, during the crystal growth step the temperature in the melt changes to remove latent heat of crystallization generated due to liquid-solid phase transition being transported through a growing crystal (not present during melting) and to adapt changes in geometry (a drop of a melt level, an increase of a crystal size etc.) in the way to keep constant temperature at the growth interface. Thus, for the purpose of the present description the **GT** covers all temperature changes in the growth furnace during the crystal growth step.

[0034] Time period for the crystal growth step mainly depends on the growth method applied, growth rate, crystal length and like, and may last between about one and hundreds of hours. Once the crystal growth step is completed, the growth furnace together with the crystal is cooled down to room temperature **RT** for a predefined period of time, typically between several and tens of hours, depending on the growth method, furnace and crystal size. During cooling down the oxygen concentration **OC** decreases from the growth oxygen concentration value **C2** to a final oxygen concentration value **C3**, which is typically lower than the growth oxygen concentration value **C2, C2', C2"**, as shown in Fig. 2B. Because the crystal has already been grown, the oxygen concentration **OC** at the cooling down step does not need to be changed in such strict manner as during heating up shown in Fig. 2A. The final value **C3** does not need to be very small and may exceed 3 vol. %, for example to tune electrical properties of the obtained crystal. However, it is preferable to achieve a small value to avoid high oxidation of iridium at low temperatures during the cooling down step. The oxygen concentration **OC** can be decreased from the growth oxygen concentration value **C2** to the final oxygen concentration value **C3** in any way, as shown by profiles **11** to **15** or in any combinations thereof. Alternatively, the final oxygen concentration value **C3** may substantially equal to the growth oxygen concentration value **C2, C2', C2"**, as shown by the profile **13** in Fig. **2B.**

[0035] A defined oxygen concentration **OC** at different stages of a growth process is provided to a growth furnace within a growth atmosphere surrounding the melt and crystal. The growth atmosphere is composed of oxygen with variable concentration and one or more of other gasses, including Ar, N_2, He, Xe, Ne, CO_2, CO and traces of H_2 or H_2O, or any combination thereof. Ar, N_2, He, Xe are Ne are neutral gasses, CO_2 is an oxidizing agent, while CO, H_2 and H_2O are reducing agents to additionally modify electrical properties of a β-Ga_2O_3 single crystal. During early heating up and cooling down steps only CO_2 can be used as an oxygen source. Additionally an external overpressure can be used, such as 1-70 bar.

EXAMPLES - GROWTH TECHNIQUES

[0036] Now different crystal growth techniques from the melt are exemplary described, which utilize an iridium (or its alloy) crucible and to which the above described invention can be applied to growth β-Ga_2O_3 single crystals or other high melting-point oxides (> 1500°C) requiring a high oxygen concentration, especially those unstable at high temperatures.

Example 1

[0037] Fig. 3 schematically shows a growth furnace **100** of the Czochralski method, which is placed within a water-cooled growth chamber (not shown). The growth furnace **100** includes an iridium crucible **101** containing a Ga_2O_3 starting material **102**, which is surrounded by a thermal insulation **103**. The crucible **101** is heated up by a heater **104**, typically an inductive or resistive heater. The heater **104** is connected to a heat generator (not shown) and a controller (not shown). Inside the growth furnace **100** a crystal seed **105** is provided being mounted within a seed holder **106** that is coupled via a pulling rod **107** with a translation and rotation mechanisms (not shown). Inside the growth furnace **100** a growth atmosphere **120** is provided, which is in communication with all furnace parts, including the crucible **101** and the Ga_2O_3 starting material **102**. During the heating up step, the oxygen concentration contained within the growth atmosphere **120** changes form the initial oxygen concentration value **C0** to the intermediate oxygen concentration value **C1** (or alternatively **C1 = C0**) and next approaches the growth oxygen concentration value **C2** around melting of the Ga_2O_3 starting material **102** in the way described in connection to Fig. 2A (or alternatively **C2 = C1**). Once the starting material **102** is molten and stabilized, the crystal seed **105** is brought into a contact with the molten starting material **102** and slowly pulled up with a pulling speed **V** (e.g. between 0.5 - 10 mm/h) while rotating with an angular speed **R** (e.g. at 2 - 30 rpm). By doing so the melt of the Ga_2O_3 starting material **102** solidifies on the crystal seed **105** to form a bulk single crystal **110**. A crystal diameter increases from a seed diameter to a predefined cylinder diameter, which is then kept

during the rest of the crystal growth step by regulating melt temperature via the controller. During the crystal growth step the oxygen concentration is maintained at the substantially constant level (profile **10**) of the growth oxygen concentration value **C2**. Alternatively, the growth oxygen concentration value **C2** can be lowered once the predefined cylinder diameter is achieved (profile **10'**). The growth oxygen concentration value **C2** can be also increased at a later stage of the crystal growth step (profile **10"**). Once a predefined crystal length (or mass) is reached, the crystal **110** is separated from the melt and slowly cooled down. During the cooling down step, the oxygen concentration within the growth atmosphere **120** decreases from the growth oxygen concentration **C2** to the final oxygen concentration value **C3** (or alternatively **C3** = **C2**) in the way described in connection with Fig. 2B.

Examples 2

[0038]   Fig. 4 schematically shows a growth furnace **200** of the Kyropolous method, which is placed within a water-cooled growth chamber (not shown). The Kyropolous method is a variant of the Czochralski method, where a single crystal **210** is rather growing from a larger surface out of the melt and partly within a molten starting material **202**. In this method a very small pulling rate **V** (smaller than that in the Czochralski method) is typically applied, possible with rotation **R.** All the components of the growth furnace **200** are very similar to those of the Czochralski method (can be identical). During the heating up step, the oxygen concentration contained within a growth atmosphere **220** changes form the initial oxygen concentration value **C0** to the intermediate oxygen concentration value **C1** (or alternatively **C1** = **C0**) and next approaches the growth oxygen concentration value **C2** (or alternatively **C2** = **C1**) around melting of the Ga_2O_3 starting material **202** in the way described in connection to Fig. 2A. During the crystal growth stage the oxygen concentration is maintained at the level of the growth oxygen concentration value **C2** or it can be changed during growth within the oxygen concentration range **SC** (e.g. decreased and/or increased). During the cooling down step, the oxygen concentration within the growth atmosphere **220** decreases from the growth oxygen concentration value **C2** to the final oxygen concentration value **C3** (or alternatively **C3** = **C2**) in the way described in connection with Fig. 2B.

Examples 3

[0039]   Fig. 5A schematically shows a growth furnace **300** of the Vertical Bridgman method or the Vertical Gradient Freeze method, which is placed within a water-cooled growth chamber (not shown). The growth furnace **300** includes an iridium crucible **301** containing a Ga_2O_3 starting material **302**, which is surrounded by a thermal insulation **303**. The crucible **301** is enclosed by a lid **308**, preferably of iridium, with an opening **309** through which a growth atmosphere **320** communicates with the Ga_2O_3 starting material **302**. The crucible **301** is heated up by a heater **304** (inductive or resistive). The heater **304** is connected to a heat generator (not shown) and a controller (not shown). At the heating up step, the oxygen concentration contained within the growth atmosphere **320** changes form the initial oxygen concentration value **C0** to the intermediate oxygen concentration value **C1** (or alternatively **C1** = **C0**) and next approaches the growth oxygen concentration value **C2** (or alternatively **C2** = **C1**) around melting of the Ga_2O_3 starting material **302** in the way described in connection to Fig. 2A. The bottom part of the crucible **301** is tapered and ended with a small diameter tube that functions as a seed holder **306**, within which a crystal seed **305** is accommodated. The iridium crucible **301** is located within vertical temperature gradients in such a way the seed holder **306** along with the crystal seed **305** are hold at lower temperature than the rest of the crucible **301** to prevent melting of the seed **305** once all the Ga_2O_3 starting material **302** is molten. The temperature within the crucible **301** typically increases from the seed holder **306** towards the top of the crucible **301**. By lowering the temperature at the crucible wall (Vertical Gradient Freeze method) the molten Ga_2O_3 starting material **302** slowly solidify on the crystal seed **305** upwards to form a single crystal **310**. Instead of lowering the temperature at the crucible wall, the crucible **301** or the whole growth furnace **300** can be lowered in a direction of lower temperatures (Bridgman method) or the heater **304** is moved in a direction opposite to the crystal seed **305**. Alternatively both lowering the temperature and moving of the crucible **301** / heater **304** can be applied. During the crystal growth step the oxygen concentration is maintained at the level of the growth oxygen concentration value **C2** or it can be changed within the oxygen concentration range **SC**. Once the crystal growth step is completed (i.e. once all the melt is solidified) the growth furnace **300** is cooled down and the oxygen concentration within the growth atmosphere **320** decreases from the growth oxygen concentration value **C2** to the final oxygen concentration value **C3** (or alternatively **C3** = **C2**) in the way described in connection with Fig. 2B.

Examples 4

[0040]   Fig. 5B schematically shows a growth furnace **400** of the Horizontal Bridgman method. The principle of this method is the same as in the case of the Vertical Bridgman method, but the solidification proceeds in a horizontal direction instead of the vertical direction. During the heating up step, the oxygen concentration contained within a growth atmosphere **420** changes form the initial oxygen concentration value **C0** to the intermediate oxygen concentration value **C1**

(or alternatively **C1** = **C0**) and next approaches the growth oxygen concentration value **C2** (or alternatively **C2** = **C1**) around melting of the Ga_2O_3 starting material **402** in the way described in connection to Fig. 2A. During the crystal growth step the oxygen concentration is maintained at the level of the growth oxygen concentration value **C2** or it can be changed during growth within the oxygen concentration range **SC**, while during the cooling down step, the oxygen concentration within the growth atmosphere **420** decreases from the growth oxygen concentration value **C2** to the final oxygen concentration value **C3** (or alternatively **C3** = **C2**) in the way described in connection with Fig. 2B.

