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(54) **METHOD OF PREPARING A COMPOUND SEMICONDUCTOR CRYSTAL**

4,478,675 A 10/1984 Akai 156/605
4,521,272 A 6/1985 Gault
4,678,534 A 7/1987 Tada et al. 156/607

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(Continued)

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FOREIGN PATENT DOCUMENTS

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EP 0 417 843 A2 3/1991
EP 0 803 593 A1 10/1997
EP 0803593 * 10/1997
EP 0927777 * 7/1999
EP 0529963 B1 4/2000

(Continued)

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OTHER PUBLICATIONS

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Related U.S. Patent Documents

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Advanced Electronics Series I-4 Bulk Crystal Growth Technology, by Keigo Hoshikawa, Baifukan, pp. 148, fig. 7.22; Oct. 6, 1997.*

Nosovsky A.M., et al., "Carbon in Undoped SI-GaAs: The Influence Of Growth Conditions," Fifth Hungarian Conference on Crystal Growth, HCCG-5, Budapest, Hungary, Nov. 14-16, 1989, vol. 70, No. 3, pp. 211-216.

(Continued)

U.S. Applications:

(63) Continuation of application No. 09/274,286, filed on Mar. 22, 1999, now Pat. No. 6,273,947.

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(57) **ABSTRACT**

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C30B 9/00 (2006.01)

A method of preparing a compound semiconductor crystal is able to dope the crystal with carbon with high reproducibility. The method includes the steps of sealing a carbon oxide gas of a predetermined partial pressure and a compound semiconductor material in a gas-impermeable airtight vessel, increasing the temperature of the vessel to melt the compound semiconductor material sealed in the vessel, and then decreasing the temperature of the vessel to solidify the melted compound semiconductor material to grow a compound semiconductor crystal containing a predetermined amount of carbon. With this method, a compound semiconductor crystal with a carbon concentration of $0.1 \times 10^{15} \text{ cm}^{-3}$ to $20 \times 10^{15} \text{ cm}^{-3}$ is prepared with high reproducibility.

(52) **U.S. Cl.** **117/73; 117/76; 117/77; 117/81; 117/83**

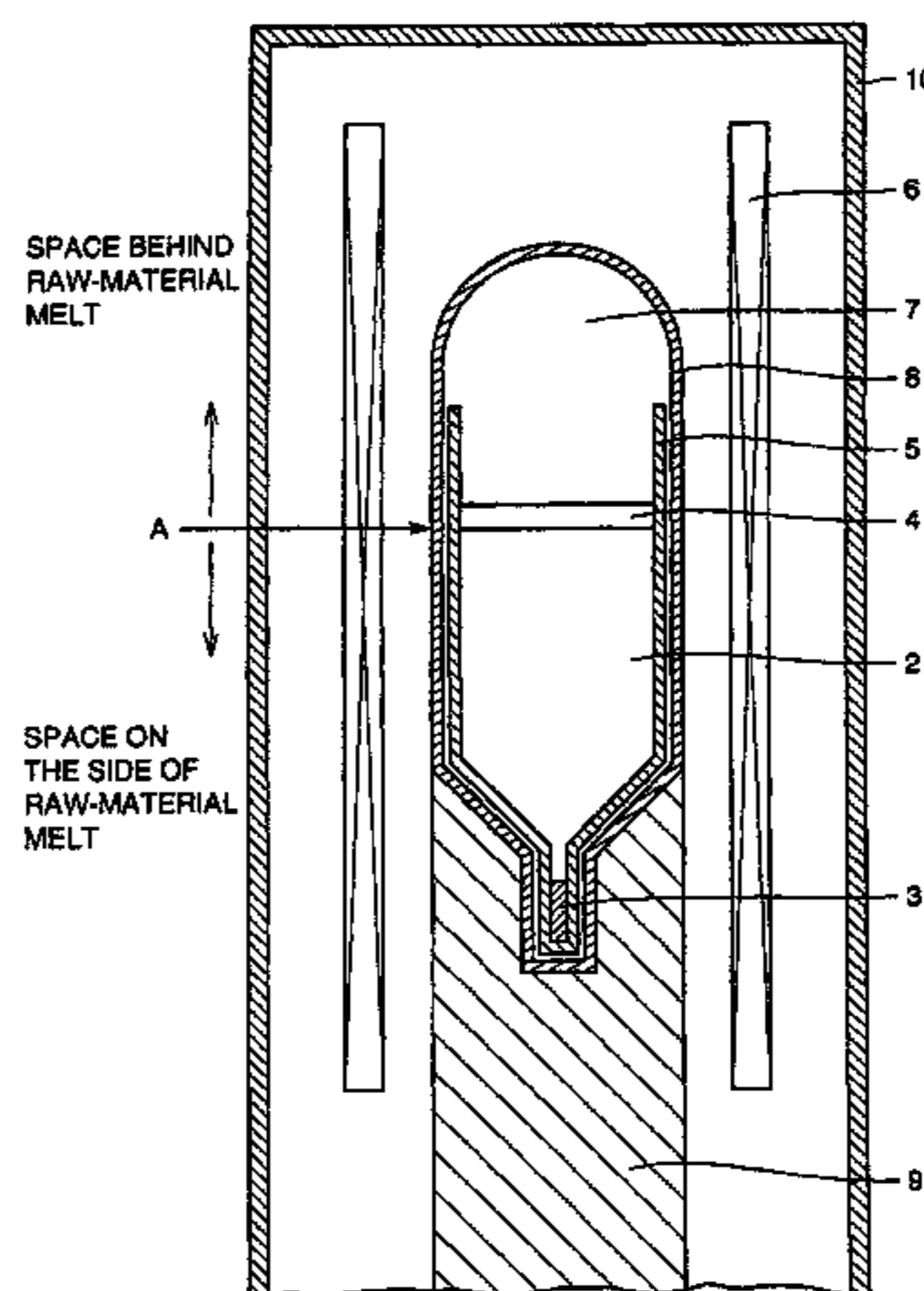
(58) **Field of Classification Search** **117/73, 117/76, 77, 81, 83, 954**
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,083,748 A 4/1978 Gault
4,404,172 A 9/1983 Gault

