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(54) **Title:** MELT-GROWN BULK ß-(AlxGa1-x)2O3 SINGLE CRYSTALS AND METHOD FOR PRODUCING BULK ß-(AlxGA1-x)2O3 SINGLE CRYSTALS

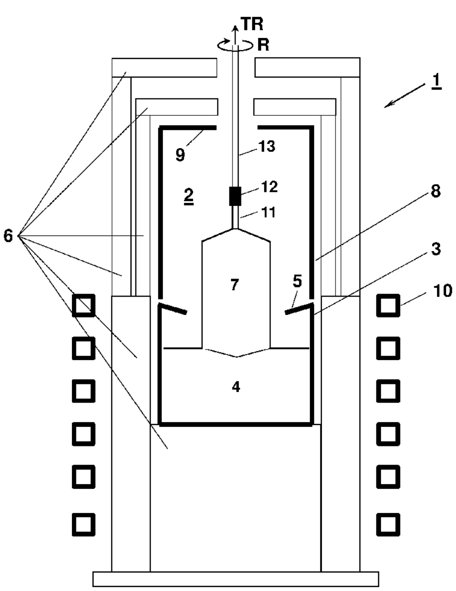

Fig. 1

(57) **Abstract:** An aluminium-containing bulk β-(AlxGa1-x)2O3 single crystal (7) directly grown from the melt with (x) between 0.1 – 0.35, that corresponds to 10 – 35 mol.% of Al. The single crystal (7) maintains its monoclinic, single crystalline structure with the following lattice parameters: a = 12.1780 – 12.0330 ± 0.015 Å, b = 3.0245 – 2.9795 ± 0.012 Å, c = 5.7870 – 5.7280 ± 0.012 Å, and β = 103.905 – 104.046 ± 0.01°, and has a volume of at least 5 cm3, preferably at least 100 cm3. The energy gap of the single crystal (7) increases in relation to pure β-Ga2O3 by 0.2 – 0.8 ± 0.05 eV for x = 0.1 – 0.35 for polarizations parallel to main crystallographic direction along the a-, b-, and c-axis. The bulk β-(AlxGa1-x)2O3 single crystal (7) can be an electrical insulator or semi-insulator, semiconductor, or degenerate semiconductor. Also, a method for producing aluminium-containing, bulk β-(AlxGa1-x)2O3 single crystal (7) directly grown from the melt, in particular from the melt contained within a metal crucible (3) is provided.

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MELT-GROWN BULK β-$(Al_xGa_{1-x})_2O_3$ SINGLE CRYSTALS AND METHOD FOR PRODUCING BULK β-$(Al_xGa_{1-x})_2O_3$ SINGLE CRYSTALS

TECHNICAL FIELD

The present invention relates to aluminium-containing, bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals directly grown from the melt, which are electrically insulating, semi-insulating, semiconducting, or degenerately semiconducting. The invention also relates to a method for producing aluminium-containing, bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals that are directly grown from the melt, especially from the melt contained within a metal crucible.

BACKGROUND OF THE INVENTION

Beta-phase of Ga_2O_3 (β-Ga_2O_3) is an emerging ultra-wide band gap n-type oxide semiconductor with high potential for UV optoelectronic and high power electronic applications. This is the result of a wide energy gap of 4.85 eV that makes that compound transparent down to UV spectral region and high theoretical breakdown field of 8 MV/cm.

For devices bulk single crystals are required, which serve as substrates for epitaxial layers and then device structure fabrication thereon. Although foreign substrates can be used for such purposes, they usually deteriorate the quality of the layers and consequently a device performance, due to the lattice mismatch between the substrate and the layer. For that reason, native substrates are demanded.

β-Ga_2O_3 – based power devices, such as Schottky diodes and field effect transistors (FETs) can be economically efficient in terms of energy saving and energy management. They can find applications in a number of industrial areas, such as mobile transportation, including electric cars, aircrafts, and vessels, as well as railways, or power grids. Generally, power switching devices can be designed in two configurations: lateral (planar) and vertical. In the lateral configuration, the substrate is electrically insulating and acts as a support for the layer with all contacts thereon, e.g. source, drain, and gate contacts in the FET device. In the vertical configuration, the substrate is highly conducting and acts as an electrical contact in addition to support the epitaxial layer. The devices in the vertical configuration can switch higher voltages as compared with the lateral configuration.

For high volume crystal production melt-grow methods are typically utilized, where a starting material is first molten within a noble metal crucible, which is then crystallized on a crystal seed. The melt-grow methods utilizing the metal crucible include the methods developed by Czochralski, Kyropolous, Bridgman method and the Vertical Gradient Freeze (VGF) method. The edge-defined film-fed growth (EFG) method is the most widely use technique in the group of shaped methods.

The Czochralski method offers the possibility of growing cylindrical bulk β-Ga_2O_3 single crystals of large volume and high structural quality. Two inch diameter electrically insulating, semiconducting, or degenerately semiconducting bulk β-Ga_2O_3 single crystals grown by the Czochralski method are for instance shown in the paper of Galazka entitled “Growth of bulk β-Ga_2O_3 single crystals by the Czochralski method”, J. Appl. Phys. 131 (2022) 031103, and Galazka et al. – “Two inch diameter, highly conducting bulk β-Ga_2O_3 single crystals grown by the Czochralski method”, Appl. Phys. Lett. 120 (2022) 152101. To grow such large crystals, a high oxygen partial pressure in a growth atmosphere is required to minimize the formation of elemental Ga in the Ga_2O_3 melt, that have a high, negative impact on the growth process, the crucible lifetime and the crystal quality. This requirement is necessary for all melt growth methods used for β-Ga_2O_3 single crystals that involve a noble metal crucible, as taught by Galazka et al. in patent descriptions No. EP 3,242,965 B1 and US 11,028,501 B2.

The Bridgman or VGF method also enable the growth of bulk β-Ga_2O_3 single crystals of two inch diameter as e.g. described by K. Hoshikawa et al. in the papers entitled “2-inch diameter (100) β-Ga_2O_3 crystal growth by the vertical Bridgman technique in a resistance heating furnace in ambient air”, J. Cryst. Growth, 545 (2020) 125724, “50 mm diameter Sn-doped (001) β-Ga_2O_3 crystal growth using the vertical Bridgeman technique in ambient air”, J. Cryst. Growth 546 (2020) 125778, and the patent document No. US10,570,528 B2, as well as by Galazka et al. in the paper entitled “Scaling-Up of Bulk β-Ga_2O_3 Single Crystals by the Czochralski Method”, ECS J. Solid State Sci. Technol. 6 (2017) Q3007-Q3011, and in the above-mentioned patent documents Nos. EP 3,242,965 B1 and US 11,028,501 B2.

The EFG method enables to grow bulk β-Ga_2O_3 single crystals in the form of slabs or sheets, which facilitate to fabricate wafers of large size (up to 6 inch in diameter) although the overall crystal volume is smaller than that grown by the Czochralski method. Examples of this method in relation to bulk β-Ga_2O_3 single crystals are disclosed in the paper to A. Kuramata et al. entitled “High-quality β-Ga_2O_3 single crystals grown by edge-defined film-fed growth”, Jpn. J. Appl. Phys. 55 (2016)

1202A2, and in the patent / patent application documents: WO 2013/172227 A1 (corresponding JP 6,421,357 B2), WO 2013/073497 A1 (corresponding JP 5,491,483 B2; EP 2,801,645 B1), WO 2014/073314 A1 (corresponding JP 5,756,075 B2, EP 2,933,359 B1, US 9,926,646 B2), WO 2014/185302 (corresponding JP 5,865,867 B2, US 9,915,009 B2), WO 2014/185304 (corresponding JP 5,836,999 B2, EP 3,006,607 B1, US 9,915,010 B2) and WO 2014/163056 (corresponding JP 5,788,925 B2, EP 2,990,509 B1, US 10,526,721 B2).