Example 5

[0041] This Example relates to shaped crystal growth techniques in general, such as the Stepanov, Noncapillary Shaping (NCS) and Edge-Defined Film-Fed Growth (EFG) methods. Fig. 6 schematically shows a growth furnace **500** of the EFG method, which is placed within a water-cooled growth chamber (not shown). Within an iridium crucible **501** an iridium die **511** is disposed. The die **511** has at least one opening being in communication with the molten Ga_2O_3 starting material **502** and a small-diameter central channel **512**, through which the melt is transported via capillary forces (capillary channel) to the top surface **513** having typically a quite small width (several millimeters) but much larger length (even several cm). If the central channel **512** is larger than the capillary constant (noncapillary channel), then the melt is transported through the channel by a pressure difference (Stepanov and NCS methods). Once the Ga_2O_3 starting material **502** is molten a crystal seed **505** is brought into the contact with the melt on the top surface **513** and pulled upwards at the pulling speed **V** to form a single crystal **510**. The pulling speed **V** is typically larger than that of the Czochralski method. A crystal rotation is typically not applied in this method. The resulted crystal shape corresponds to the geometry of the top surface **513** which can be different (e.g. rectangular or circular). Once the crystal growth is completed it is separated from the melt and cooled down. During the heating up step, the oxygen concentration contained within a growth atmosphere **520** changes form the initial oxygen concentration value **C0** to the intermediate oxygen concentration value **C1** (or alternatively **C1** = **C0**) and next approaches the growth oxygen concentration value **C2** (or alternatively **C2** = **C1**) around melting of the Ga_2O_3 starting material **502** in the way described in connection to Fig. 2A. During the crystal growth step the oxygen concentration is maintained at the level of the growth oxygen concentration value **C2** or it can be changed during growth within the oxygen concentration range **SC**, while during the cooling down step, the oxygen concentration within the growth atmosphere **520** decreases from the growth oxygen concentration value **C2** to the final oxygen concentration value **C3** (or alternatively **C3** = **C2**) in the way described in connection with Fig. 2B.

Example 6

[0042] Fig. 7 schematically shows a growth furnace **600** of the Levitation-Assisted Self-Seeding Crystal Growth Method (LASSCGM), which is placed within a water-cooled growth chamber (not shown). An iridium crucible **601** containing Ga_2O_3 starting material **602** is located within a thermal insulation **603**. The crucible **601** is covered by a lid **608** with an opening 609 for a communication of a growth atmosphere **620** with the Ga_2O_3 starting material **602**. A heater **604** must be an inductive heater in this case. In this method it is required that the Ga_2O_3 starting material is highly conducting in the liquid phase which is then coupled with the electromagnetic field of the inductive heater **604** through the crucible wall and it is levitated. By levitating a portion of the melt a liquid neck **605** is formed, which acts as a seed during solidification. After melting and levitating a portion of the melt, the furnace **600** is cooled down and the molten Ga_2O_3 starting material solidifies on the neck **605** to form two single crystals **610** on the opposite sides of the self-created neck **605**. More details of the LASSCGM can be found in document WO 2013/159808 to Galazka et al.. During the heating up step, the oxygen concentration contained within a growth atmosphere **620** changes form the initial oxygen concentration value **C0** to the intermediate oxygen concentration value **C1** (or alternatively **C1** = **C0**) and next approaches the growth oxygen concentration value **C2** (or alternatively **C2** = **C1**) at or preferably after melting of the Ga_2O_3 starting material **602** in the way described in connection to Fig. 2A. To obtain a high electrical conductivity of the liquid Ga_2O_3 starting material **602** the growth oxygen concentration value **C2** during the crystal growth step should be kept rather at lower level, e.g. 5 - 10 vol. %. Additionally an intentional doping with tetravalent ions (Si, Sn) can be used. During the crystal growth step the oxygen concentration is maintained at the level of the growth oxygen concentration value **C2** (or alternatively **C2** = **C1**), while during the cooling down step, the oxygen concentration within the growth atmosphere **620** decreases from the growth oxygen concentration value **C2** to the final oxygen concentration value **C3** (or alternatively **C3** = **C2**) in the way described in connection with Fig. 2B.

Example 7

[0043] In addition to the above-mentioned techniques, the present invention can also be applied to the micro-pulling down technique. This technique involves a small diameter metal (e.g. iridium) crucible with a small diameter aperture

at the bottom part, which prevents the starting material to flow out from the crucible after melting by holding it via capillary forces. Then a seed is brought into a contact with the melt in the aperture and pulled down. In this way a crystal fiber of about 1-2 mm in diameter can be grown. During the heating up step, the oxygen concentration contained within a growth atmosphere changes form the initial oxygen concentration value **C0** to the intermediate oxygen concentration value **C1** (or alternatively **C1** = **C0**) and next approaches the growth oxygen concentration value **C2** (or alternatively **C2** = **C1**) around melting of the Ga_2O_3 starting material in the way described in connection to Fig. 2A. During the crystal growth step the oxygen concentration is maintained at the level of the growth oxygen concentration value **C2** or it can be changed during the crystal growth step within the oxygen concentration range **SC**, while during the cooling down step, the oxygen concentration within the growth atmosphere **420** decreases from the growth oxygen concentration value **C2** to the final oxygen concentration value **C3** (or alternatively **C3** = **C2**) in the way described in connection with Fig. 2B. Due to small crucible dimensions, possible fast heating and fast crystal growth rates, oxygen concentration can be as high as 100 vol. % during the entire growth process (i.e. **C0** = **C1** = **C2** = **C3** = 100 vol. %).

EXAMPLES - OXYGEN CONCENTRATIONS

Example 8 (comparative)

[0044] The Czochralski method **100** (Fig. 3, Example 1) was used with an iridium crucible of 40 mm in diameter and height (the amount of the Ga_2O_3 was 1 mole only). The growth atmosphere was CO_2 which provided oxygen concentration at the level of about 1.2 vol. % at the melting temperature **MT**. This means the oxygen concentration was increased from room temperature **RT** to the melting temperature **MT** from substantially 0 vol. % to about 1.2 vol. %, which was then kept constant during the crystal growth step at the growth temperature **GT**. During the cooling down step the oxygen concentration was decreased from 1.2 vol. % at the growth temperature **GT** to about 0 vol. % at room temperature **RT**. The obtained crystal was of 20 mm in diameter and 60 mm in length. The crystal quality was relatively good, although contained crystallographic twins and moderate dislocation density. Moreover, the crystal surface was rough as the result of noticeable Ga_2O_3 decomposition. Due relatively high Ga_2O_3 decomposition the melt was unstable leading to difficulties in seeding and early stage of the crystal growth step. Additionally, some signs of crucible degradation due to eutectic formed between Ga and Ir metals were visible. Similar results were obtained in the case of a growth atmosphere consisting with O_2 = 2 vol. % and N_2 0 98 vol. %. This example demonstrates that relatively good crystals of β-Ga_2O_3 could be grown with a very low oxygen concentration if the amount of the staring material was very small (1 mole). In reference to Fig. 1A, the amount of metallic Ga produced during Ga_2O_3 decomposition was very small, yet below **CR1** curve, therefore not critical at all. However, first sings of problems associated with growth stability, crystal quality and crucible durability have been recognized.

Example 9 (comparative)

[0045] The Czochralski method **100** (Fig. 3, Example 1) was used with much larger iridium crucible of 100 mm in diameter and height. The growth atmosphere was CO_2, identical to that of Example 8. The only difference was much larger iridium crucible and amount of the Ga_2O_3 starting material by factor of 18 (18 mole of Ga_2O_3). In this case it was almost impossible to start growing a crystal due to a high concentration of metallic Ga being created due to insufficient oxygen concentration in relation to the amount of the Ga_2O_3 starting material. The high concentration of metallic Ga changes the melt temperature and the melt chemistry. Even the growth could be eventually started, only a short crystal could obtained (30 mm), although large diameter (50 mm). This was due to high growth instabilities caused by Ga metal. Due to this negative effects the crystal quality was much worse than that of smaller crystal of Example 8. More importantly, usually after a first growth run the crucible was heavily damaged due to eutectic formed between Ga and Ir metals and could not be reused. Crucible damage and lack of a crystal of a reasonable size and quality lead to high economical losses. This example clearly shows that with increasing amount of the Ga_2O_3 starting material the oxygen concentration must correspondingly increase to obtain: low level of Ga_2O_3 decomposition (i.e. low density of metallic Ga and low evaporation rate), a stable melt flow, much larger crystal size of high structural quality and lower risk of iridium crucible damage.

Example 10

[0046] The Czochralski method **100** (Fig. 3, Example 1) was used with an iridium crucible of 100 mm in diameter and height, the same as in Example 9, but a different growth atmosphere was used. During the heating up step, the oxygen concentration was increased from substantially 0 vol. % (the initial oxygen concentration value **C0**) to about 1 vol. % (the intermediate oxygen concentration value **C1**) between room temperature **RT** and the intermediate temperature value **T1** of about 1300°C. This was achieved by using CO_2 only. Then the CO_2 growth atmosphere was replaced with

a mixture of Ar = 95 vol. % + O_2 = 5 vol. % as the growth atmosphere at and next with Ar = 92 vol. % + O_2 = 8 vol. % at the beginning of melting of the Ga_2O_3 starting material (the growth oxygen concentration value **C2**), which was kept constant during the rest of the heating up step until complete melting of the Ga_2O_3 starting material (the melting temperature **MT**) and during the entire crystal growth step at the growth temperature **GT**. Once the crystal growth step was completed, the growth atmosphere of Ar (92 vol. %) + O_2 (8 vol. %) was replaced again with CO_2. Oxygen produced during CO_2 decomposition was decreased to 0 - 1 vol. % (the final oxygen concentration value **C3**) at room temperature **RT**. As the result only a very small concentration of metallic Ga was present at the melt surface and it was much easier to start growing a crystal. The obtained crystal was a semiconductor with the free electron concentration of 6×10^{17} cm^{-3}. It was 50 mm in diameter and 125 mm in length, i.e. much longer than that of the comparable Example 9 and of much better structural quality. The crystal was transparent with smooth surface and with no iridium particles therein. Moreover, the iridium crucible has not been damaged by Ga - Ir eutectic and it could be re-used several times.