72 Claims, 3 Drawing Sheets



U.S. PATENT DOCUMENTS

4,923,561	A	5/1990	Chemmanur et al.	
4,946,544	A	8/1990	Ejima	
4,999,082	A	3/1991	Kremer et al.	156/605
5,041,186	A	8/1991	Nishio et al.	
5,057,287	A	* 10/1991	Swiggard	117/219
5,131,975	A	7/1992	Bourret-Courchesne	156/616.2
5,145,550	A	9/1992	Tada et al.	
5,186,784	A	2/1993	Rau et al.	
5,256,381	A	10/1993	Tada et al.	
5,259,916	A	11/1993	Rau et al.	
5,342,475	A	8/1994	Yoshida et al.	117/83
5,387,544	A	2/1995	Hayafuji	
5,400,742	A	3/1995	Nishio et al.	
5,415,125	A	5/1995	Fujita et al.	
5,454,346	A	10/1995	Uchida et al.	117/13
5,471,945	A	12/1995	Nishio et al.	
5,515,810	A	* 5/1996	Yamashita	117/17
5,685,907	A	* 11/1997	Fujikawa et al.	117/205
5,968,260	A	* 10/1999	Saishouji et al.	117/13
6,007,622	A	* 12/1999	Kawase et al.	117/82
6,273,947	B1	* 8/2001	Kawase et al.	117/73

FOREIGN PATENT DOCUMENTS

JP	59-054699	3/1984
JP	60210599	* 10/1985
JP	64-037833	2/1989
JP	6479087	* 3/1989
JP	1239089	* 9/1989
JP	2-48496	* 2/1990
JP	02034597	* 2/1990
JP	02-074597	3/1990
JP	3-122097	* 5/1991
JP	04-104989	4/1992
JP	06-128096	5/1994
JP	09-030887	2/1997
JP	10-167898	6/1998
JP	11-147785	6/1999
JP	11-228292	8/1999

OTHER PUBLICATIONS

Bourret, E.D., et al., "Effects of Total Liquid Encapsulation on the Characteristics of GaAs Single Crystals Grown . . ." J. Cryst. Gr. 11 (1991), pp. 395-404.

Declaration of Hunter D. Marshall, undated (5 pp.).

Desnica et al., "Distribution coefficient of carbon in gallium arsenide," Inst. Phys. Conf. Ser. No. 83, ch. 2, pp. 33-38 (1986).

Desnica et al., "Distribution coefficient of carbon in melt-grown GaAs," J. Appl. Phys. 62(9) (Nov. 1, 1987).

Diploma paper Matthias Muller, Sep. 15, 1993, Universitat Erlangen-Nurnberg (D5A Letter re Publication Date)—with available translation of sections.

Dissertation of Christian Frank, 1995, Technische Universitat-Bergakademie Freiberg (D4A Catalogue Data re Publication Year)—with available translation of sections.

Doering et al., "Carbon incorporation into LEC GaAs" in Semi-Insulating III-V Materials, 1990.

Doering et al., "Carbon Incorporation Into LEC GaAs", Malmö, Sweden (1984).

Flade, "Entwicklung großflächiger GaAs-Substrate," Freiburger Elektronik GmbH (Hannover, Germany, Feb. 19, 1996)—with available translation of sections.

Frank, Ch., et al., "Description of Facet Growth During VGF Growth," Cryst. Res. Technol. 29 (1994) 1, pp. K12-16.

Hein et al., "Die Kristallisation aus Schmelzen als metallurgischer Prozeß," Metall, v. 47, No. 10, pp. 924-928 (Oct. 1993)—with available translation of sections.

Hein, "Growth of Semiinsulating GaAs Crystals by Vertical Gradient Freeze Technique," Crystal Research Technology v. 30, No. 7, pp. 897-909 (1995).

Influence of Melt Preparation on Residual Impurity Concentration in Semi-Insulating LEC GaAs, Johji Nishio and Kazutaka Terashima, Journal of Crystal Growth 96 (1989) 605-608, North-Holland, Amsterdam.

Kawasw et al., "Low-dislocation-density and Low residual-strain Semi-insulating GaAs Grown by VB Method," 9th Conf. on Semiconducting & Insulating Materials, -Abstracts, title, contents and p. 47 (Apr. 29-May 3, 1996).

Kawase et al., "Low-dislocation-density and Low-residual-strain Semi-insulating GaAs Grown by Vertical Boat Method," 9th Conf. on Semiconducting & Insulating Materials-Proceedings, title, pp. ii-iii, vii-viii, xv, 275-278 (1996).

Marshall et al., "A novel technique to reduce the concentration of Carbon in LEC gallium arsenide," J. Cryst. Growth, 110 (1991), pp. 960-962.

Müller et al., "Current issues in bulk growth of s.i. III-V materials" in Semi-Insulating III-V Materials, 1992.

Parsey, "Relative virtues of different growth techniques" in Semi-Insulating III-V Materials, 1988.