To further increase the breakdown field enabling switching higher voltages, which is directly correlated with the energy gap, solid-solution β-Ga_2O_3 – Al_2O_3 single crystals were proposed in the art, as the energy gap of Al_2O_3 is close to 9 eV. Also, the melting point of Al_2O_3 is higher than that of β-Ga_2O_3 by about 260 K. Solid-solution β-Ga_2O_3 – Al_2O_3 systems can be described as β-$(Al_xGa_{1-x})_2O_3$. Because of different crystal systems of β-Ga_2O_3 (monoclinic) and Al_2O_3 (hexagonal), the solubility of Al_2O_3 in Ga_2O_3 is limited to about 50 mol.%. A large gap between liquidus and solidus in the β-Ga_2O_3 – Al_2O_3 systems and the increasing growth temperature makes the growth of large β-$(Al_xGa_{1-x})_2O_3$ single crystals difficult. In fact, the state of the art demonstrated the growth of β-$(Al_xGa_{1-x})_2O_3$ single crystals from the melt contained within a metal crucible with up to x = 0.1 (10 mol.% of Al). For instance, Galazka et al. in the papers entitled “Czochralski-grown bulk β-Ga_2O_3 single crystals doped with mono-, di-, tri-,and tetravalent ions”, J. Cryst. Growth 529 (2020) 125297; “Bulk β-Ga_2O_3 single crystals doped with Ce, Ce+Si, Ce+Al, and Ce+Al+Si for detection of nuclear radiation”, J. Alloy. Compd. 818 (2020) 152842; and “Two inch diameter, highly conducting bulk β-Ga_2O_3 single crystals grown by the Czochralski method”, Appl. Phys. Lett. 120 (2022) 152101, demonstrated the grow of bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals with x = 0.05 (5 mol.%) by the Czochralski method, including two inch diameter ones. The crystals were either electrically insulating, semiconducting, or degenerately semiconducting. Bauman et al. in the paper entitled “High-Quality Bulk β-Ga_2O_3 and β-$(Al_xGa_{1-x})_2O_3$ Crystals: Growth and Properties”, Phys. Status Solidi A 218 (2021) 2100335 discussed Czochralski-grown β-$(Al_xGa_{1-x})_2O_3$ crystals with x = 0.075, while Jesenovec et al. in the paper entitled “Alloyed β-$(Al_xGa_{1-x})_2O_3$ bulk Czochralski single β-$(Al_{0.1}Ga_{0.9})_2O_3$ and polycrystals β-$(Al_{0.33}Ga_{0.66})_2O_3$, β-$(Al_{0.5}Ga_{0.5})_2O_3$, and property trends”, J. Appl. Phys. 131 (2022) 155702, demonstrated the growth of bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals by the Czochralski method with x = 0.1, but higher Al concentrations resulted in polycrystals, not usable for any electronic applications. In both cases the crystals were electrically insulating.

Because of lack of bulk single crystals with yet higher Al content in the monoclinic β-Ga_2O_3 system, thin films demonstrated so far were grown heteroepitaxially on pure β-Ga_2O_3. However, all lattice constants of β-$(Al_xGa_{1-x})_2O_3$ shrink with Al content, and the lattice mismatch between the film and the substrate increases. As the result, the films are of poor structural quality, full of structural defects, often polycrystalline and/or cracked. Such structures are not suitable for fabrication electronic devices.

Therefore, there is a high demand on bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals with $x \geq 0.1$ ($\geq$ 10 mol.% of Al), that are of high structural quality and large volume, enabling wafer preparation for homoepitaxial growth of β-$(Al_xGa_{1-x})_2O_3$ films and electronic device fabrication.

SUMMARY OF THE INVENTION

The first object of the present invention is to provide bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals with $x \geq 0.1$ ($\geq$ 10 mol.% of Al) of high structural quality and large size, that are suitable for wafer fabrication to be used for homoepitaxial growth of thin films of the same composition.

The second object of the present invention is to provide bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals with $x \geq 0.1$ ($\geq$ 10 mol.% of Al) which are either electrically insulating (or semi-insulating), or semiconducting, or degenerately semiconducting, suitable for electronic devices in the lateral and vertical configurations.

The third object of the present invention is to provide a method for producing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals with $x \geq 0.1$, which are directly grown from the melt contained within a metal crucible, having large size, high structural quality, and tuneable electrical properties.

According to the first and second aspect of the invention, an aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal directly grown from the melt is provided. The aluminium content (x) in the obtained single crystal is between 0.1 – 0.35, that corresponds to 10 – 35 mol.% of Al, while the crystal maintains its monoclinic, single crystalline structure with the following lattice parameters a = 12.1780 – 12.0330 $\pm$ 0.015 Å, b = 3.0245 – 2.9795 $\pm$ 0.015 Å, c = 5.7870 – 5.7280 $\pm$ 0.015 Å, and the angle between a- and c-axis, β = 103.905 – 104.040 $\pm$ 0.015°, while the volume of the single crystal is at least 5 cm^3. Such crystal composition and crystal size will allow to fabricate substrates for homoepitaxial growth of thin films having the same or similar composition, i.e. a wide range of Al content while keeping high structural quality due to perfect lattice match between the substrate and the film.

Preferably, the measured energy gap of β-$(Al_xGa_{1-x})_2O_3$ single crystal is larger in relation to pure β-Ga_2O_3 by 0.2 – 0.8 ± 0.05 eV for x = 0.1 – 0.35 and polarizations parallel to main crystallographic direction along the a-, b-, and c-axis.

In a preferred embodiment the bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal is a semiconductor with the free electron concentration of 1 – 5×10^{17} cm^{-3}, electron mobility of 40 – 80 $cm^2V^{-1}s^{-1}$, and resistivity of 0.1 – 1 Ωcm, as measured by the Hall effect. In another preferred embodiment, the bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal is intentionally co-doped with at least one of tetravalent ions selected from the group consisting of Si^{4+} and Sn^{4+} at concentration of 10^{18} – 10^{19} cm^{-3}, and it constitutes a semiconductor or degenerated semiconductor with the free electron concentration of 1×10^{17} – 5×10^{18} cm^{-3}, electron mobility of 10 – 60 $cm^2V^{-1}s^{-1}$, and resistivity of 0.02 – 2 Ωcm, as measured by the Hall effect. Co-doping with tetravalent ions enables to tune electrical properties of the crystal in a wider range, in particular, it allows to achieve high electrical conductivity suitable for electronic devices in the vertical configuration.

In an alternative embodiment, the bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal is intentionally co-doped with at least one of divalent ions selected from the group consisting of Mg^{2+}, Co^{2+}, and Ni^{2+} at concentration of 10^{17} – 10^{18} cm^{-3}, and it constitutes an electrical insulator or semi-insulator with the electrical resistivity of at least 10^8 Ωcm. This solution provides single crystals suitable for electronic devices in the lateral configuration.

Advantageously, the bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal has a volume of at least 5 cm^3, preferably at least 100 cm^3. Large crystal volume enables a fabrication of a number of substrates for homoepitaxial growth and significantly lowers production costs.

Preferably, the bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal is fabricated into wafers for homoepitaxial growth of thin films, wherein the wafers have the full width at half maximum (FWHM) of the rocking curve is between 10 – 100 arcsec. High structural quality of the wafers enables high structural quality of thin films deposited thereon, and good electrical properties suitable for electronic device fabrication of high performance.