Example 11

[0047]　This Example is very similar to that of Example 10 (the Czochralski method **100,** iridium crucible of 100 mm in diameter and height), but a different oxygen concentration was used. The initial oxygen concentration value **C0** was about 0 vol. %, which was increased during the heating up step to about 1.1 vol. % (the intermediate oxygen concentration value **C1**) at about 1700°C (the intermediate temperature value **T1**). This was achieved by using a CO_2 growth atmosphere. Then the oxygen concentration was increased to 12 vol. % (the growth oxygen concentration value **C2**) at the beginning of melting of Ga_2O_3 (the melting temperature **MT**), by replacing the CO_2 growth atmosphere with a mixture of Ar = 88 vol. % + O_2 = 12 vol. % as the growth atmosphere. The growth oxygen concentration value **C2** of 12 vol. % was kept constant during the entire crystal growth step at the growth temperature **GT**. During the cooling down step, the oxygen concentration was decreased to 0 - 1 vol. % (the final oxygen concentration value **C3**) at room temperature **RT**. The metallic Ga concentration was still lower than that in Example 9 and there was quite easy to initiate crystal seeding and growth. The obtained crystal was a semiconductor with the free electron concentration of 2×10^{17} cm^{-3}, which was lower than that in Example 10 due to higher oxygen concentration. The crystal was 50 mm in diameter and 100 mm in length. It was transparent with a very smooth surface. The overall crystal quality was much better as compared with a crystal grown under low oxygen concentration (comparative Example 9). No iridium particles were present inside the crystal and no damage sings of the crucible were visible.

Example 12

[0048]　This Example is very similar to Examples 10 and 11 (the Czochralski method **100** with 100 mm iridium crucible). The initial oxygen concentration value **C0** was about 0 vol. % which was next increased to the intermediate oxygen concentration value **C1** of about 1 vol. % at about 1500 °C (the intermediate temperature value **T1**), and then to the growth oxygen concentration value **C2** of 20 vol. % just below the melting temperature **MT**. Similar to Example 11, initially CO_2 was used as the growth atmosphere, which was then replaced with a mixture of Ar = 80 vol. % + O_2 = 20 vol. % as the growth atmosphere. The growth oxygen concentration value **C2** of 20 vol. % was kept constant during the entire crystal growth step at the growth temperature **GT**. During the cooling down step, the oxygen concentration was decreased from the growth oxygen concentration value **C2** of 20 vol. % to the final oxygen concentration value **C3** of 0-1 vol. % at room temperature **RT**. This was achieved by replacing the Ar + O_2 growth atmosphere with the CO_2 growth atmosphere during the cooling down step. The obtained crystal was a semiconductor with the free electron concentration of 7×10^{16} cm^{-3}, which was lower than that in Examples 10 and 11 due to yet higher oxygen concentration. The results in terms of the crystal size, appearance and quality, as well as crucible stability were similar to those of Example 10 and 11.

Example 13

[0049]　This Example is similar to Example 8 (the Czochralski method **100**), but a different growth atmosphere was used. The crucible diameter and height were 40 mm. Additionally the Ga_2O_3 starting material was doped with Mg at a very low level of 0.05 mol. %. The initial oxygen concentration value **C0** at room temperature **RT** was about 0 vol. % which was next increased to the intermediate oxygen concentration value **C1** of about 1 vol. % (by using CO_2) at the intermediate temperature value **T1** of 1460 °C, and then to the growth oxygen concentration value **C2** of 35 vol. % by using a mixture of N_2 = 65 vol. % + O_2 = 35 vol. % as the growth atmosphere at temperature below the melting temperature **MT**, which was then kept constant during the entire crystal growth step at the growth temperature **GT**. Oxygen concentration changes during the heating up step were step-wise (oxygen was increased in steps of about 5 vol. % in temperature intervals of about 50 - 100 K by changing a N_2/O_2 ratio). During the cooling down step, the oxygen concentration was decreased from the growth oxygen concentration value **C2** of 35 vol. % at growth temperature **GT** to the final oxygen concentration value **C3** of about 1 vol. % at room temperature **RT** in the step-wise manner by changing the N_2/O_2 ratio.

The obtained crystal of 20 mm in diameter and 60 mm in length was an electrical insulator. The structural quality of the crystal was as good as that in Examples 10-12.

Example 14

[0050]   This Example is similar to the Example 13 (the Czochralski method **100**), but a different growth atmosphere was used. The crucible diameter and height were 40 mm. The initial oxygen concentration value **C0** at room temperature **RT** was 3 vol. % (a mixture of Ar = 97 vol. % + O_2 = 3 vol. %) which was kept constant as the intermediate oxygen concentration value **C1** (**C1 = C0**) until the intermediate temperature value **T1** of 1820 °C which is equal to the melting temperature **MT** (**T1 = MT**), that is when the all Ga_2O_3 starting material was in the liquid phase. Next the oxygen concentration at the melting temperature **MT** was abruptly increased from the intermediate oxygen concentration value **C1** to the growth oxygen concentration value **C2** of 12.5 vol. % by an increase of the O_2 flow with respect to the Ar flow. The growth oxygen concentration value **C2** was kept constant at the growth temperature **GT** during seeding, growth of the crystal shoulder and the beginning of the crystal cylinder. Next the growth oxygen concentration value **C2** was decreased (as shown by the profile **10'** in fig. 2A) to a second growth oxygen concentration value **C2'** of 9.7 vol. % (**C2'** < **C2**), which was kept constant during growth of most of the crystal cylinder. When the crystal cylinder achieved of about 2/3 of the final length, the second growth oxygen concentration value **C2'** was increased (as shown by the profile **10"** in fig. 2B) to a third growth oxygen concentration value **C2"** of 13.8 vol. % (**C2"** > **C2**). During the cooling down step, just after the crystal growth step was completed, the growth atmosphere consisting of Ar+O_2 was replaced with CO_2, and the final oxygen concentration value **C3** was 0-1 vol. % at room temperature **RT**. The obtained crystal 20 mm in diameter and 60 mm in length was a semiconductor with the free electron concentration of 6×10^{17} cm^{-3}. Other features were very similar to those in previous Examples 10 - 13.

Example 15

[0051]   In this Example the Kyropoluos method **200** was utilized, as schematically shown in Fig. 4. The iridium crucible diameter and height were 40 mm. The initial oxygen concentration value **C0** was about 0 vol. % at room temperature **RT**, which was next increased to the intermediate oxygen concentration value **C1** of about 1.1% (from CO_2) at the intermediate temperature value **T1** of 1630 °C, and then to the growth oxygen concentration value **C2** of 16 vol. % just below the melting temperature **MT**. This was obtained by replacing CO_2 with a mixture of N_2 = 84 vol. % + O_2 = 16 vol. %. The growth oxygen concentration value **C2** of 16 vol. % was kept constant during the initial stage of crystal growth at the growth temperature **GT**. Once the initial stage of crystal growth was completed (seeding and crystal shoulder), the growth oxygen concentration value **C2** of 16 vol. % was decreased to a second oxygen concentration value **C2'** of 8 %, which was kept constant to the end of the crystal growth step at the growth temperature **GT**. The final oxygen concentration value **C3** at room temperature **RT** was 3 vol. %, obtained by a decrease (from the growth oxygen concentration value **C2** in a step-wise manner) of the O_2 flow in relation to the N_2 flow. The resulted crystal was of 32 mm in diameter and 20 mm in length. Similar to the above-described Examples 9 - 14, the obtained crystal was a transparent semiconductor with the free electron concentration of 1×10^{17} cm^{-3} and high structural quality. No signs of a crucible damage were observed.

Example 16

[0052]   In this example the Vertical Bridgman or VGF method **300** was utilized as schematically shown in Fig. 5A. The cylindrical part of the crucible was of 60 mm and 80 mm in diameter and length, respectively. The bottom conical part of the crucible of 25 mm in length was ended with a 5 mm tube acting as a seed holder. In this experiment Sn (0.1 mol % of SnO_2 in the Ga_2O_3 starting material) was used as an intentional dopant to obtain high electrical conductivity of the obtained crystal despite of a very high oxygen concentration. The initial oxygen concentration value **C0** was 0 vol. % at room temperature **RT**, which was then increased to the intermediate oxygen concentration value **C1** of about 1 vol. % (from the CO_2 growth atmosphere) at the intermediate temperature value **T1** of 1430 °C. During the next stage of the heating up step the intermediate oxygen concentration value **C1** of 1 vol. % was increased to the growth oxygen concentration value **C2** of 17 vol. % (by replacing CO_2 with a mixture of N_2 = 83 vol. % + O_2 = 17 vol %) below the melting temperature **MT**. The value **C2** of 17 vol. % was kept constant during melting and during the crystal growth step at the growth temperature **GT**. Once the crystal growth step was completed and after an initial stage of the cooling down step, the growth oxygen concentration value **C2** was decreased during the next stage of the cooling down step to the final oxygen concentration value **C3** of about 0 - 1 vol. % (by replacing N_2 + O_2 with CO_2) at room temperature **RT**. The obtained crystal was 50 mm in diameter and 35 mm long. It was a transparent semiconductor with the free electron concentration of 5×10^{18} cm^{-3}. No signs of crucible damage was observed.