* cited by examiner

FIG. 1

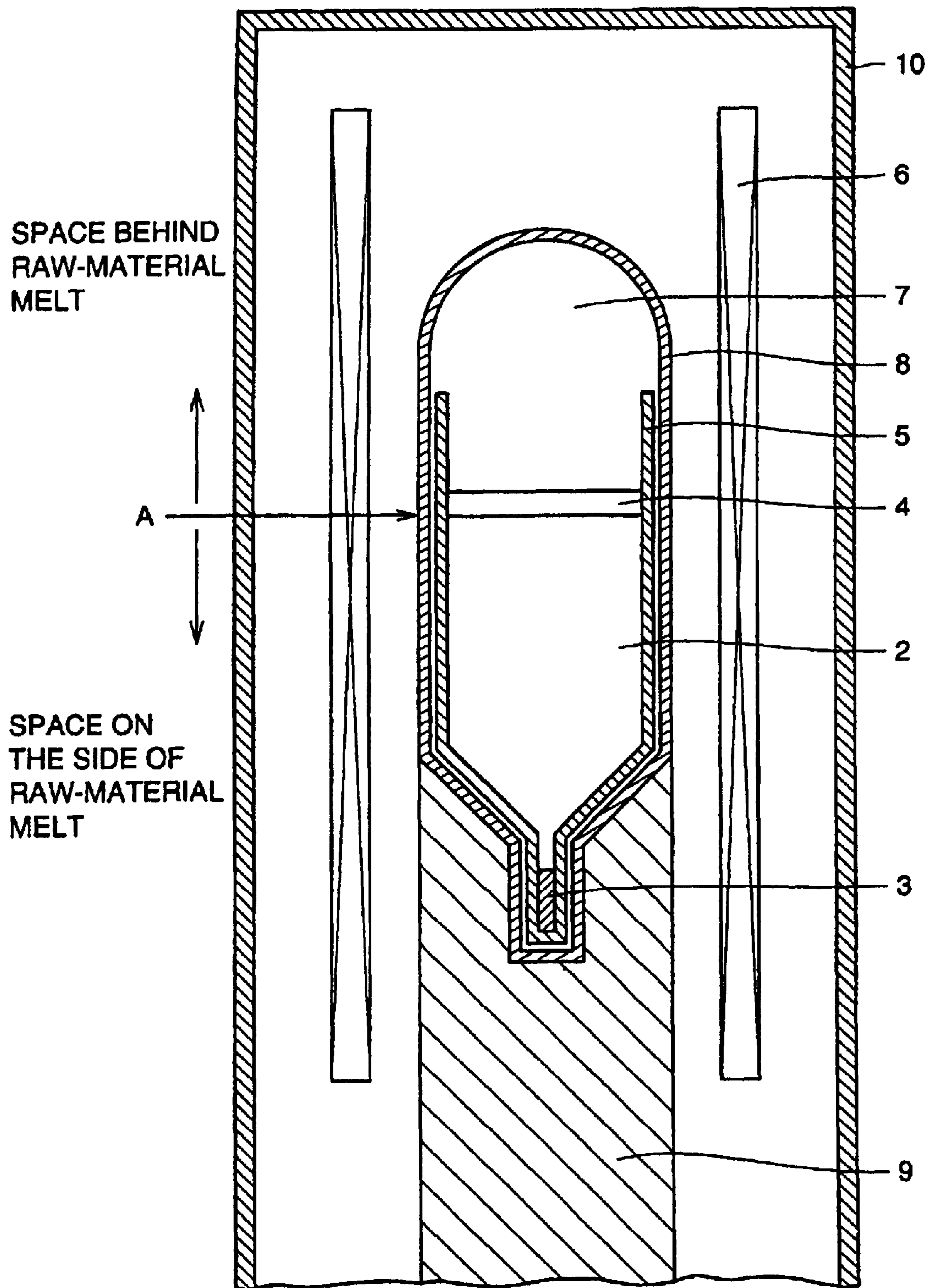


FIG. 2

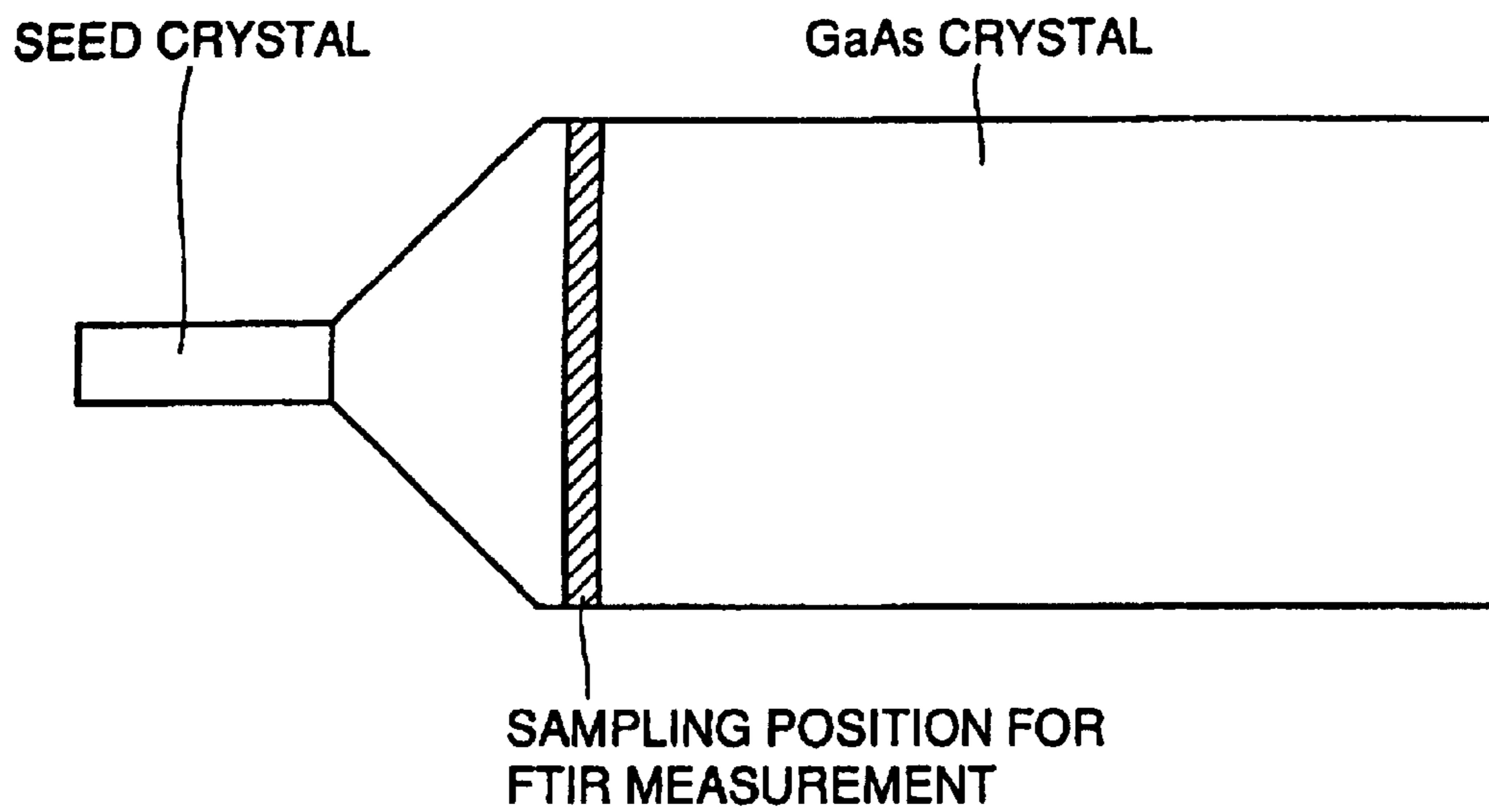


FIG. 3

PRIOR ART

CARBON
CONCENTRATION
IN CRYSTAL
($\times 10^{15} \text{cm}^{-3}$)