According to the third aspect of the invention, a method for producing aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal directly grown from the melt contained within a metal crucible is provided. The method comprises the steps of:

- providing into a growth chamber a thermal system or growth furnace (1) comprising the metal crucible containing a starting material consisting of Ga_2O_3 + Al_2O_3, a thermal insulation surrounding the metal crucible, and a heater disposed around the metal crucible and thermal insulation;

- providing a crystal seed within the growth furnace;

- introducing 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 + Al_2O_3 starting material until melting;

- contacting the crystal seed with the molten Ga_2O_3 + Al_2O_3 starting material contained within the metal crucible;

- growing a β-$(Al_xGa_{1-x})_2O_3$ single crystal on the crystal seed by temperature gradients between the crystal seed and the melt;

- cooling down the grown β-$(Al_xGa_{1-x})_2O_3$ single crystal to room temperature once the crystal growth step has been completed.

In this method, the provided Ga_2O_3 + Al_2O_3 starting material for growing β-$(Al_xGa_{1-x})_2O_3$ single crystal contains 9 – 30 mol.% of Al_2O_3 corresponding to (x) = 0.09 – 0.30, the oxygen concentration in the growth atmosphere is between 0.5 – 25 vol.%, while the crystal seed contacting the melt has a composition of β-$(Al_xGa_{1-x})_2O_3$ with (x) = 0.1 – 0.30 ± 0.1, preferably with (x) = 0.1 – 0.30 ± 0.05. Due to segregation coefficient of Al in the $(Al_xGa_{1-x})_2O_3$ melt of 1.1 – 1.2, the obtained β-$(Al_xGa_{1-x})_2O_3$ single crystal results in (x) = 0.1 – 0.36. The method enables to provide large crystal volume or size of high structural quality and yield, and thus to produce a number of wafers or substrates suitable for homoepitaxial growth of thin films having in a wide range of Al content, while keeping low production costs.

Preferably, the oxygen in the growth atmosphere is decreased to a value of 0 – 0.5 vol.% at the end of crystal growth or during cooling down of the grown aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal at a heating power of 50 – 97 % in relation to a heating power at crystal seeding. More preferably, the oxygen in the growth atmosphere is switched-off during cooling down of the grown aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal, most preferably, just after completing of the growth. Such solution constitutes an additional tool for tuning electrical properties of obtained single crystals to some extent, especially by reducing the formation of gallium vacancies in the single crystals.

In a preferred embodiment, Al_2O_3 in the starting material is selected from the group consisting of an Al_2O_3 powder mixed with a Ga_2O_3 powder, an Al_2O_3 layer deposited, at least partly, on the inner surface of the metal crucible, or a combination thereof. Al_2O_3 in the form of the powder enables easy preparation of the starting material, while in the form of the deposited layer partly protects metal crucible from oxidation, extend crucible lifetime, and minimizes contamination of obtained crystals with crucible metal element as the result of oxidation.

Advantageously, the starting material additionally contains at least one oxide of a tetravalent ion selected from the group consisting of SiO_2 and SnO_2 at concentration of 0.05 – 3 mol.% to enhance the electrical conductivity, or at least one oxide of a divalent ion selected from the group consisting of MgO, CoO, and NiO at concentration of 0.05 – 2 mol.% to compensate the electrical conductivity. Intentional co-dopants have a strong impact on the electrical properties of obtained bulk single crystals, either by enhancing the electrical conductivity, or by compensating the electrical conductivity.

Preferably, the pressure in the growth chamber is selected from the group consisting of atmospheric pressure, underpressure down to 0.01 bar, or overpressure up to 100 bar. Such solution provides a tool to control, to some extent, the growth temperature, and thermal decomposition of Ga_2O_3.

In a preferred embodiment, the aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal is grown by the Czochralski method, the Kyropolous method, by a shaped technique selected from the group consisting of Stepanov, Noncapillary Shaping, and Edge-Defined Film-Fed Growth methods, or their modifications, the Bridgman or Vertical Gradient Freeze method, or the horizontal Bridgman method. The growth technique according to the teaching of the present invention enables to utilize all melt growth methods known in the state of the art. In addition to the methods involving a metal crucible, also other melt growth methods can be applied, in particular methods free of metal crucibles, such as Verneuil, optical floating zone, and cold crucible methods while keeping substantially the same physical properties of the single crystals. Also, non-metal crucibles, like alumina or sapphire can be used in a combination with resistive heating instead of inductive heating.

More advantages and other features of the inventive material and method for producing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals or other solid-solution oxide single crystals will be apparent from the detailed description of the embodiments in reference to the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic growth furnace for oxide single crystals grown by the Czochralski method in a cross-sectional view;

Figure 2 shows a change of lattice constants of bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals; and

Figure 3 shows a change of the energy gap of bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals.

DETAILED DESCRIPTION OF THE EMBODIMENTS

The thermal system or growth furnace **1** shown in Fig. 1 is adapted for growing bulk oxide single crystals by the Czochralski method in general, and in particular for growing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals. The growth furnace **1** is accommodated within a water-cooled growth chamber (not shown) to which a pre-defined growth atmosphere **2** is introduced. The growth furnace **1** consists of a noble metal crucible **3** containing a β-$(Al_xGa_{1-x})_2O_3$ starting material **4**, preferably with a metal lid **5** thereon, and a thermal insulation **6** surrounding the metal crucible **3** from all sides. Above the crucible there is a free space (growth zone) that accommodates a growing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal **7**. The growth furnace **1** further includes a metal afterheater **8** with a metal lid **9** to assure low temperature gradients in the growth zone. The noble metal crucible **3** is heated by a heater **10** preferably inductively by an RF coil situated outside the thermal insulation **6** and powered by a RF generator (not shown). Instead of an RF heater, a resistive heater can also be utilized as well. The bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal **7** is grown on a crystallographically oriented β-$(Al_xGa_{1-x})_2O_3$ crystal seed **11** that is fixed to a seed holder **12** connected to a pulling rod **13**. The pulling rod **13** is connected to a pulling and rotation mechanisms (not shown) for translating **TR** and rotating **R** the growing β-$(Al_xGa_{1-x})_2O_3$ single crystal **7**, and to a scale (not shown) for weighting the growing β-$(Al_xGa_{1-x})_2O_3$ single crystal **7**. Alternatively, the scale is coupled with the growth furnace **1**. In each case, the scale indicates the growth rate of the growing single crystal **7** by weighting directly the crystal mass or a mass difference between the furnace **1** and the growing crystal **7**. A signal from the scale is coupled to a controller that controls the generator power, and thus the melt temperature.

The thermal insulation **6** is a refractory material that withstands high temperatures, depending on the melting point of an oxide crystal to be grown. The melting point of $(Al_xGa_{1-x})_2O_3$ increases from about 1800°C for **x** = 0 to about

1900°C for **x** = 0.35. The thermal insulation **6** typically includes alumina and/or zirconia tubes, granules, felts, and possible quartz tubes on outer parts of the growth furnace **1**. The aim of the thermal insulation **6** is to decrease heat losses and establish pre-defined temperature gradients in the metal crucible **3** and in the growth zone to minimize thermal stresses and associated structural and point defects in the growing crystal **7**, as well as to minimize melt decomposition.

The noble metal crucible **3** for growing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals is iridium or its alloys, like iridium-platinum alloy. Such crucible materials can withstand growth temperatures of β-$(Al_xGa_{1-x})_2O_3$.