Example 17

[0053] In this example two shaped crystal growth techniques were used: the NCS and EFG methods **500**, as schematically shown in Fig. 6. The cylindrical iridium crucible diameter and height were 40 mm. The die was made of iridium and had a conically-shaped circular top surface of 16 mm to obtain a cylindrical crystal of the same diameter. The central channel **512** was of 12 mm in diameter in the case of the NCS variant and 1 mm in diameter in the case of the EFG variant. The initial oxygen concentration value **C0** was about 0 % at room temperature **RT**, which was next increased to the intermediate oxygen concentration value **C1** of 1 % (from CO_2) at the intermediate temperature value **T1** of 1400 °C, and then to the growth oxygen concentration value **C2** of 12 % just below the melting temperature **MT**. This was obtained by replacing CO_2 with a mixture of Ar = 88 vol. % + O_2 = 12 vol. %. The growth oxygen concentration value **C2** of 12 % was kept constant during the entire crystal growth step at the growth temperature **GT**. The final oxygen concentration value **C3** at room temperature **RT** was about 0 - 1 vol. %, obtained by replacing N_2 + O_2 with CO_2. The resulted single crystals were semiconductors of 16 mm in diameter and 50 mm in length. No iridium crucible and die damage was observed.

Example 18

[0054] In this example the Levitation-Assisted Self-Seeding Crystal Growth Method **600** was utilized as schematically shown in Fig 7. The iridium crucible was of 40 mm in diameter and height. To obtain a very high electrical conductivity of Ga_2O_3 in the liquid phase an intentional doping with Sn (0.2 mol % of SnO2 in the Ga_2O_3 starting material) was used. The initial oxygen concentration value **C0** was 2 vol. % at room temperature **RT**, which was kept constant to the intermediate temperature value **T1** of 1500 °C, that is **C1** = **C0**. Next, the intermediate oxygen concentration value **C1** of 2 vol. % (a mixture of N_2 = 98 vol. % + O_2 = 2 vol. %) was increased to the growth oxygen concentration value **C2** of 5 vol. % (by an increase of the O_2 flow with respect to the N_2 flow) below the melting temperature **MT**. The value **C2** of 5 vol. % was kept constant during melting and during the crystal growth step at the growth temperature **GT**. Once the crystal growth step was completed and after the initial stage of the cooling down step, the growth oxygen concentration value **C2** was decreased during the next stage of the cooling down step to the final oxygen concentration value **C3** of about 1 vol. % (by a decrease of the O_2 flow with respect to the N_2 flow) at room temperature **RT**. The obtained crystal was 35 mm in diameter and 20 mm long with relatively good structural quality. It was a transparent semiconductor with the free electron concentration of 1×10^{19} cm^{-3}. No signs of a crucible damage was observed.

[0055] The growth atmosphere in addition to main constituents (O_2, CO_2, N_2, Ar) and depending on a growth process contained also other gases, such as H_2O between 0 - 1.5 vol. %, H_2 between 0 - 0.1 vol. %, CO between 0 - 2 vol. % (mainly from CO_2 decomposition) and He between 0 - 100 vol. ppm. Typically the growth atmosphere contained several gases, especially in the case of replacing one atmosphere with another one.

[0056] Using the growth atmosphere according to the teaching of the present invention significantly decreases eutectic formation between solid iridium crucible and metallic gallium formed during decomposition of Ga_2O_3. This is of particular importance when using large growth systems to obtain large single crystals of several kg by weight (e.g. cylindrical crystals of 2-4 inch in diameter grown by the Czochralski method), what is required at the industrial level. At the same time also evaporation of volatile species of Ga_2O_3 have been minimized or eliminated. Secondly, the obtained crystals, whether small or large, were of high structural quality when using the inventive growth atmosphere. The full with of half maximum (FWHM) of the rocking curve (determining structural quality) was around or below 50 arcsec when using the novel growth atmosphere indicating an improvement by factor of two or three when compared with crystals grown at low oxygen concentration (around 100-150 arcsec). Furthermore, the crystals obtained under the novel growth atmosphere had lower dislocation density (not exceeding several thousand per cm^2) by factor of 10-100 as compared with the crystals grown with use of the atmosphere containing lower oxygen concentration. Moreover, the inventive growth atmosphere minimized or even eliminated crystallographic twinning, cleaving and cracking. Also the crystal surface became smooth and shiny as the decomposition of Ga_2O_3 was significantly reduced. In additions to much improved crystal quality, high oxygen concentration at liquid Ga_2O_3 contained within a metal crucible allowed for much easier seeding and more stable crystal growth process. A combination of the above-mentioned advantages of the present inventions led to a high overall production yield of the crystals (a combination of crystal size and quality as well as extended life of an iridium crucible). Yet another advantage of the present invention is the possibility of modifying electrical and optical properties of the crystals by using different oxygen concentrations during the growth and/or cooling down steps. For example, crystals grown at very high oxygen concentrations (> 25 vol %) my turn into semi-insulating or insulating state, while at lower values of the oxygen concentration the crystals remain semiconducting. Therefore depending on needs the crystals can be grown either as insulators, semi-insulators or semiconductors, with yet different electrical properties.

[0057] Unexpectedly and surprisingly, the obtained crystals did not contained any iridium particles, in contrast to low oxygen concentrations, when iridium particles are often present in the obtained crystals. This is due to very high iridium

oxide partial pressure at high temperatures, which evaporates very effectively just after creation. If high oxygen concentration is used at moderate temperatures (600 - 1000°C), then iridium oxide partial pressure is very low and may simple contaminate the starting material contacting the iridium crucible. Despite of extremely high oxygen concentration according to the present invention (up to 100 vol. %) at high temperatures iridium losses due to oxidation and evaporation are quite low and acceptable, between 2 - 9 wt. % per growth run depending on oxygen concentration and duration of the growth run. In the case of 100 vol. % of oxygen, 9 wt. % of iridium loss relates to one-day growth run, while at lower oxygen concentrations several wt. % of iridium loss relates to several-day grow runs.

[0058] The present invention can be applied for obtaining β-Ga_2O_3 single crystals which are either undoped or intentionally doped with a number of elements to further modify (if needed), in addition to oxygen concentration, electrical and optical properties of the crystals. Some of the crystals described in reference to Examples 10-18 were undoped, while other ones were doped either with divalent ions (Mg) to obtained insulating crystals or tetravalent ions (Sn) to increase the electrical conductivity of the crystals despite of high oxygen concentration. In connection to the inventive growth atmosphere any dopants can be used, as required.

[0059] The crystal growth atmosphere according to the present invention has a very broad spectrum of applications, as it may be applied to any crystal growth method utilizing a metal crucible comprising iridium or its alloys. These methods have been described in connection with Examples 1-18 and Figs. 3-7. Any modifications or adaptations of these methods may also encompassed, as long as a metal crucible is used at high temperatures (> 1500°C).

[0060] High structural quality of the obtained β-Ga_2O_3 crystals allows for fabrication of high quality wafers or substrates for depositing thereon homo- or heteroepitaxial films or layers with use of various epitaxial techniques. Homoepitaxial films or layers may include β-Ga_2O_3 single crystal films of different conductivity than the substrate, while heteroepitaxial films involve other compounds, such as different oxides or nitrides (GaN, AlN, AlGaN, InN, InGaN and like). The epitaxial techniques include, but not limited to Molecular Beam Epitaxy (MBE), Metal-Organic Chemical Vapor Deposition (MOCVD), Pulsed Laser deposition (PLD), Sputtering, Electron Beam Evaporation and like. Wafers or substrates prepared from β-Ga_2O_3 single crystals can also be used as seeds for other growth techniques, such as, but not limited to Chemical Vapor Transport (CVT), Physical Vapor Transport (PVT) and like.

[0061] β-Ga_2O_3 single crystals can be used in a diversity of applications, such as, but not limited to: light emitting diodes, solid-state lasers, transparent or high power field-effect transistors (such as MISFET and MOSFET), Schottky diodes and high temperature gas sensors (electrical properties change on oxidizing and reducing conditions at elevated temperatures).

[0062] The essence of the present invention is the use of a very high oxygen concentration (5 - 100 vol. %) in connection with an iridium crucible (or its alloys) at high temperatures (> 1500°C) for the growth of β-Ga_2O_3.

[0063] It is important to note that the operating conditions, arrangement and design of the methods as shown in the various embodiments are illustrative only. Although only exemplary embodiments of the present invention have been described in detail in this disclosure, those skilled in the art will readily appreciate that many modifications are possible, e.g., variations in values of crystal growth parameters, crystal growth atmosphere compositions, use of materials, use of crystal growth techniques, process designs etc. without materially departing from the novel teachings and advantages of the subject matter recited in the claims.

Reference numeral list

[0064]

1 - 9	Oxygen concentration profiles vs. temperature during heating up step
10, 10', 10"	Oxygen concentration profiles during crystal growth step
11-15	Oxygen concentration profiles vs. temperature during cooling down step
100, 200, 300, 400, 500, 600	Crystal growth furnace
101, 201, 301, 401, 501, 601	Metal crucible
102, 202, 302, 402, 502, 602	Ga_2O_3 starting material
103, 203, 303, 403, 503, 603	Thermal insulation
104, 204, 304, 404, 504, 604	Heater
105, 205, 305, 405, 505, 605	Crystal seed
106, 206, 306, 406, 506	Seed holder
107, 207, 507	Pulling rod
110, 210, 310, 410, 510, 610	Single crystal
120, 220, 320, 420, 520, 620	Growth atmosphere
308, 408, 608	Lid covering the crucible 301, 401, 601
309, 409, 609	Opening in the lid 308, 408, 308
511	Die of the metal crucible 501

512	Central channel of the die 511
513	Top surface of the die 511
OC	Oxygen concentration
C0, C1, C2, C2', C2", C3	Oxygen concentration values: initial, intermediate, growth and final
T1	Intermediate temperature value
ST	Range of temperature values T1
SC	Range of oxygen concentrations at the growth temperature
MT	Melting temperature
GT	Growth temperature
RT	Room temperature
V	Pulling speed
R	Rotation rate

Claims

1. A method for growing beta phase of gallium oxide (βGa_2O_3) single crystals from the melt contained within a metal crucible, comprising the steps of:

   - providing into a growth chamber a thermal system or growth furnace (**100, 200, 300, 400, 500, 600**) comprising the metal crucible (**101, 201, 301, 401, 501, 601**) containing the Ga_2O_3 starting material (**102, 202, 302, 402, 502, 602**), a thermal insulation (**103, 203, 303, 403, 503, 603**) surrounding the metal crucible (**101, 201, 301, 401, 501, 601**) and a heater (**104, 204, 304, 404, 504, 604**) disposed around the metal crucible (**101, 201, 301, 401, 501, 601**);
   - providing or creating a crystal seed (**105, 205, 305, 405, 505, 605**) within the growth furnace (**100, 200, 300, 400, 500, 600**);
   - introducing at least into the growth furnace (**100, 200, 300, 400, 500, 600**) a growth atmosphere (**120, 220, 320, 420, 520, 620**) containing oxygen;
   - heating up the metal crucible (**101, 201, 301, 401, 501, 601**) by the heater (**104, 204, 304, 404, 504, 604**), which in turns heats up the Ga_2O_3 starting material (**102, 202, 302, 402, 502, 602**) until melting;
   - contacting the crystal seed (**105, 205, 305, 405, 505, 605**) with the molten Ga_2O_3 starting material (**102, 202, 302, 402, 502, 602**) contained within the metal crucible (**101, 201, 301, 401, 501, 601**);
   - growing a β-Ga_2O_3 single crystal (**110, 210, 310, 410, 510, 610**) on the crystal seed (**105, 205, 305, 405, 505, 605**) by temperature gradients between the crystal seed and the melt;
   - cooling down the grown β-Ga_2O_3 single crystal (**110, 210, 310, 410, 510, 610**) to room temperature (**RT**) once the crystal growth step has been completed;

   characterized in that it further comprises the steps of:

   i) providing into the growth furnace (**100, 200, 300, 400, 500, 600**) the growth atmosphere (**120, 220, 320, 420, 520, 620**) with a variable oxygen concentration (**OC**) or partial pressure in such a way that the oxygen concentration (**OC**) reaches a growth oxygen concentration value (**C2, C2', C2"**) in the concentration range (**SC**) of 5 - 100 vol. % below (**8, 9**) the melting temperature (**MT**) of Ga_2O_3 or at (**6, 7**) the melting temperature (**MP**) or after (**5**) complete melting of the Ga_2O_3 starting material (**102, 202, 302, 402, 502, 602**) adapted to minimize creation of metallic gallium amount (**CR1, CR2, CR3**) and thus eutectic formation with the metal crucible (**101, 201, 301, 401, 501, 601**) and to improve stoichiometry of the Ga_2O_3 starting material (**102, 202, 302, 402, 502, 602**) and crystal growth stability; and

   ii) maintaining the growth oxygen concentration value (**C2, C2', C2"**) within the oxygen concentration range (**SC**) during the crystal growth step of the β-Ga_2O_3 single crystal (**110, 210, 310, 410, 510, 610**) from the melt at the growth temperature (**GT**), wherein the oxygen concentration (**OC**):

   iii) does not exceed an intermediate oxygen concentration value (**C1**) in the range of 0 - 5 vol. % during the heating up step from room temperature (**RT**) to an intermediate temperature value (**T1**), intermediate temperature value (**T1**) being located within the temperature range (**ST**) between 1000 C and the melting temperature (**MT**) of Ga_2O_3;

   iv) increases from the intermediate oxygen concentration value (**C1**) to the growth oxygen concentration value (**C2, C2', C2"**) in the oxygen concentration range (**SC**) of 5 - 100 vol. % during the heating up step from the intermediate temperature value (**T1**) to the melting temperature (**MT**) of Ga_2O_3 or at the melting temperature (**MT**) or after complete melting of the Ga_2O_3 starting material (**102, 202, 302, 402, 502, 602**) if the intermediate

temperature value (**T1**) substantially equals to the melting temperature (**MT**).

2. The method according to claim 1, wherein the oxygen concentration (**OC**):
   v) decreases from the growth oxygen concentration value (**C2, C2', C2"**) to a final oxygen concentration value (**C3**) being lower than the growth oxygen concentration value (**C2, C2', C2"**) during the cooling down step from the growth temperature (**GT**) to room temperature (**RT**).

3. The method according to claim 1, wherein the growth oxygen concentration value (**C2**) is substantially constant (**10**) within the oxygen concentration range (**SC**) at the growth temperature (**GT**) during the entire crystal growth step.

4. The method according to claim 1, wherein the growth oxygen concentration value (**C2**) decreases (**10'**) to a second growth oxygen concentration value (**C2'**) within the oxygen concentration range (**SC**) at the growth temperature (**GT**) after an early stage of the crystal growth step.

5. The method according to claim 1, wherein the growth oxygen concentration value (**C2**) increases (**10"**) to a third growth oxygen concentration value (**C2"**) within the oxygen concentration range (**SC**) at the growth temperature (**GT**) at the later stage of the crystal growth step.

6. The method according to claim 1, wherein the growth oxygen concentration value (**C2**) first decreases (**10'**) to a second growth oxygen concentration value (**C2'**) within the oxygen concentration range (**SC**) at the growth temperature (**GT**) after an early stage of the crystal growth step, and increases (**10"**) to a third growth oxygen concentration value (**C2"**) within the oxygen concentration range (**SC**) at the growth temperature (**GT**) at the later stage of the crystal growth step.

7. The method according to any one of the preceding claims 1-6, wherein the growth atmosphere (**120**) is applied to the Czochralski method (**100**).

8. The method according to any one of the preceding claims 1-6, wherein the growth atmosphere (**220**) is applied to the Kyropolous method (**200**).

9. The method according to any one of the preceding claims 1-6, wherein the growth atmosphere (**320**) is applied to the vertical Bridgman or Vertical Gradient Freeze method (**300**).

10. The method according to any one of the preceding claims 1-6, wherein the growth atmosphere (**420**) is applied to the horizontal Bridgman method (**400**).

11. The method according to any one of the preceding claims 1-6, wherein the growth atmosphere (**520**) is applied to shaped crystal growth techniques selected from the group consisting of the Stepanov, Noncapillary Shaping and Edge-Defined Film-Fed Growth methods (**500**).

12. The method according to any one of the preceding claims 1-6, wherein the growth atmosphere (**620**) is applied to the Levitation Assisted Self-Seeding Crystal Growth method (**600**).

13. The method according to any one of the preceding claims 1-6, wherein the growth atmosphere is applied to the Micro-Pulling Down method.

Patentansprüche

1. Verfahren zum Züchten von Beta-Phase von Galliumoxid (β-Ga$_2$O$_3$)-Einkristallen aus der in einem Metalltiegel enthaltenen Schmelze, umfassend die Schritte:

   - Bereitstellen eines thermischen Systems oder eines Wachstumsofens (**100, 200, 300, 400, 500, 600**) in einer Wachstumskammer, umfassend einen Metalltiegel (**101, 201, 301, 401, 501, 601**), der das Ga$_2$O$_3$-Ausgangs-material (**102, 202, 302, 402, 502, 602**) enthält, eine den Metalltiegel (**101, 201, 301, 401, 501, 601**) umgebende Wärmedämmung (**103, 203, 303, 403, 503, 603**) und eine um den Metalltiegel (**101, 201, 301, 401, 501, 601**) angeordnete Heizung (**104, 204, 304, 404, 504, 604**);
   - Bereitstellen oder Erzeugen eines Kristallkeims (**105, 205, 305, 405, 505, 605**) innerhalb des Wachstumsofens

(100, 200, 300, 400, 500, 600);
- Einbringen einer sauerstoffhaltigen Wachstumsatmosphäre (120, 220, 320, 420, 520, 620) zumindest in den Wachstumsofen (100, 200, 300, 400, 500, 600);
- Erwärmen des Metalltiegels (101, 201, 301, 401, 501, 601) durch das Heizgerät (104, 204, 304, 404, 504, 604), das wiederum das Ga_2O_3-Ausgangsmaterial (102, 202, 302, 402, 502, 502, 602) bis zur Schmelze erwärmt;
- Kontaktieren des Kristallkeimes (105, 205, 305, 405, 505, 505, 605) mit dem geschmolzenen Ga_2O_3-Ausgangsmaterial (102, 202, 302, 402, 502, 602), das in dem Metalltiegel (101, 201, 301, 401, 501, 601) enthalten ist;
- Züchten eines β-Ga_2O_3-Einkristalls (110, 210, 310, 410, 510, 610) auf dem Kristallkeim (105, 205, 305, 405, 505, 605) durch Temperaturgradienten zwischen dem Kristallkeim und der Schmelze;
- Abkühlen des gezüchteten β-Ga_2O_3-Einkristalls (110, 210, 310, 410, 510, 610) auf Raumtemperatur (RT), nachdem der Kristallwachstumsschritt abgeschlossen ist;

dadurch gekennzeichnet, dass es ferner die Schritte umfasst:

i) Bereitstellen der Wachstumsatmosphäre (120, 220, 320, 420, 520, 620) mit einer variablen Sauerstoffkonzentration (OC) oder einem Partialdruck in dem Wachstumsofen (100, 200, 300, 400, 500, 600), so dass die Sauerstoffkonzentration (OC) einen Wachstums-Sauerstoffkonzentrationswert (C2, C2', C2") im Konzentrationsbereich (SC) von 5 - 100 Vol. % unterhalb (8, 9) der Schmelztemperatur (MT) von Ga_2O_3 oder bei (6, 7) der Schmelztemperatur (MP) oder nach (5) vollständigem Schmelzen des Ga_2O_3-Ausgangsmaterials (102, 202, 302, 402, 502, 602), angepasst, um die Bildung einer metallischen Galliummenge (CR1, CR2, CR3) und damit eutektische Bildung mit dem Metalltiegel (101, 201, 301, 401, 501, 601) zu minimieren und die Stöchiometrie des Ga_2O_3-Ausgangsmaterials (102, 202, 302, 402, 502, 502, 602) und der Kristallzuchtstabilität zu verbessern; und
ii) Aufrechterhalten des Wachstums-Sauerstoffkonzentrationswertes (C2, C2', C2''') innerhalb des Sauerstoffkonzentrationsbereichs (SC) während des Kristallwachstumsschritts des β-Ga_2O_3-Einkristalls (110, 210, 310, 410, 510, 610) aus der Schmelze bei der Wachstumstemperatur (GT), wobei die Sauerstoffkonzentration (OC):
iii) einen mittleren Sauerstoffkonzentrationswert (C1) im Bereich von 0 - 5 Vol. % während des Aufheizschritts von Raumtemperatur (RT) auf einen mittleren Temperaturwert (T1) nicht überschreitet, wobei der mittlere Temperaturwert (T1) innerhalb des Temperaturbereichs (ST) zwischen 1000 °C und der Schmelztemperatur (MT) von Ga_2O_3 liegt;
iv) vom mittleren Sauerstoffkonzentrationswert (C1) auf den Wachstumssauerstoffkonzentrationswert (C2, C2', C2''') im Sauerstoffkonzentrationsbereich (SC) von 5 - 100 Vol. % während des Aufheizschritts vom mittleren Temperaturwert (T1) auf die Schmelztemperatur (MT) von Ga_2O_3 oder bei der Schmelztemperatur (MT) oder nach vollständigem Schmelzen des Ga_2O_3-Ausgangsmaterials (102, 202, 302, 402, 502, 602) ansteigt, wenn der mittlere Temperaturwert (T1) im Wesentlichen der Schmelztemperatur (MT) entspricht.

2. Verfahren nach Anspruch 1, wobei die Sauerstoffkonzentration (OC):
v) vom Wachstumssauerstoffkonzentrationswert (C2, C2', C2''') auf einen Endsauerstoffkonzentrationswert (C3) abnimmt, der niedriger ist als der Wachstumssauerstoffkonzentrationswert (C2, C2', C2") während des Abkühlungsschritts von der Wachstumstemperatur (GT) auf die Raumtemperatur (RT).

3. Verfahren nach Anspruch 1, wobei der Wert der Wachstums-Sauerstoffkonzentration (C2) innerhalb des Sauerstoffkonzentrationsbereichs (SC) bei der Wachstumstemperatur (GT) während des gesamten Kristallwachstumsschrittes im Wesentlichen konstant (10) ist.

4. Verfahren nach Anspruch 1, wobei der Wachstums-Sauerstoffkonzentrationswert (C2) nach einem frühen Stadium des Kristallwachstumsschrittes innerhalb des Sauerstoffkonzentrationsbereichs (SC) bei der Wachstumstemperatur (GT) auf einen zweiten Wachstums-Sauerstoffkonzentrationswert (C2') sinkt (10').

5. Verfahren nach Anspruch 1, wobei der Wachstums-Sauerstoffkonzentrationswert (C2) innerhalb des Sauerstoffkonzentrationsbereichs (SC) bei der Wachstumstemperatur (GT) in der späteren Phase des Kristallzüchtungsschritts auf einen dritten Wachstums-Sauerstoffkonzentrationswert (C2") ansteigt (10'').

6. Verfahren nach Anspruch 1, wobei der Wachstums-Sauerstoffkonzentrationswert (C2) zunächst auf einen zweiten Wachstums-Sauerstoffkonzentrationswert (C2') innerhalb des Sauerstoffkonzentrationsbereichs (SC) bei der Wachstumstemperatur (GT) nach einem frühen Stadium des Kristallwachstumsschrittes sinkt (10") und auf einen dritten Wachstums-Sauerstoffkonzentrationswert (C2") innerhalb des Sauerstoffkonzentrationsbereichs (SC) bei der Wachstumstemperatur (GT) in dem späteren Stadium des Kristallwachstumsschrittes steigt (10'').

7. Verfahren nach einem der vorhergehenden Ansprüche 1-6, wobei die Wachstumsatmosphäre **(120)** auf das Czochralski-Verfahren **(100)** angewendet wird.

8. Verfahren nach einem der vorhergehenden Ansprüche 1-6, wobei die Wachstumsatmosphäre **(220)** auf das Kyropolous-Verfahren **(200)** angewendet wird.

9. Verfahren nach einem der vorhergehenden Ansprüche 1-6, wobei die Wachstumsatmosphäre **(320)** auf das vertikale Bridgman- oder das vertikale Gradientenfrostverfahren **(300)** angewendet wird.

10. Verfahren nach einem der vorhergehenden Ansprüche 1-6, wobei die Wachstumsatmosphäre **(420)** auf das horizontale Bridgman-Verfahren **(400)** angewendet wird.

11. Verfahren nach einem der vorhergehenden Ansprüche 1-6, worin die Wachstumsatmosphäre **(520)** auf geformte Kristallzüchtungstechniken angewendet wird, die aus der Gruppe ausgewählt sind, die aus den Stepanov-, Nicht-kapillarformungs- und Kantenformungsverfahren **(500)** besteht.

12. Verfahren nach einem der vorhergehenden Ansprüche 1-6, wobei die Wachstumsatmosphäre **(620)** auf das levitationsunterstützte selbstaussäende Kristallwachstumsverfahren **(600)** aufgebracht wird.

13. Verfahren nach einem der vorhergehenden Ansprüche 1-6, worin die Wachstumsatmosphäre auf das Micro-Pulling Down-Verfahren aufgebracht wird.

Revendications

1. Procédé de croissance d'une phase bêta de cristaux uniques d'oxyde de gallium (β-Ga_2O_3) à partir de la masse fondue contenue à l'intérieur d'un creuset métallique, comprenant les étapes consistant à :

- obtenir, dans une chambre de croissance, un système thermique ou un four de croissance **(100, 200, 300, 400, 500, 600)** comprenant le creuset métallique **(101, 201, 301, 401, 501, 601)** contenant le matériau de départ Ga_2O_3 **(102, 202, 302, 402, 502, 602)**, une isolation thermique **(103, 203, 303, 403, 503, 603)** entourant le creuset métallique **(101, 201, 301, 401, 501, 601)** et un appareil de chauffage **(104, 204, 304, 404, 504, 604)** disposé autour du creuset métallique **(101, 201, 301, 401, 501, 601)** ;
- obtenir ou créer un germe de cristal **(105, 205, 305, 405, 505, 605)** situé à l'intérieur du four de croissance **(100, 200, 300, 400, 500, 600)** ;
- introduire au moins dans le four de croissance **(100, 200, 300, 400, 500, 600)** une atmosphère de croissance **(120, 220, 320, 420, 520, 620)** contenant de l'oxygène ;
- chauffer le creuset métallique **(101, 201, 301, 401, 501, 601)** au moyen de l'appareil de chauffage **(104, 204, 304, 404, 504, 604)**, qui à son tour chauffe le matériau de départ Ga_2O_3 **(102, 202, 302, 402, 502, 602)** jusqu'à ce qu'il fonde ;
- mettre en contact le germe de cristal **(105, 205, 305, 405, 505, 605)** avec le matériau de départ Ga_2O_3 **(102, 202, 302, 402, 502, 602)** fondu contenu à l'intérieur du creuset métallique **(101, 201, 301, 401, 501, 601)** ;
- faire croître un cristal unique de β-Ga_2O_3 **(110, 210, 310, 410, 510, 610)** sur le germe de cristal **(105, 205, 305, 405, 505, 605)** au moyen de gradients de température entre le germe de cristal et la masse fondue ;
- refroidir le cristal de croissance unique de β-Ga_2O_3 **(110, 210, 310, 410, 510, 610)** à température ambiante **(RT)** une fois l'étape de croissance de cristal achevée ;

caractérisé en ce qu'il comprend en outre les étapes consistant à :

i) obtenir dans le four de croissance **(100, 200, 300, 400, 500, 600)** l'atmosphère de croissance **(120, 220, 320, 420, 520, 620)** contenant une concentration variable en oxygène **(OC)** ou une pression partielle de telle sorte que la concentration en oxygène **(OC)** atteigne une valeur de croissance de concentration en oxygène **(C2, C2', C2'')** située dans la plage de concentration **(SC)** comprise entre 5 et 100 % en volume inférieure **(8, 9)** à la température de fusion **(MT)** de Ga_2O_3 ou à **(6, 7)** la température de fusion **(MP)** ou après **(5)** fusion totale du matériau de départ Ga_2O_3 **(102, 202, 302, 402, 502, 602)** conçu pour minimiser la création d'une quantité de gallium métallique **(CR1, CR2, CR3)** et ainsi la formation eutectique avec le creuset métallique **(101, 201, 301, 401, 501, 601)** et pour améliorer la stoechiométrie du matériau de départ Ga_2O_3 **(102, 202, 302, 402, 502, 602)** et la stabilité de croissance de cristal ; et

ii) maintenir la valeur de croissance de concentration en oxygène **(C2, C2', C2")** située dans la plage de concentration **(SC)** pendant l'étape de croissance de cristal du cristal unique de β-Ga$_2$O$_3$ **(110, 210, 310, 410, 510, 610)** à partir de la masse fondue à la température de croissance **(GT)**, dans lequel la concentration en oxygène **(OC)** :

iii) ne dépasse pas une valeur intermédiaire de concentration en oxygène **(C1)** dans la gamme comprise entre 0 et 5 % en volume pendant l'étape de chauffage à partir de la température ambiante **(RT)** à une valeur de température intermédiaire **(T1)**, la valeur de température intermédiaire **(T1)** étant située à l'intérieur de la plage de température **(ST)** entre 1000 °C et la température de fusion **(MT)** de Ga$_2$O$_3$;

iv) augmente de la valeur intermédiaire de concentration en oxygène **(C1)** à la valeur de croissance de concentration en oxygène **(C2, C2', C2")** située dans la plage de concentration **(SC)** comprise entre 5 et 100 % en volume pendant l'étape de chauffage à partir de la valeur de température intermédiaire **(T1)** à la température de fusion **(MT)** de Ga$_2$O$_3$ ou à la température de fusion **(MT)** ou après fusion totale du matériau de départ Ga$_2$O$_3$ **(102, 202, 302, 402, 502, 602)** si la valeur de température intermédiaire **(T1)** est sensiblement égale à la température de fusion **(MT)**.