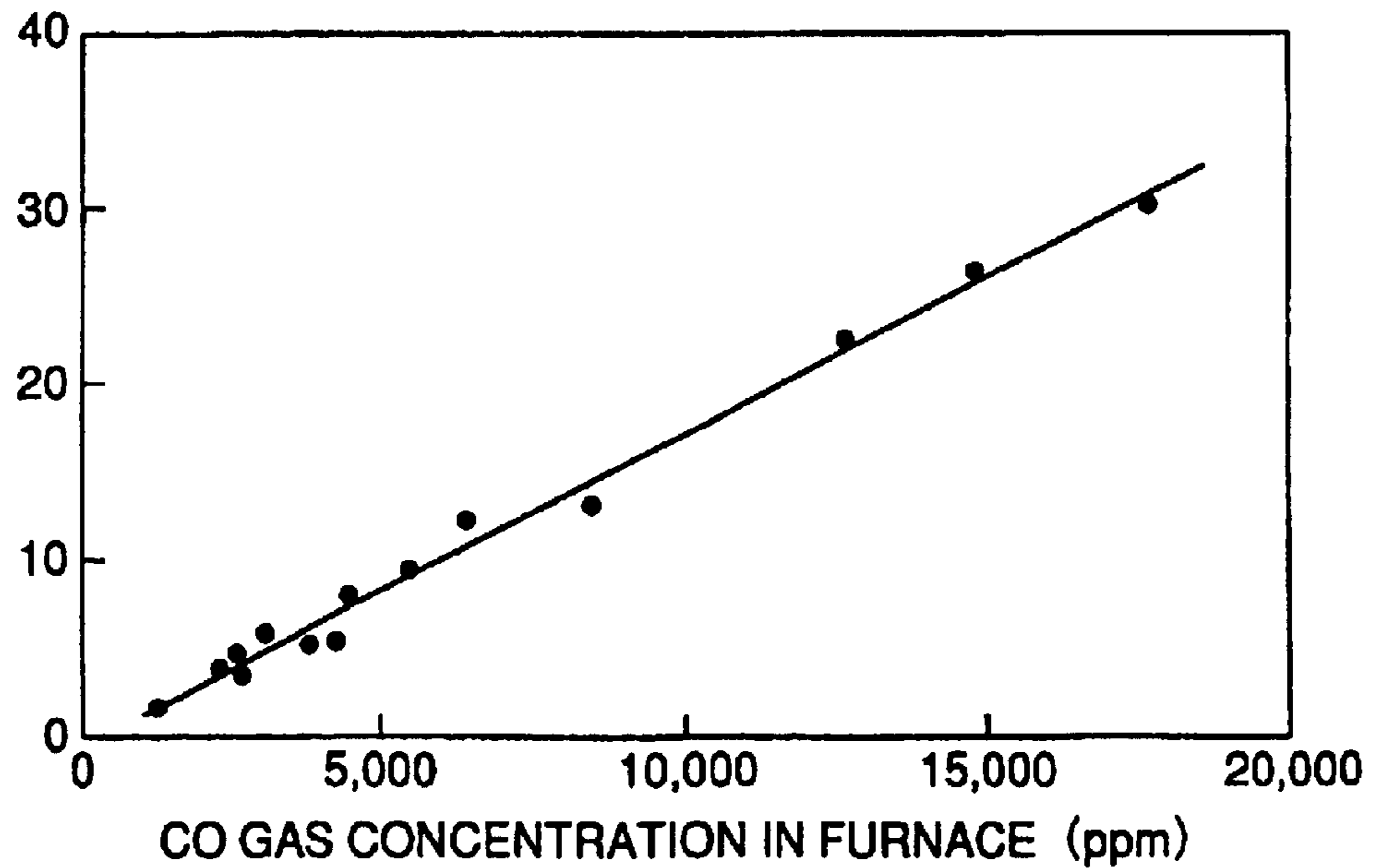
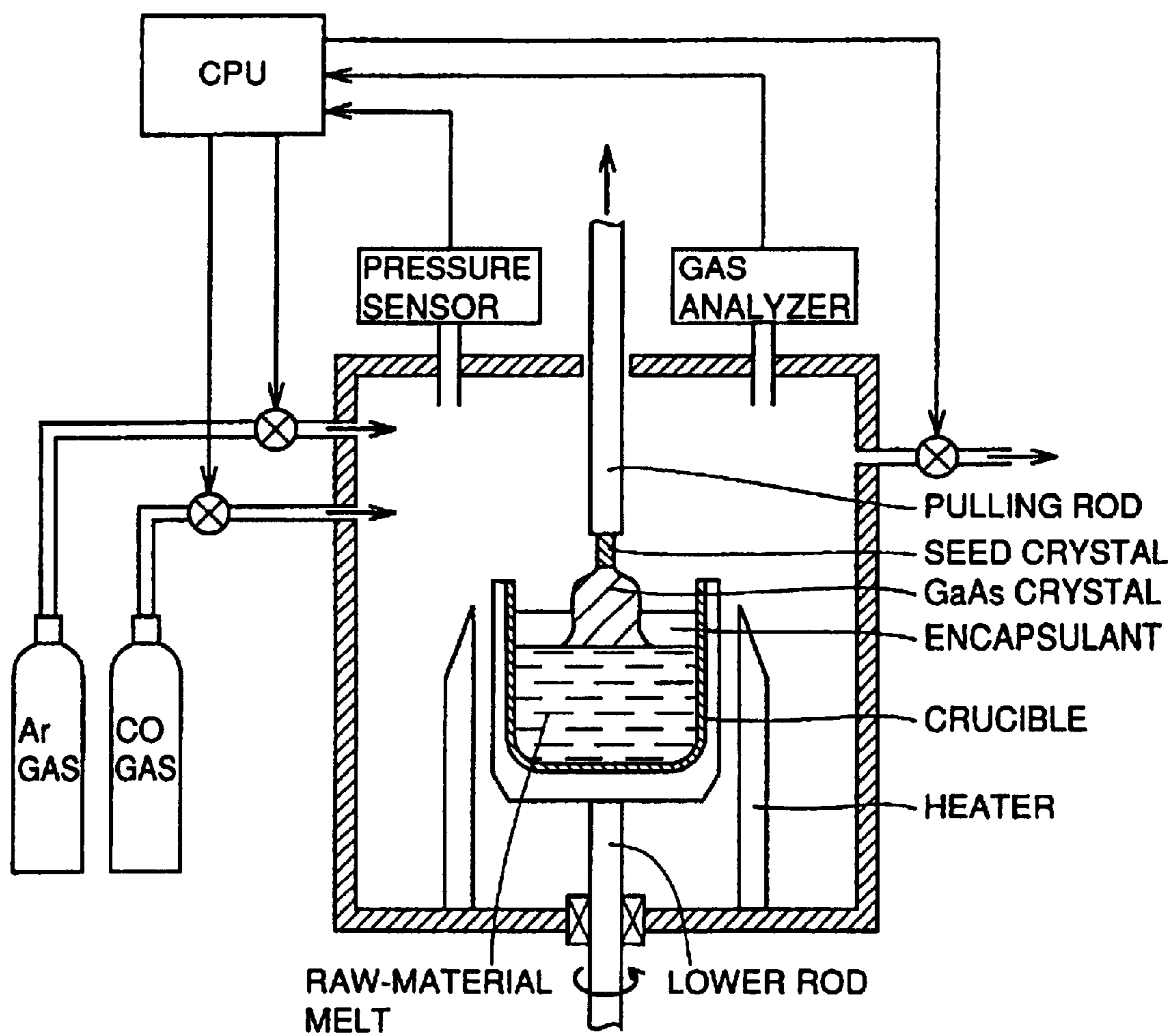