The starting material **4** typically consists of mixed Ga_2O_3 and Al_2O_3 powders of high purity (minimum 4N, preferably 5N) with a pre-defined molar composition. Prior mixing the powders are dried to remove any moisture and possible carbonates. After mixing the powders can be pressed to decrease its volume, and preferably sintered. Instead of powder, previously solidified β-$(Al_xGa_{1-x})_2O_3$ can be used as the starting material **4**, for instance previous crystals. In an alternative solution, at least part of the inner surface of the noble metal crucible **3** is coated with an Al_2O_3 (alumina or sapphire) layer of a predefined amount **x**, which reacts with the Ga_2O_3 powder in the metal crucible **3** at high temperatures and forms $(Al_xGa_{1-x})_2O_3$ starting material **4**. Al_2O_3 layer as the Al_2O_3 source can be used alone, or in a combination with Ga_2O_3 + Al_2O_3 powders in such a way that Al_2O_3 content in both the layer and powder corresponds to the predefined content **x**.

The growth atmosphere **2** for growing the β-$(Al_xGa_{1-x})_2O_3$ single crystal **7** contains oxygen at concentration of minimum 0.5 vol.% for crystal diameter below 1 inch, and at least 5 vol.%, preferably between 5 – 25 mol.% for a crystal diameter of 2 inch and larger (such as 3 – 6 inch diameter), which is mixed with at least one another non-reducing gas, like Ar, N_2, CO_2, He, Xe, and Ne, as described in the patent No. US 11,028,501 B2 to Galazka et al., incorporated here as a reference. The growth atmosphere **2** for growing the β-$(Al_xGa_{1-x})_2O_3$ single crystal **7** can be lower as compared with pure β-Ga_2O_3 due to better thermal stability.

As the result of differences in chemical composition and lattice constants between β-$(Al_xGa_{1-x})_2O_3$ and β-Ga_2O_3 the crystal seed **11** should have a composition similar to the composition of the grown crystal **7** with a deviation not higher than 10 mol.% of Al (**x** = 0.1), preferably not higher than 5 mol.% of Al (**x** = 0.05). So, the seed composition can be described as β-$(Al_xGa_{1-x})_2O_3$ with **x** = 0 – 0.3 ± 0.1. The effective segregation coefficient for Al in the Ga_2O_3 melt is between 1.1 – 1.2 for x = 0 – 0.3 meaning that the Al content in β-$(Al_xGa_{1-x})_2O_3$ is higher in the crystal **7** than that in the starting material **4**. The differences increase with Al content. For instance, to produce β-$(Al_xGa_{1-x})_2O_3$ single crystals with **x** = 0.1 and 0.35, the melt composition contains **x** = 0.09 and 0.3, respectively. Taking this into the account, the Al content in the crystal seed **11** is more preferably higher than that in the starting material **4** by 1 – 5 mol.% for **x** = 0.09 – 0.3 in the starting material **4**. The crystal seed **11** is preferably crystallographically oriented along the [010] direction, parallel to both easy (100) and (001) cleavage planes that are present in the monoclinic system of β-$(Al_xGa_{1-x})_2O_3$. Other seed orientations inclined to the [010] direction, e.g. [110], can be used as well.

A crystal growth process is as follows. After assembling the growth furnace **1**, the noble metal crucible **3** with the starting material **4** is heated up by the RF heater **10** (e.g. for 5 to 20 h) until melting the β-$(Al_xGa_{1-x})_2O_3$ starting material **4**. Once the $(Al_xGa_{1-x})_2O_3$ melt is thermally and chemically homogenized, the oriented β-$(Al_xGa_{1-x})_2O_3$ crystal seed **11** is dipped into the β-$(Al_xGa_{1-x})_2O_3$ melt while rotating at the rotation rate **R**. Next, the oriented β-$(Al_xGa_{1-x})_2O_3$ crystal seed **11** is pulled upwards at the translation rate **TR** while expanding its diameter to a predefined cylindrical diameter, by a gradual decrease of the melt temperature via the RF generator. When the crystal achieves a pre-defined cylindrical length, it is separated from the melt, slowly cooled down to room temperature (e.g. for 10 – 30 h depending on the crystals size), and removed from the growth furnace **1**. Just after crystal separation, or during cooling down of the grown aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal **7**, oxygen concentration in the growth atmosphere **2** is preferably decreased to a low level or entirely switched-off, to minimize the formation of gallium vacancies that compensates the electrical conductivity to some extent. The oxygen in the growth atmosphere **2** is therefore decreased to a value of 0 – 0.5 vol.% at a heating power of 50 – 97 % in relation to a heating power at the seeding step.

Although the exemplary growth of bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals is described in relation to the Czochralski method, other melt growth techniques involving noble metal crucibles can be utilized, as for instance those shown in the patent No. US 11,028,501 B2 to Galazka et al., incorporated here as a reference. These methods include the Kyropolous method, Vertical or Horizontal Bridgman method, Vertical Gradient Freeze method, and shaped crystal growth techniques in general, such as the Stepanov, Noncapillary Shaping, and Edge-Defined Film-Fed Growth (EFG) methods, and their modifications. Although the main furnace components and growth process remain substantially the same, these methods differ in arrangement, geometry, growth conditions and operating parameters, the way of growth control, and the direction of the crystallization. For instance, in the Vertical Bridgman and Vertical Gradient Freeze methods a seed is located at the bottom part of a crucible and the growth proceeds on the top of the seed either by moving the crucible towards lower temperatures, or changing the heating power. In the EFG method, a shaper is disposed within the metal crucible, which transports the melt to the top of the shaper via capillary forces, and the crystal is pulled up from a shallow basin of the melt on the top of the shaper. In all of these methods the pressure in a growth chamber can be atmospheric pressure, lower than the atmospheric pressure (underpressure), preferably down to 0.01 bar to decrease the growth temperature, or higher than the atmospheric pressure (overpressure), preferably up to 100 bar to minimize the thermal decomposition of Ga_2O_3. It is also obvious for those skilled in the art that yet other melt growth methods can be applied for growing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals according to the teaching of the present invention, in particular crucible-free methods, such as Verneuil method, optical floating zone method, and cold crucible (also called skull melting) method. The cold crucible method can be carried out either without a crystal seed, or with a crystal seed that is dipped into the melt from the top, which is then pulled up in the same way as in the Czochralski method. Although in these methods there is no metal crucible, physical properties of the bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals are substantially the same as those grown from a metal crucible, because they constitute intrinsic properties. The lack of the metal crucible enables to use any oxygen concentration, up to 100 vol.%, including underpressure or overpressure, in the same way as in the case of melt growth methods involving the metal crucible. In yet alternative solutions when using the above-mentioned melt-growth methods, non-metal crucibles, such as alumina or sapphire can be used in a combination with resistive heating instead of inductive heating typically utilized for metal crucibles. Here, the alumina or sapphire crucible can act as a source for Al_2O_3, that reacts with Ga_2O_3.

The crystal size or volume is important for industrial applications, to provide a number of wafers (substrates) from one crystal and minimize the costs per volume unit. The crystal shape and volume depend on the growth method and the growth furnace. The methods may provide crystal slabs (horizontal Bridgman and EFG methods) or cylindrical crystals (other, above-listed methods). Preferably, the crystal volume is at least 5 cm^3, more preferably at least 10 cm^3, most preferably at least 100 cm^3.