2. Procédé selon la revendication 1, dans lequel la concentration en oxygène **(OC)** :
v) diminue de la valeur de croissance de concentration en oxygène **(C2, C2', C2")** à une valeur finale de concentration en oxygène **(C3)** étant inférieure à la valeur de croissance de concentration en oxygène **(C2, C2', C2")** pendant l'étape de refroidissement à partir de la température de croissance **(GT)** à la température ambiante **(RT)**.

3. Procédé selon la revendication 1, dans lequel la valeur de croissance de concentration en oxygène **(C2)** reste essentiellement constante **(10)** à l'intérieur de la plage de concentration **(SC)** à la température de croissance **(GT)** pendant la totalité de l'étape de croissance du cristal.

4. Procédé selon la revendication 1, dans lequel la valeur de croissance de concentration en oxygène **(C2)** diminue **(10')** à une seconde valeur de croissance de concentration en oxygène **(C2')** située à l'intérieur de la plage de concentration **(SC)** à la température de croissance **(GT)** après un stade précoce de l'étape de croissance de cristal.

5. Procédé selon la revendication 1, dans lequel la valeur de croissance de concentration en oxygène **(C2)** augmente **(10")** à une troisième valeur de croissance de concentration en oxygène **(C2")** située à l'intérieur de la plage de concentration **(SC)** à la température de croissance **(GT)** au stade ultérieur de l'étape de croissance de cristal.

6. Procédé selon la revendication 1, dans lequel la valeur de croissance de concentration en oxygène **(C2)** diminue **(10')** à une seconde valeur de croissance de concentration en oxygène **(C2')** située à l'intérieur de la plage de concentration **(SC)** à la température de croissance **(GT)** après un stade précoce de l'étape de croissance de cristal, et augmente **(10")** à une troisième valeur de croissance de concentration en oxygène **(C2")** située à l'intérieur de la plage de concentration **(SC)** à la température de croissance **(GT)** au stade ultérieur de l'étape de croissance de cristal.

7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel l'atmosphère de croissance **(120)** est appliquée au procédé Czochralski (100).

8. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel l'atmosphère de croissance **(220)** est appliquée au procédé Kyropoulos (200).

9. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel l'atmosphère de croissance **(320)** est appliquée au procédé vertical de Bridgman ou au procédé de congélation à gradient vertical **(300)**.

10. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel l'atmosphère de croissance **(420)** est appliquée au procédé horizontal de Bridgman **(400)**.

11. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel l'atmosphère de croissance **(520)** est appliquée à des techniques de croissance de cristal façonné choisies dans le groupe constitué des procédés de Stepanov, de mise en forme non capillaire et de croissance à partir d'un film délimité par un contour **(500)**.

12. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel l'atmosphère de croissance **(620)** est appliquée au procédé de croissance de cristal à auto-amorçage assisté par lévitation **(600)**.

13. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel l'atmosphère de croissance est appliquée au procédé de micro-démolition.

Fig. 1A

Fig. 1B

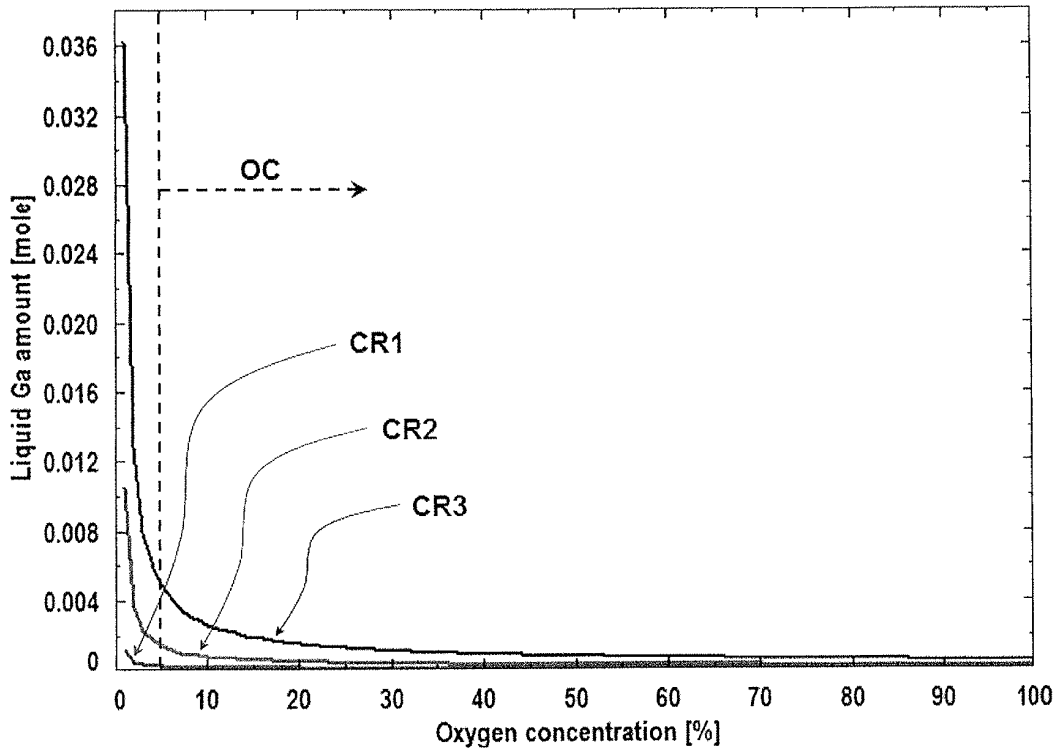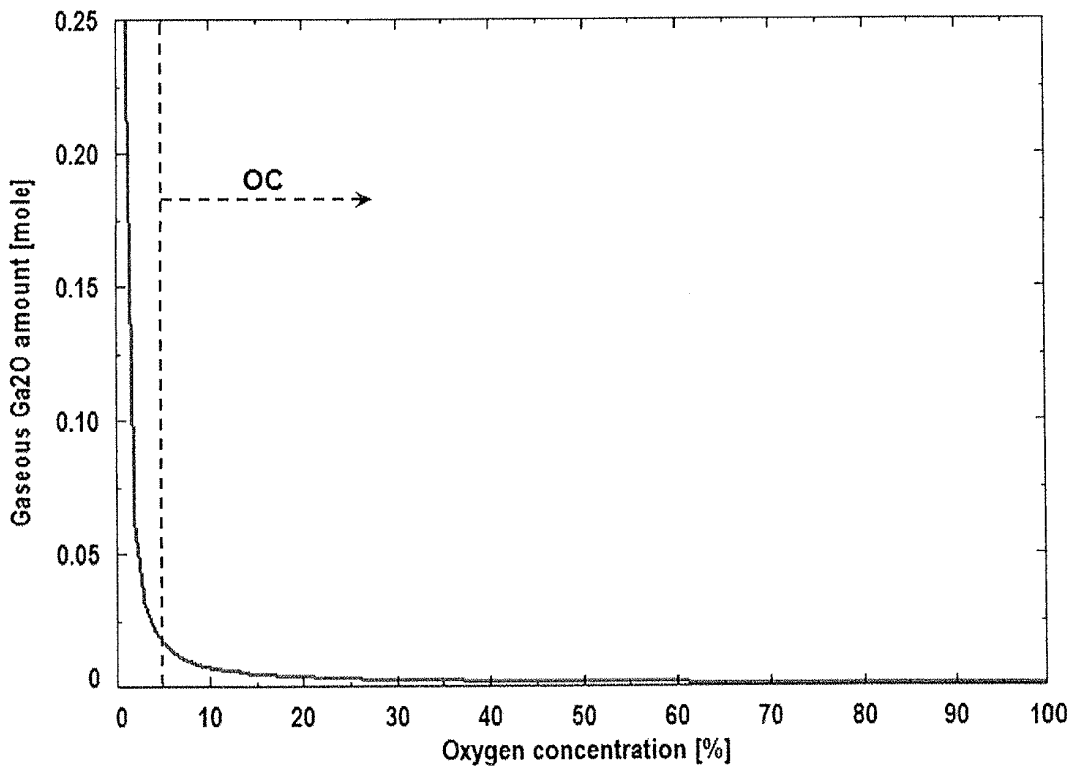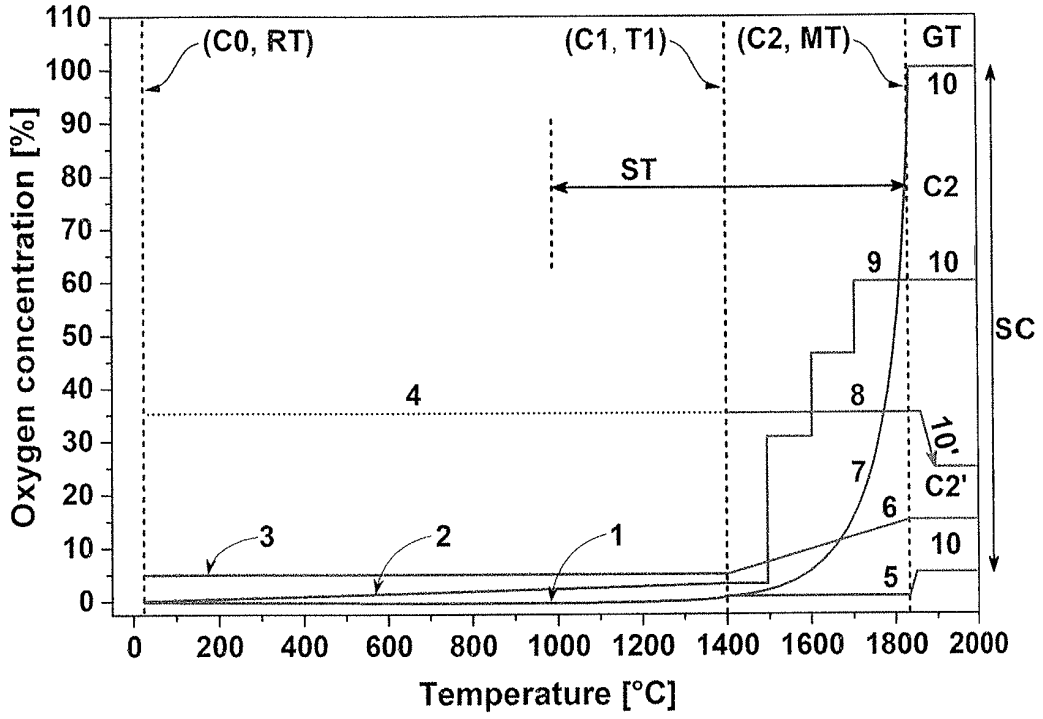**Fig. 2A**