FIG. 4 PRIOR ART



METHOD OF PREPARING A COMPOUND SEMICONDUCTOR CRYSTAL

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a Continuation of U.S. application Ser. No. 09/274,286 filed Mar. 22, 1999 now U.S. Pat. No. 6,273,947.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to methods of preparing a compound semiconductor crystal and to the compound semiconductor crystals prepared thereby, and particularly to methods of preparing a carbon-containing, compound semiconductor crystal and compound semiconductor crystals obtained thereby.

2. Description of the Background Art

It has been conventionally well known that as for an LEC method using a stainless chamber there is a correlation between the CO gas concentration provided in the chamber and the carbon concentration of a GaAs crystal in a high-pressure Ar gas ambient.

FIG. 3 is a graph of carbon concentration in a GaAs crystal versus CO gas concentration in a LEC furnace found in Advanced Electronics Series I-4 Bulk Crystal Growth Technology, Keigo Hoshikawa, BAIFUKAN, p.184, Fig. 7.22. FIG. 3 shows that carbon concentration in a GaAs crystal and CO gas content in the LEC furnace are correlated by a straight line. In the LEC method, the correlation represented in the graph is applied to the adjustment of carbon concentration in a GaAs crystal. The carbon concentration in a GaAs crystal can be controlled by adjusting the CO gas content in the ambient gas using a CO gas cylinder and an Ar gas cylinder for dilution connected to the stainless chamber.

FIG. 4 shows an exemplary GaAs crystal growth equipment for the LEC method disclosed in Japanese Patent Laying-Open No. 1-239089. Referring to FIG. 4, Japanese Patent Laying-Open No. 1-239089 discloses a method of preparing a single crystal of compound semiconductor by placing in a predetermined gas ambient a raw-material housing portion housing a raw-material melt, detecting at least the concentration of one of H₂, O₂, CO₂ and CO corresponding to components of the ambient gas, and controlling the detected concentration of a component at a predetermined value to keep over the entirety of an ingot a predetermined concentration of a residual impurity mixed into a resulting single crystal.

This method can, however, not be applied in preparing a compound semiconductor crystal in a gas-impermeable airtight vessel incapable of supplying a gas from outside the airtight vessel, such as a quartz ampoule.

Japanese Patent Laying-Open No. 3-122097 discloses a method of preparing a GaAs crystal in a quartz ampoule wherein a carbon source is arranged internal to the ampoule and external to a crucible in fluid communication with a polycrystalline compound provided as a raw material to allow the GaAs crystal to be doped with carbon. "Fluid communication" means a free flow of vapor and heat between the inside and outside of the crucible which allows carbon to be

transferred into the crucible and thus to a melt. In accordance with the method, a carbon disk is arranged on an opening of a cap. It discloses that the ingots of various doped levels can be provided by varying the amount of carbon arranged external to the opening and/or the crucible.

With this method, however, a large amount of carbon source is placed above the melt. Thus fine powder of carbon falls thereon and can thus vary the carbon concentration thereof. Particularly, the controllability can be poor at a slight carbon concentration corresponding to a level of $0.1 \times 10^{15} \text{ cm}^{-3}$ to $2 \times 10^{15} \text{ cm}^{-3}$.

Japanese Patent Laying-Open No. 64-79087 discloses a method of preparing a single crystal of GaAs doped with carbon to reduce dislocation, using a reactor or a boat for crystal growth at least partially formed of carbon. It discloses that when a graphite boat is used, a part of the carbon boat changes into a gas (CO or CO₂) due to oxygen derived from a small amount of As₂O₃, Ga₂O or the like remaining in the quartz reactor and the gas is thus added to the single crystal of GaAs in synthesis reaction or in single-crystal growth.

In accordance with this method, however, it is difficult to control the carbon concentration in the crystal due to the difficulty of controlling the amount of As₂O₃, Ga₂O or the like remaining in the quartz reactor. In particular, the controllability can be poor at a slight carbon concentration corresponding to a level of $0.1 \times 10^{15} \text{ cm}^{-3}$ to $2 \times 10^{15} \text{ cm}^{-3}$.