Obtained bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals have a monoclinic system, wherein all lattice constants “a”, “b”, and “c” decrease with Al content, as shown in Fig. 2:

a = 12.2289 – 12.0330 ± 0.015 Å, b = 3.04 – 2.9795 ± 0.015 Å, and c = 5.8074 – 5.7280 ± 0.015 Å for **x** = 0 – 0.35, and a = 12.1780 – 12.0330 ± 0.015 Å, b = 3.0245 – 2.9795 ± 0.012 Å, and c = 5.7870 – 5.7280 ± 0.012 Å, for **x** = 0.1 – 0.35. As the result of the lattice shrinkage, the angle β between a- and c-axis of the monoclinic system increase from 103.849 to 104.040 ± 0.015° for **x** = 0 – 0.35, and from 103.905 to 104.040 ± 0.015° for **x** = 0.1 – 0.35. They define a real crystal structure of β-$(Al_xGa_{1-x})_2O_3$ single crystals which enable to select a proper crystal composition for substrates to be used for homoepitaxial growth of β-$(Al_xGa_{1-x})_2O_3$ thin films of the same or similar composition. Lattice match between the substrate and the epitaxial thin film is critical for obtaining high structural quality thin films with good electrical properties, and thus electronic devices of high performance. It is known in the state of the art that β-$(Al_xGa_{1-x})_2O_3$ thin films grown heteroepitaxially on pure β-Ga_2O_3 are structurally deteriorated, often cracked, have low crystallinity, and even contain other phases. Therefore, the availability of substrates with a composition that match the composition of the thin films is crucial in developing electronic devices, like power field-effect transistors at industrial scale. In addition, for homoepitaxial growth of β-$(Al_xGa_{1-x})_2O_3$ thin films, the substrates should be of high structural quality to avoid deterioration of thin films in terms of structural defects and electrical properties. In particular, the substrates should be free from twins and low-angle grain boundaries. One of the main parameters defining the structural quality of the substrates is X-ray rocking curve, and its full-width at half maximum (FWHM). Bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals according to the present invention have high structural quality defined by narrow FWHM values, between 10 – 100 arcsec for the whole Al doping range of 0 – 35 mol.%, therefore the fabricated substrates assure high structural quality of homoepitaxial thin films grown thereon.

As the result of the incorporation of Al into the β-Ga_2O_3 crystal lattice, the energy gap of β-$(Al_xGa_{1-x})_2O_3$ single crystals increases with Al content, as demonstrated in Fig. 3, for two different polarization, parallel to b- and c-axis of the monoclinic system. It also increases in the same manner for polarization parallel to other crystallographic axes, including a-axis (not shown). In relation to pure β-Ga_2O_3, the energy gap increases by 0.8 ± 0.05 eV at **x** = 0.35, while for the range **x** = 0.1 – 0.35, the energy gap increases by 0.2 – 0.8 ± 0.05 eV. The larger the energy gap, the larger the critical electric field (scales with the energy gap in power 2.5), which will enable switching higher voltages before breakdown.

The demanded electrical state of bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal depends on applications. For instance, substrates for powder devices in the lateral configuration should be electrically insulating or semi-insulating, while for powder devices in the vertical configuration they should be semiconducting or degenerately semiconducting. Bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals according to the teaching of the present invention enable all demanded electrical states. Bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals (**x** = 0 – 0.35) with no intentional co-dopants are semiconductors with the free electron concentration of 2.5×10^{16} – 5×10^{17} cm^{-3}, electron mobility of 40 – 160 $cm^2V^{-1}s^{-1}$, and resistivity of 0.1 – 1.5 Ωcm as measured by the Hall effect. For **x** = 0.1 – 0.35 in bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals, the free electron concentration = 1 – 5×10^{17} cm^{-3}, electron mobility of 40 – 80 $cm^2V^{-1}s^{-1}$, and resistivity of 0.1 – 1 Ωcm, as measured by the Hall effect. To further increase the electrical conductivity the crystals can be intentionally co-doped with tetravalent ions, such as Si^{4+} and Sn^{4+} at concentration around or above 10^{18} cm^{-3}, preferably between 10^{18} – 10^{19} cm^{-3}. Such concentration can be achieved by adding to the starting material **4** SiO_2 or SnO_2 powder at concentration of 0.05 – 3 mol. %. For SiO_2 the concentration can be in a range of 0.05 – 1 mol.%, while for SnO_2 should be higher, preferably 1 – 3 mol.%, due to its thermal instability at high temperatures and losses of Sn-containing species via evaporation. Such crystals with **x** = 0 – 0.35 revealed the following electrical properties: free electron concentration = 1×10^{17} – 1×10^{19} cm^{-3}, electron mobility = 10 – 103 $cm^2V^{-1}s^{-1}$, and resistivity = 0.01 – 2 Ωcm according to Hall effect measurements. For **x** = 0.1 – 0.35, the electrical properties were as follows: free electron concentration = 1×10^{17} – 5×10^{18} cm^{-3}, electron mobility = 10 – 60 $cm^2V^{-1}s^{-1}$, and resistivity = 0.02 – 2 Ωcm. On the other hand, to get electrically insulating or semi-insulating state (resistivity > 10^8 Ωcm), the β-$(Al_xGa_{1-x})_2O_3$ single crystals over the entire range x = 0 – 0.35 can be doped with compensating divalent ions, such as Mg^{2+}, Co^{2+}, Ni^{2+}, or Fe^{2+} at concentration of 10^{17} – 10^{18} cm^{-3}, to compensate residual impurities, mainly Si and hydrogen. The doping is performed by adding corresponding oxides of MgO, CoO, NiO, or FeO to the starting material **4** at a concentration of 0.05 – 2 mol.%.

EXAMPLES

Example 1

A series of bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals with x = 0 – 0.3 and 20 mm in diameter were grown by the Czochralski method in 5 mol.% steps (Δx = 0.05), with the use of iridium crucible having diameter and height of 40 mm. The starting material consisted of Ga_2O_3 and Al_2O_3 powders, that were dried, mixed, and pressed. The growth atmosphere was a mixture of O_2 = 2 vol.% ± 0.5 vol.% + Ar = 98 vol.% ± 0.5 vol.%. The heating rate was 180 – 190 K/h and the growth rate between 1.25 – 1.5 mm/h with a crystal rotation rate of 9 rpm.

Crystal seeds were prepared from previously grown crystals, therefore, their composition was β-$(Al_xGa_{1-x})_2O_3$ with x = 0.05 – 0.25. Then, having crystals with x = 0 – 0.3, next crystal seeds with the same as crystal composition were prepared. These seeds were used for growing further crystals, wherein the crystal seed composition was the same as the melt composition, or higher than the melt composition by Δx = 0.05. It has been concluded that bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals could be grown on crystal seeds having the same composition as the melt composition, lower by Δx = -0.05 or higher by Δx = +0.05 than the melt composition $(Al_xGa_{1-x})_2O_3$.

Once the crystals achieved a pre-defined length, typically 50 mm, they were separated from the melt, and cooled down to room temperature at a rate of 120 – 130 K/h. The crystal diameter and length resulted in a volume of about 16 cm^3. Just after crystal separation, or later during cooling the crystal down, O_2 flow was switched-off to minimize the formation of gallium vacancies, that would compensate, to some extent, the electrical conductivity. In yet other experiments, O_2 flow was reduced to a small concentration, not higher than 0.5 vol.%. Lowering O_2 concentration in the growth atmosphere or switching it off was carried out at the heating power of 50 – 97 % in relation to the heating power during seeding.

Bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals were substantially free of macro structural defects, and the measured X-ray rocking curves were smooth and narrow. The full width at half maximum of the rocking curves was between 10 – 100 arcsec, suitable for homoepitaxial growth of β-$(Al_xGa_{1-x})_2O_3$ thin films of high structural quality, and thus electronic device fabrication of high performance.

The obtained bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals with x = 0 – 0.35 were semiconductors with the following electrical properties measured by the Hall effect:

free electron concentration = 2.5×10^{16} – 5×10^{17} cm^{-3}, electron mobility = 40 – 160 $cm^2V^{-1}s^{-1}$, and resistivity = 0.1 – 1.5 Ωcm. The energy gaps, gathered either from the absorption edge, or from ellipsometry, continuously increase with Al content substantially by the same amount for polarizations parallel to all main crystallographic a-, b-, and c-axis. For instance, the energy gap for polarization parallel to b-axis increases from 4.82 to 5.66 for x = 0 (Al content = 0 mol.%) to x = 0.35 (Al content = 35 mol.%).