Fig. 2B
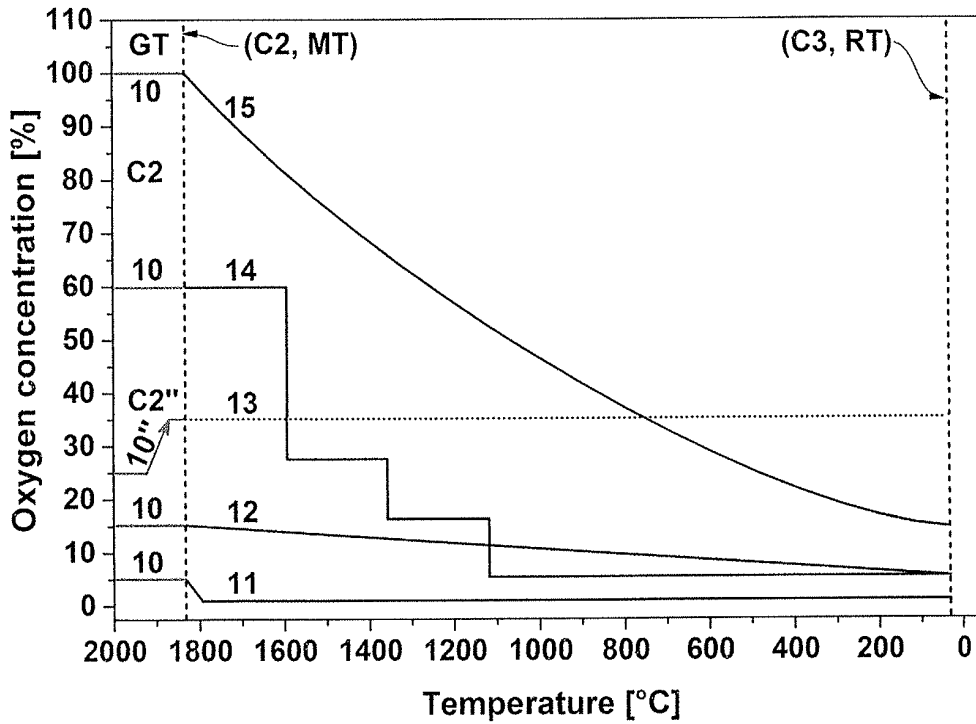
Fig. 4

Fig. 3

Fig. 5B

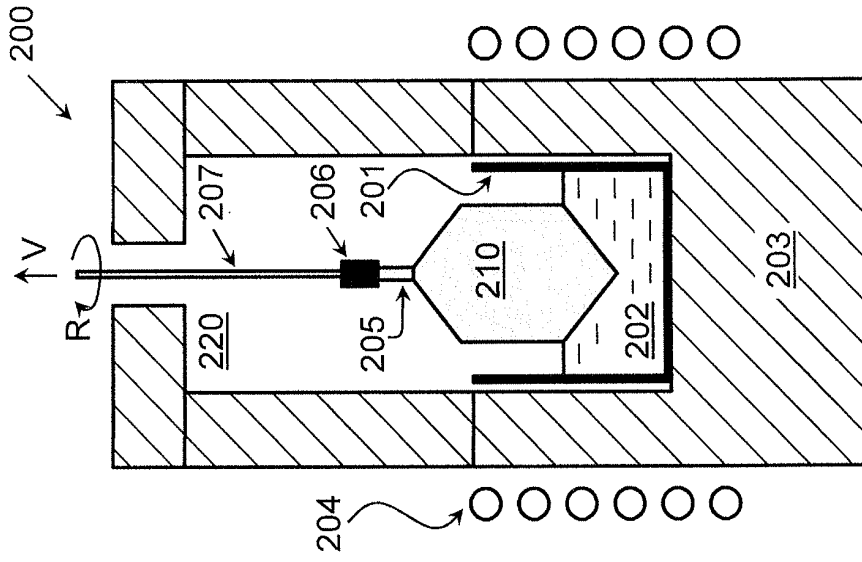Fig. 5A
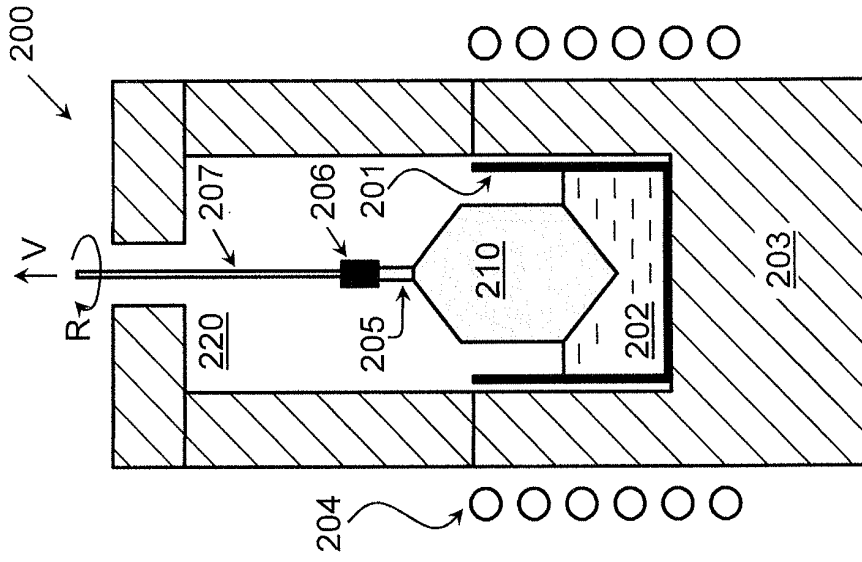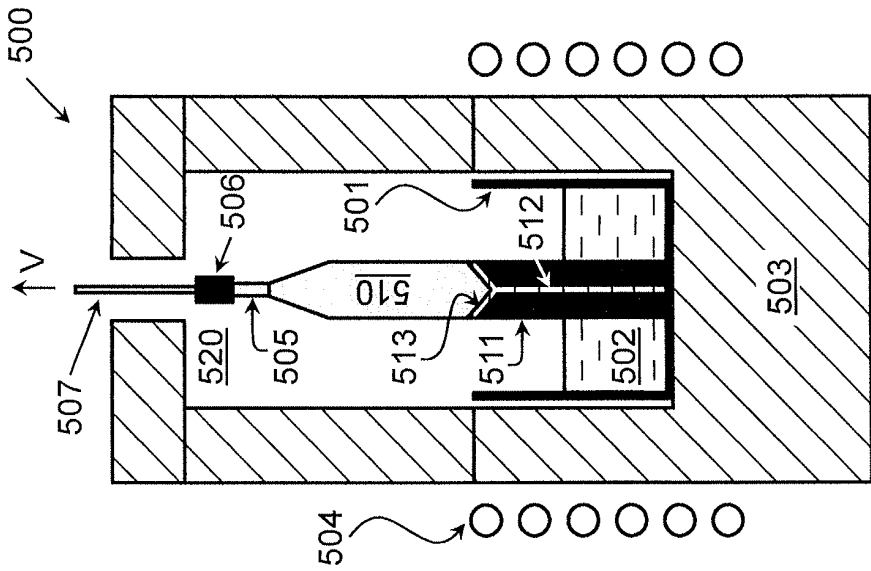
Fig. 7

Fig. 6
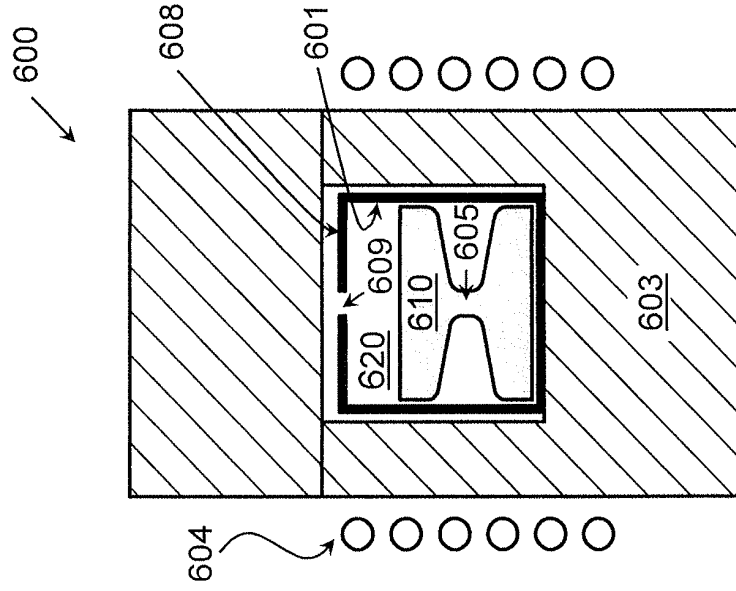
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