Japanese Patent Laying-Open No. 2-48496 discloses a method of preparing a Cr-doped, semi-insulating GaAs crystal wherein a quartz boat or a quartz crucible is used to grow the crystal under the existence of nitrogen oxide or carbon oxide. It discloses that when a GaAs crystal is grown under the existence of nitrogen oxide or carbon oxide, the oxide serves as an oxygen doping source to reduce the Si concentration of the grown crystal so that a semi-insulating crystal is reliably provided.

However, this method contemplates control of oxygen concentration and does not describe control of carbon concentration.

SUMMARY OF THE INVENTION

One object of the present invention is to provide a method of preparing a compound semiconductor crystal allowing the compound semiconductor crystal to be doped with carbon in high reproducibility, and a compound semiconductor crystal prepared thereby.

In one aspect of the present invention, a method of preparing a compound semiconductor crystal includes the steps of sealing carbon oxide gas of a predetermined partial pressure and a compound semiconductor provided as a raw material in a gas-impermeable airtight vessel, increasing the temperature of the airtight vessel to melt the compound semiconductor material sealed in the airtight vessel, and thereafter decreasing the temperature of the airtight vessel to solidify the melted compound semiconductor material to grow a compound semiconductor crystal containing a predetermined amount of carbon.

The carbon oxide gas includes at least one type of gas selected from the group consisting of CO gas and CO₂ gas.

In growing the crystal, preferably the melted compound semiconductor material is at least partially kept in contact with boron oxide (B₂O₃).

In growing the crystal, more preferably the melted compound semiconductor material has its upper surface entirely covered with boron oxide (B₂O₃).

Preferably, the boron oxide (B_2O_3) has a water content of no more than 300 ppm, more preferably no more than 100 ppm.

Preferably, variation of the water content of the boron oxide (B_2O_3) is controlled to fall within a range from +20% to -20%.

In accordance with the present invention, the carbon oxide gas sealed in the airtight vessel preferably has a partial pressure of 0.1 to 100 Torr at 25° C.

In accordance with the present invention, carbon oxide gas is preferably sealed in an airtight vessel according to an expression:

$$C_{CARBON} = \alpha \times P^{0.5} \quad (1),$$

wherein C_{CARBON} (cm^{-3}) represents carbon concentration in a compound semiconductor crystal, P (Torr) represents partial pressure of the carbon oxide gas, and α represents any coefficient.

In expression (1) coefficient α preferably ranges from 0.25×10^{15} to 4×10^{15} $cm^{-3}/Torr$, more preferably 0.5×10^{15} to 2×10^{15} $cm^{-3}/Torr$.

In accordance with the present invention, preferably the step of subjecting the airtight vessel to a vacuum heat treatment is also provided before the step of sealing carbon oxide gas in the airtight vessel.

The vacuum heat treatment is preferably provided at a temperature of no more than 350° C.

In accordance with the present invention, at least the internal wall of the airtight vessel and at least the outer surface of the contents of the airtight vessel other than the compound semiconductor material and the boron oxide are preferably formed from a material which does not contain carbon.

The material which does not contain carbon includes at least one material selected from the group consisting, e.g., of quartz, silicon nitride, boron nitride, pyrolytic boron nitride and alumina.

In accordance with the present invention, the gas-impermeable airtight vessel can at least partially be formed from quartz.

Preferably, the portion formed from quartz has a thickness of no less than 1.5 mm.

In growing the crystal, preferably the portion formed from quartz is controlled to have a temperature of at most 1270° C.

In accordance with the present invention, in growing the crystal a space behind a raw-material melt of melted compound preferably has its most heated portion and its least heated portion with a temperature difference of no more than 300° C. therebetween.

In accordance with the present invention, the space behind the raw-material melt is preferably larger, more preferably no less than twice larger in volume than the space on the side of the raw-material melt.

A method of preparing a compound semiconductor crystal in accordance with the present invention is applicable to preparing a compound semiconductor crystal of GaAs.

In another aspect, the present invention provides a compound semiconductor crystal prepared in accordance with the above-described method of preparing a compound semiconductor crystal, having a carbon concentration of 0.1×10^{15} cm^{-3} to 20×10^{15} cm^{-3} .

In accordance with the present invention, the compound semiconductor includes GaAs.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows preparation of a GaAs crystal as one example of a method of preparing a compound semiconductor crystal in accordance with the present invention.

FIG. 2 shows a position of a sample for FTIR measurement in a crystal.

FIG. 3 is a graph of carbon concentration in a GaAs crystal versus CO gas concentration in a conventional LEC furnace.

FIG. 4 shows one example of conventional GaAs crystal growth equipment for the LEC method.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is based on a method of preparing a compound semiconductor crystal in a sealed system (a system incapable of supplying a gas from outside an airtight vessel) using a gas-impermeable airtight vessel.

In accordance with the present invention, carbon oxide gas of a predetermined partial pressure as well as a compound semiconductor provided as a raw material are sealed in a gas-impermeable airtight vessel, the temperature of the airtight vessel is increased to melt the compound semiconductor material and the temperature of the airtight vessel is then decreased to solidify the melted compound semiconductor material to grow a compound semiconductor crystal to thereby allow the compound semiconductor crystal to be doped with carbon with high reproducibility.

As the carbon oxide gas, a stable CO or CO_2 gas can be used to allow the crystal to be doped with carbon in particularly high reproducibility.

In growing the crystal, preferably at least a portion of the melt of the compound semiconductor material can be kept in contact with boron oxide (B_2O_3) and more preferably the upper surface of the melt can be entirely covered with boron oxide (B_2O_3) to prevent other elements of impurities from being introduced into the melt so as to further enhance the reproducibility of the carbon concentration of the crystal.

To reduce an influence of the water contained in B_2O_3 to control the carbon concentration of the crystal in high reproducibility, B_2O_3 preferably has a water content of no more than 300 ppm, more preferably no more than 100 ppm. To reduce an influence of variation of the water content of B_2O_3 to control the carbon concentration of the crystal in high reproducibility, the variation of the water content of B_2O_3 is preferably controlled to fall within a range from +20% to -20%.