Example 2

The same series of bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals with x = 0 – 0.35 was grown under the same conditions and parameters as in Example 1, but the starting material was additionally co-doped with SiO_2 at concentration between 0.2 – 1 mol.%, to dope growing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals with Si^{4+} ions that increases the electrical conductivity. Even lower SiO_2 concentration of 0.05 mol.% is sufficient to increase the electrical conductivity by factor of 5 – 10. Other crystals were co-doped with Sn^{4+}ions. In this case the doping level of SnO_2 in the starting material was between 1 – 3 mol.% to cover losses of Sn-containing species due to its thermal instability at high temperatures. Although this example shows doping with Si^{4+} and Sn^{4+} ions, it is obvious from the state of the art, that other tetravalent or pentavalent ions can be utilized for that purpose, such as Zr^{4+}, Hf^{4+}, and Nb^{5+}. The length of the crystals was typically 25 – 30 mm, resulted in a volume of 8 – 10 cm^3.

The obtained bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals co-doped with Si were either degenerate semiconductors at x = 0 – 0.15, semiconductors at x = 0.15 – 0.25, or electrical insulators (or semi-insulators) at x > 0.25. Crystal having high electrical conductivity are suitable for wafer fabrication particularly dedicated for electronic devices in the vertical configuration. The electrical properties for the semiconducting and degenerately semiconducting states, measured by Hall effect, were as follows: free electron concentration = 1×10^{17} – 1×10^{19} cm^{-3}, electron mobility = 10 – 103 $cm^2V^{-1}s^{-1}$, and resistivity = 0.01 – 2 Ωcm. The structural quality and energy gaps were substantially the same as in Example 1.

Example 3

The same series of single crystals was grown under the same conditions and parameters as in Example 1, but the starting material was additionally doped with MgO at concentration of 0.3 mol.%, to dope growing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals with Mg^{2+} ions that compensate the electrical conductivity and make the crystals electrically insulating or semi-insulating. Indeed, the resistivity higher than 10^8 Ωcm clearly indicates the electrically insulating or semi-insulating state. Instead of Mg^{2+} other divalent ions can be used to compensate the electrical conductivity, in particular Co^{2+}, Ni^{2+}, and Fe^{2+}, as shown in the state of the art. The concentration of MgO, CoO, NiO, or FeO in the starting material is preferably between 0.05 – 2 mol.%., which results in atomic concentration of the divalent ions at a level of 1 – 10×10^{17} cm^{-3}. Such concentration will sufficiently compensate shallow donors arising from residual Si^{4+} and hydrogen. The crystals in this example had the structural quality and energy gaps substantially the same as those in Example 1. The length of the crystals was typically 50 mm, resulted in a volume of 16 cm^3.

Example 4

55 mm diameter (2 inch) bulk β-$(Al_xGa_{1-x})_2O_3$ single crystals with x = 0 – 0.2 were grown by the Czochralski method with an iridium crucible of diameter and height of 100 and 80 mm, respectively. The starting material was prepared in the same way as in Example 1. The growth atmosphere was a mixture of O_2 = 10 – 14 vol.% ± 1 vol.% + Ar = 86 – 90 vol.% ± 1 vol.%. The oxygen concentration in the growth atmosphere must be higher as compared to Examples 1 – 3 because of much larger melt volume that leads to formation of elemental Ga having a distractive impact on the growth process and iridium crucible. This is discussed in the patent No. US 11,028,501 B2 to Galazka et al., incorporated here as a reference. Incorporation of Al into Ga_2O_3 increases thermal stability of the $(Al_xGa_{1-x})_2O_3$ melt to some extent, therefore, O_2 concentration can be lower as compared to pure Ga_2O_3 and the same melt volume by 20 – 50 %. The heating rate was 150 – 160 K/h and the growth rate between 1.25 – 1.5 mm/h with a crystal rotation rate of 5 – 7 rpm. The starting material $(Al_xGa_{1-x})_2O_3$ was co-doped with MgO = 0.5 mol.% to achieve electrically insulating or semi-insulating state, which is dedicated for electronic devices in lateral configuration.

Once the crystals achieved a pre-defined length of 50 – 60 mm, they were separated from the melt, and cooled down to room temperature at a rate of 100 – 110 K/h. The crystal diameter and length resulted in a volume of about 120 – 140 cm^3. Although not necessary, due to electrically insulating or semi-insulating state, O_2 concentration in the growth atmosphere can be lowered or switched-off just after crystal separation or later during cooling down. This will decrease overall iridium losses.

It is important to note that the operating conditions, arrangements and designs 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. Accordingly, all such modifications are intended to be included within the scope of the present invention as defined in the appended claims. Other substitutions, modifications, changes and omissions may be made in the operating conditions and arrangements of the preferred and other exemplary embodiments without departing from the scope of the present invention.

CLAIMS

1. An aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal (**7**) directly grown from the melt,

characterized in that

the aluminium content (**x**) in the obtained single crystal (**7**) is between 0.1 – 0.35, that corresponds to 10 – 35 mol.% of Al, while the single crystal (**7**) maintains its monoclinic, single crystalline structure with the following lattice parameters: a = 12.1780 – 12.033 ± 0.015 Å, b = 3.0245 – 2.9795 ± 0.015 Å, c = 5.7870 – 5.7280 ± 0.015 Å, and the angle between a- and c-axis, β = 103.905 – 104.040 ± 0.015°, wherein a volume of the single crystal (**7**) is at least 5 cm^3.

2. The aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal according to claim 1, characterized in that its energy gap is larger in relation to pure β-Ga_2O_3 by 0.2 – 0.8 ± 0.05 eV for x = 0.1 – 0.35 and polarizations parallel to main crystallographic direction along the a-, b-, and c-axis.

3. The aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal according to claim 1 or 2, characterized in that it is a semiconductor with the free electron concentration of 1-5×10^{17} cm^{-3}, electron mobility of 40 – 80 $cm^2V^{-1}s^{-1}$, and resistivity of 0.1 – 1 Ωcm, as measured by the Hall effect.

4. The aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal according to claim 1 or 2, characterized in that it is intentionally co-doped with at least one of tetravalent ions selected from the group consisting of Si^{4+} and Sn^{4+}, especially at a concentration of 10^{18} – 10^{19} cm^{-3}, and it constitutes a semiconductor or degenerated semiconductor with the free electron concentration of 1×10^{17} – 5×10^{18} cm^{-3}, electron mobility of 10 – 60 $cm^2V^{-1}s^{-1}$, and resistivity of 0.02 – 2 Ωcm, as measured by the Hall effect.

5. The aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal according to claim 1 or 2, characterized in that it is intentionally co-doped with at least one of divalent ions selected from the group consisting of Mg^{2+}, Co^{2+}, and Ni^{2+}, especially at a concentration of 10^{17} – 10^{18} cm^{-3}, and it constitutes an electrical insulator or semi-insulator with the electrical resistivity of at least 10^8 Ωcm.

6. The aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal according to any of the preceding claims 1-5, characterized in that it has a volume of at least 10 cm^3 preferably at least 100 cm^3.

7. An aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal according to any of preceding claims 1-6, characterized in that it is fabricated into wafers for homoepitaxial growth of thin films, wherein the wafers have the full width at half maximum (FWHM) of the rocking curve between 10 – 100 arcsec.

8. A method for producing aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal directly grown from the melt contained within a metal crucible, comprising the steps of:

i) providing into a growth chamber a thermal system or growth furnace (**1**) comprising the metal crucible (**3**) containing a starting material (**4**) consisting of Ga_2O_3 + Al_2O_3, a thermal insulation (**6**) surrounding the metal crucible (**3**), and a heater (**10**) disposed around the metal crucible (**3**) and thermal insulation (**6**);

ii) providing a crystal seed (**11**) within the growth furnace (**1**);

iii) introducing into the growth furnace (**1**) a growth atmosphere (**2**) containing oxygen;

iv) heating up the metal crucible (**3**) by the heater (**10**), which in turns heats up the Ga_2O_3 + Al_2O_3 starting material (**4**) until melting;

v) contacting the crystal seed (**11**) with the molten Ga_2O_3 + Al_2O_3 starting material (**4**) contained within the metal crucible (**3**);

vi) growing a β-$(Al_xGa_{1-x})_2O_3$ single crystal (**7**) on the crystal seed (**11**) by temperature gradients between the crystal seed (**7**) and the melt;

vii) cooling down the grown β-$(Al_xGa_{1-x})_2O_3$ single crystal (**7**) to room temperature once the crystal growth step has been completed;

characterized in that:

the provided Ga_2O_3 + Al_2O_3 starting material (**4**) in step (i) for growing β-$(Al_xGa_{1-x})_2O_3$ single crystal (**7**) contains 9 – 30 mol.% of Al_2O_3 corresponding to (**x**) = 0.09 – 0.3; the oxygen concentration in the growth atmosphere (**2**) in step (iii) is between 0.5 – 25 vol.%, while the crystal seed (**11**) contacting the melt in step (v) has a composition of β-$(Al_xGa_{1-x})_2O_3$ with (**x**) = 0.1 – 0.3 $\pm$ 0.1.

9. The method according to claim 8, characterized in that the crystal seed (**11**) has a composition of β-$(Al_xGa_{1-x})_2O_3$ with (**x**) = 0.1 – 0.3 $\pm$ 0.05.

10. The method according to claim 8 or 9, characterized in that the oxygen in the growth atmosphere (**2**) is decreased to a value of 0 – 0.5 vol.% at the end of crystal growth or during cooling down of the grown aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal (**7**) at a heating power of 50 – 97 % in relation to a heating power at crystal seeding.

11. The method according to any of the preceding claims 8-10, characterized in that Al_2O_3 in the starting material (**4**) is selected from the group consisting of an Al_2O_3 powder mixed with a Ga_2O_3 powder, an Al_2O_3 layer deposited, at least partly, on the inner surface of the metal crucible (**3**), or a combination thereof.

12. The method according to any of the preceding claims 8-11, characterized in that the starting material (**4**) additionally contains at least one oxide of a tetravalent ion selected from the group consisting of SiO_2 and SnO_2 at a concentration of 0.05 – 3 mol.%.

13. The method according to any of the preceding claims 8-11, characterized in that the starting material (**4**) additionally contains at least one oxide of a divalent ion selected from the group consisting of MgO, CoO, and NiO at a concentration of 0.05 – 2 mol.%.

14. The method according to any of the preceding claims 8-13, characterized in that the pressure in the growth chamber is selected from the group consisting of atmospheric pressure, underpressure down to 0.01 bar, or overpressure up to 100 bar.

15. The method according to any of the preceding claims 8-14, characterized in that aluminium-containing bulk β-$(Al_xGa_{1-x})_2O_3$ single crystal (**7**) is grown by the Czochralski, Kyropolous, horizontal Bridgman, vertical Bridgman, or by Vertical Gradient Freeze method, or by a shaped technique selected from the group consisting of Stepanov, Noncapillary Shaping, and Edge-Defined Film-Fed Growth methods, or their modifications.