To obtain a practical carbon concentration for a compound semiconductor crystal, i.e., 0.1×10^{15} cm^{-3} to 20×10^{15} cm^{-3} , carbon oxide gas requires a partial pressure of 0.1 to 100 Torr at 25° C., substantially establishing the relation: (carbon concentration in a compound semiconductor crystal) = $\alpha \times$ (partial pressure of carbon oxide gas)^{0.5}, wherein α represents any coefficient and is preferably 0.25×10^{15} to 4×10^{15} $cm^{-3}/Torr$, more preferably 0.5×10^{15} to 2×10^{15} $cm^{-3}/Torr$.

Conventionally in the prior art, the ambient gas has been represented or quantified by its concentration. For example, an ambient gas for GaAs crystal growth typically has a pressure of 1 to 30 atm. When an ambient gas of 1 atm and an ambient gas of 30 atm which have the same gas concentration are converted into terms of partial pressure, the partial pressure of the latter is 30 times larger than that of the former.

The invention of the present invention have found that in a method of preparing a compound semiconductor crystal in a

sealed system (a system incapable of supplying a gas from outside an airtight vessel) using a gas-impermeable airtight vessel, the carbon concentration in the crystal is correlated to the partial pressure of the carbon oxide gas sealed in the airtight vessel rather than the concentration of the carbon oxide gas sealed in the airtight vessel.

Herein the carbon oxide gas sealed in the airtight vessel is represented in the partial pressure at 25° C., since the partial pressure of the carbon oxide gas increases as the temperature of the airtight vessel is increased in growing a crystal. Since a GaAs crystal has a melting point of approximately 1238° C., the partial pressure of the carbon oxide gas sealed at a room temperature (of 25° C.) is considered to be increased by approximately five times during the crystal growth.

While in accordance with the present invention, carbon oxide gas having a predetermined partial pressure is sealed in an airtight vessel, carbon oxide gas may be sealed together with another gas, which can include inert gases, such as helium, neon, argon, krypton, xenon, and nitride gas. When carbon oxide gas is only sealed, it has a concentration of 100%. When carbon oxide gas is sealed, e.g., together with any of the above gases of 50%, the carbon oxide gas has a concentration of 50%. It should be noted, however, that if carbon oxide gas is thus sealed together with any of the above gases, the expression: (carbon concentration in a compound semiconductor crystal) = $\alpha \times (\text{partial pressure of carbon oxide gas})^{0.5}$ is sufficiently satisfied by the coefficient α preferably having the value of 0.25×10^{15} to $4 \times 10^{15} \text{ cm}^{-3} / \text{Torr}$, more preferably 0.5×10^{15} to $2 \times 10^{15} \text{ cm}^{-3} / \text{Torr}$.

Removal of water absorbed in the airtight vessel further enhances the reproducibility of the carbon concentration in the crystal. Accordingly it is preferable to apply a vacuum heat treatment to the airtight vessel before it is sealed. The vacuum heat treatment applied immediately before the vessel is sealed is applied preferably at no more than 350° C., at which temperature B_2O_3 does not soften or deform.

To control the carbon concentration of the crystal in high reproducibility, at least the internal wall of the airtight vessel and at least the outer surface of the contents of the vessel other than the compound semiconductor as a raw material and boron oxide are preferably formed from a material which does not contain carbon, so that further generation of carbon oxide gas can be prevented in the vessel. More specifically, the airtight vessel is preferably formed from a material which does not contain carbon, or the vessel preferably has its internal wall coated with a material which does not contain carbon. It is also preferable that the contents of the airtight vessel other than the compound semiconductor material and boron oxide be formed from a material which does not contain carbon or that the contents have the outer surface coated with a material which does not contain carbon. The material which does not contain carbon is preferably quartz, silicon nitride, boron nitride, pyrolytic boron nitride or alumina.

Furthermore, the gas-impermeable airtight vessel of the present invention can at least partially be formed from quartz, since quartz has superior airtightness and hardly reacts with elements forming the compound semiconductor or carbon oxide gas.

In accordance with the present invention, carbon oxide gas having a predetermined partial pressure is sealed in a gas-impermeable airtight vessel. However, when the airtight vessel is deformed and its internal volume is changed, the partial pressure of the sealed carbon oxide gas is changed and the carbon concentration of the resulting compound semiconductor crystal will deviate from a targeted carbon concentration.

The strength of quartz is reduced at high temperature and is significantly reduced at a temperature at which a GaAs crystal is grown, i.e., 1238° C. If a gas-impermeable airtight vessel is at least partially formed from quartz, the difference between the pressure internal to the vessel and that external to vessel deforms the quartz portion of the vessel and thus changes the internal volume of the vessel. The inventors of the present invention have found that as the vessel's quartz portion is increased in thickness, deformation of the quartz portion is reduced at high temperatures and variation in the vessel's internal volume is thus reduced. The inventors have also found that the quartz portion of the vessel preferably has a thickness of no less than 1.5 mm, more preferably no less than 2.0 mm, still more preferably no less than 2.5 mm.

The inventors have also found that as temperature is decreased, deformation of quartz is reduced and variation in the vessel's internal volume is reduced. The inventors have also found that the quartz portion of the vessel preferably has a temperature of at most 1270° C., more preferably at most 1260° C., further still more preferably at most 1250° C.

In accordance with the present invention, carbon oxide gas of a predetermined partial pressure is sealed in a gas-impermeable airtight vessel. When the temperature of the airtight vessel varies, however, the partial pressure of the sealed carbon oxide gas changes and the carbon concentration of the resulting compound semiconductor crystal thus deviates from a targeted carbon concentration.

In particular, the hollow gas-filled space on the side of the raw-material melt, more specifically, the space between the crucible **5** and the ampoule **8** located below the interface (labeled A in FIG. 1) of raw-material melt **2** and boron oxide **4**, i.e., the space on the side of the seed crystal has its temperature reduced as crystal growth proceeds. When this hollow space on the side of the raw-material melt is large in volume, the average temperature and hence partial pressure of the carbon oxide gas in the airtight vessel are reduced significantly.