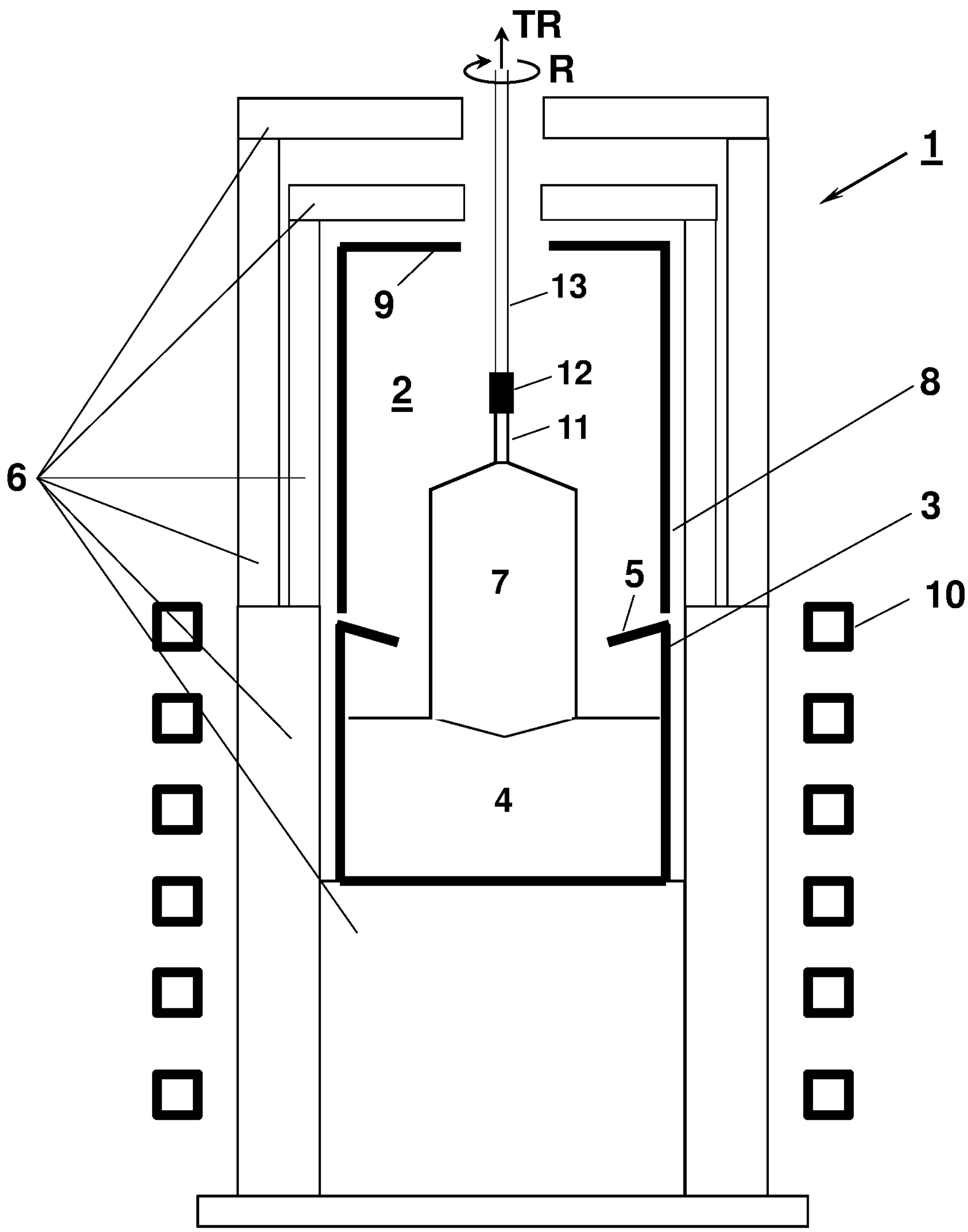

Fig. 1

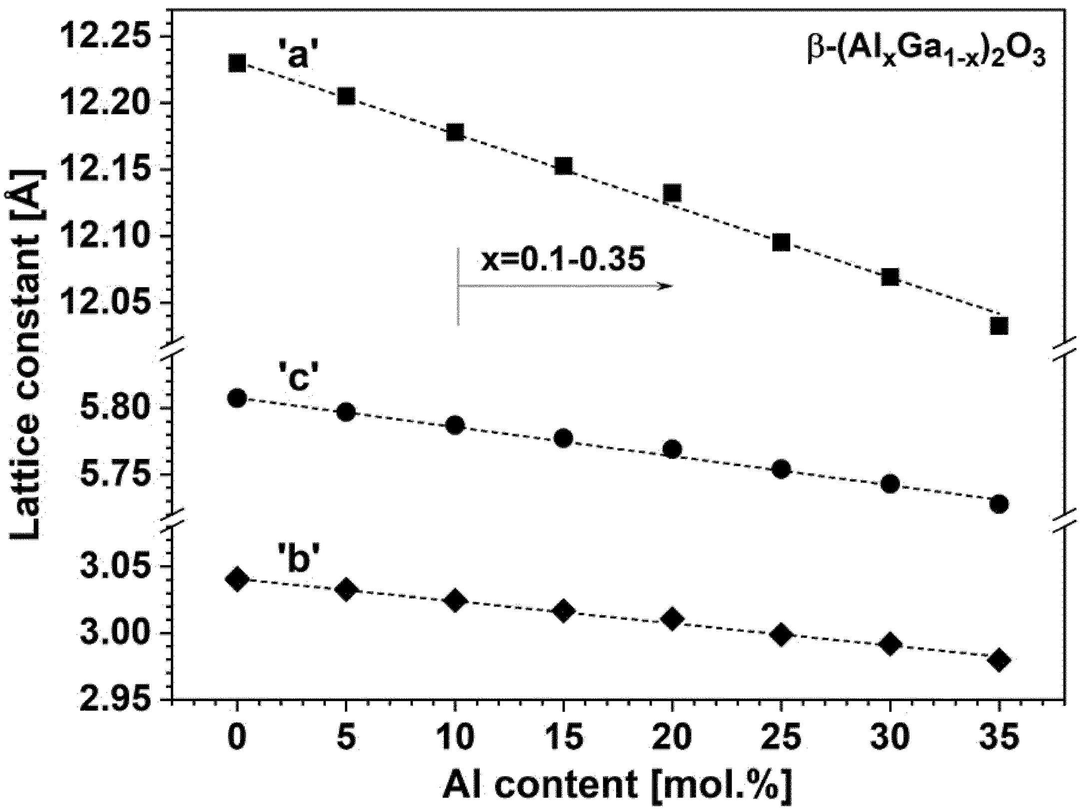
β-(Al$_x$Ga$_{1-x}$)$_2$O$_3$
'a'
'c'
'b'
x=0.1-0.35
Lattice constant [Å]
12.25
12.20
12.15
12.10
12.05
5.80
5.75
3.05
3.00
2.95
0
5
10
15
20
25
30
35
Al content [mol.%]

Fig. 2

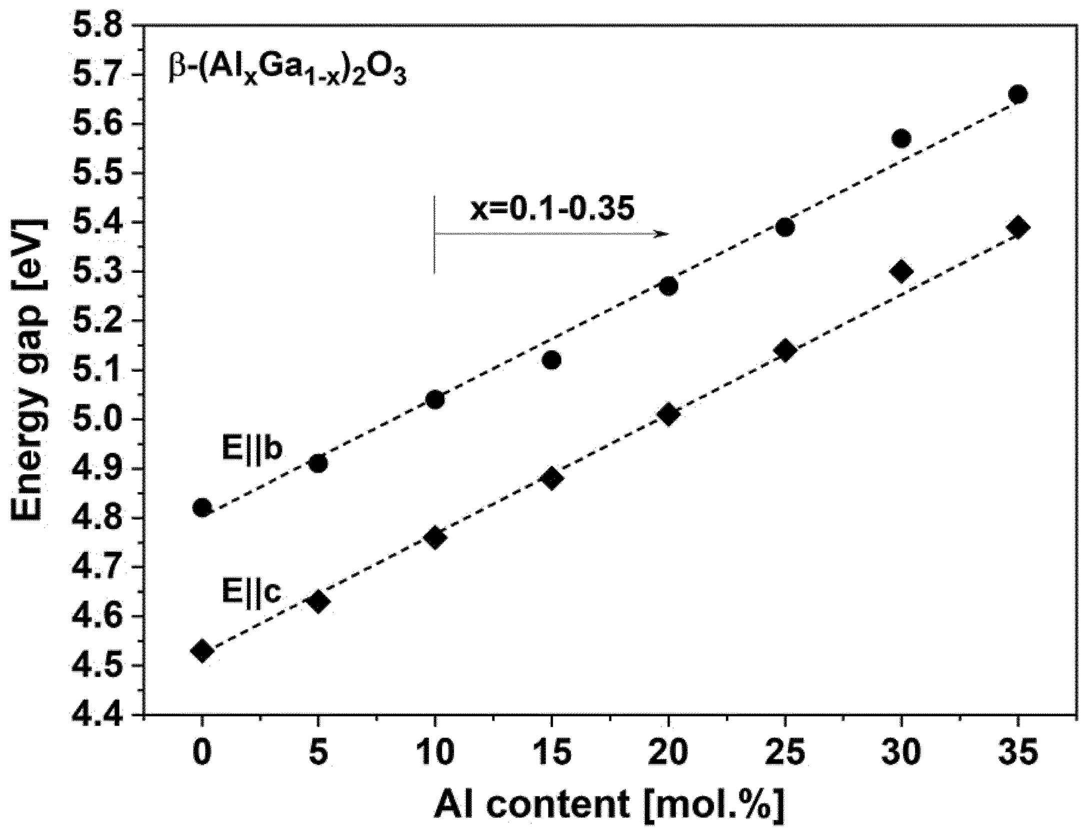
β-(Al$_x$Ga$_{1-x}$)$_2$O$_3$
x=0.1-0.35
E||b
E||c
Energy gap [eV]
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
0
5
10
15
20
25
30
35
Al content [mol.%]

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/078252

A. CLASSIFICATION OF SUBJECT MATTER
INV. C30B15/00 C30B29/22
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JANI JESENOVEC ET AL: "Alloyed B-(AlxGa1-x)2O3 bulk Czochralski single B-(Al0.1Ga0.9)2O3 and polycrystals B-(Al0.33Ga0.66)2O3, B-(Al0.5Ga0.5)2O3), and property trends", ARXIV.ORG, CORNELL UNIVERSITY LIBRARY, 201 OLIN LIBRARY CORNELL UNIVERSITY ITHACA, NY 14853, 10 January 2022 (2022-01-10), XP091196269, DOI: 10.1063/5.0073502	1-8, 10-12, 14,15
Y	I. Introduction	9
A	II. Methods III.D. Electrical Properties figures 1c, 3, 4c, 11 -----	13

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 April 2023	28/04/2023

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Schmitt, Christian

2

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	ZAKGEIM DMITRII ET AL: "Growing of bulk [beta]-(AlxGa1-x)2O3 crystals from the melt by Czochralski method and investigation of their structural and optical properties", APPLIED PHYSICS EXPRESS, [Online] vol. 15, 17 January 2022 (2022-01-17), pages 025501-1, XP093040035, DOI: 10.35848/1882-0786/ac44ca Retrieved from the Internet: URL:https://iopscience.iop.org/article/10.35848/1882-0786/ac44ca/pdf> [retrieved on 2023-04-18] the whole document -----	9
A	JP 2009 013028 A (NIPPON LIGHT METAL CO) 22 January 2009 (2009-01-22) the whole document -----	1-15
A	CN 113 035 999 A (HANGZHOU FUJIA GALLIUM TECH CO LTD) 25 June 2021 (2021-06-25) the whole document -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2022/078252

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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CN 113035999 A	25-06-2021	NONE	