In contrast, the temperature of the hollow gas-filled space behind the raw-material melt, i.e., the hollow gas-filled space within the ampoule **8** located above interface A can be controlled regardless of crystal growth. Thus, controlling the temperature of this space behind the raw-material melt, can prevent reduction of the average temperature of the carbon oxide gas in the airtight vessel and reduce reduction of the partial pressure of the carbon oxide gas in the vessel. Reducing the temperature difference between the most and least heated portions of the space behind the raw-material melt can reduce reduction of the partial pressure of the carbon oxide gas in the vessel. The temperature difference between the most and least heated portions of the space behind the melt is preferably no more than 300° C., more preferably no more than 200° C., still more preferably no more than 100° C.

When the hollow gas-filled space behind the raw-material melt is larger in volume than the hollow gas-filled space on the side of the raw-material melt, this can further reduce the reduction of the partial pressure of the carbon oxide gas in the vessel that is caused when the average temperature of the gas in the vessel is reduced. The space behind the raw-material melt is preferably no less than twice, more preferably no less than three times, still more preferably no less than four times larger in volume than that on the side of the raw-material melt.

Furthermore, the method of the present invention is particularly applicable to preparation of GaAs crystal.

Hereinafter, an example of actual preparation of a GaAs crystal in accordance with the present invention will now be described in detail.

FIG. 1 shows an exemplary method of preparing a compound semiconductor crystal in accordance with the present invention, using a gas-impermeable airtight vessel formed from quartz (referred to as a "quartz ampoule" hereinafter) to prepare a GaAs crystal.

Referring to FIG. 1, a GaAs seed crystal 3 of orientation $\langle 100 \rangle$, 5 kg of GaAs 2 as a raw material, and 50 g of boron oxide 4 (referred to as "B₂O₃" hereinafter) with a water content of 70 ppm were initially placed in a crucible 5 formed from pyrolytic boron nitride (referred to as "pBN" hereinafter) and having an inner diameter of 80 mm and also having a cylindrical portion of approximately 30 cm in length, and crucible 5 was housed in a quartz ampoule 8 of 2.5 mm thick. The space behind the raw-material melt placed in quartz ampoule 8, i.e., that located above the interface denoted by arrow A in FIG. 1 was adapted to be four times larger in volume than the space on the side of the raw-material melt, i.e., that located below interface A.

Quartz ampoule 8 has vacuumed to 1×10^{-6} Torr and also heated to 300° C. to remove water adsorbed on the internal wall of ampoule 8 and the raw material. Then, CO₂ gas 7 of 3 Torr was introduced and sealed in ampoule 8. Ampoule 8 was mounted on a support 9 and thus set internal to a vertical heater 6 provided in a chamber 10, and the temperature of heater 6 was increased to melt GaAs material 2 and an upper portion of seed crystal 3.

Then the temperature profile of the heater was adjusted to decrease the temperature from the side of the seed crystal 3 and the entirety of raw-material melt 2 was thus solidified to grow a crystal. In the crystal growth, the highest temperature of ampoule 8 was also controlled not to exceed 1250°. Furthermore, the temperature of an upper portion of ampoule 8 was controlled so that the space located behind the raw-material melt, i.e., that located above interface A shown in FIG. 1 had its most heated portion and its least heated portion with a temperature difference of no more than 100° C. therebetween.

The temperature was reduced to a room temperature and quartz ampoule 8 was then cut and opened to separate a GaAs crystal from crucible 5.

The resulting GaAs crystal had a diameter of 80 mm, and the portion having the diameter of 80 mm was approximately 18 cm long. A sample of 5 mm thick for measurement of carbon concentration was cut out at the position of a shoulder of the crystal (fraction solidified: g of 0.1). FIG. 2 shows the position of the shoulder of the crystal from which the sample was cut out. Fourier Transform Infrared Spectroscopy (FTIR) was used to measure the concentration of the carbon substituted at an arsenic site (referred to as "C_{As}" hereinafter). The measured C_{As} concentration was 2.1×10^{15} cm⁻³.

The C_{As} concentration in the crystal grown under a different partial pressure of sealed CO₂ was similarly measured. The measured results are provided in Table 1.

TABLE 1

Partial pressure of sealed CO ₂ gas and C _{As} concentration in GaAs crystal	
Partial pressure of sealed CO ₂ gas (Torr)	C _{As} concentration in GaAs crystal (cm ⁻³)
0.5	0.8×10^{15}
3.0(embodiment)	2.1×10^{15}
4.5	2.7×10^{15}
6.0	3.1×10^{15}
10.0	4.0×10^{15}
30.0	6.5×10^{15}
60.0	10.0×10^{15}
100.0	13.2×10^{15}

It has been found from the results presented in Table 1 that the relation: (carbon concentration in a compound semiconductor crystal) = $\alpha \times (\text{partial pressure of carbon oxide gas})^{0.5}$ can be substantially established, wherein $\alpha \approx 1.25 \times 10^{15}$ cm⁻³/Torr, under the conditions of the first embodiment.

As a result of experimentally growing a crystal under various conditions, it has been revealed that to obtain a value of a practical carbon concentration in a compound semiconductor crystal, i.e., 0.1×10^{15} to 20×10^{15} cm⁻³, a preferable partial pressure of carbon oxide gas is 0.1 to 100 Torr at 25° C., substantially establishing the relation: (carbon concentration in a compound semiconductor crystal) = $\alpha \times (\text{partial pressure of carbon oxide gas})^{0.5}$ and that coefficient α preferably ranges from 0.25×10^{15} to 4×10^{15} cm⁻³/Torr, more preferably 0.5×10^{15} to 2×10^{15} cm⁻³/Torr^{0.5}, since the coefficient can vary with the conditions of the experiment carried out.

It has also been found as a result of an experiment using B₂O₃ with its water content varied from 30 to 1000 ppm that the carbon concentration in the crystal can be controlled in higher reproducibility when the water content of B₂O₃ is lower and has less variation. Satisfactory reproducibility of the carbon concentration in crystal is achieved when the water content of B₂O₃ is no more than 300 ppm, particularly no more than 100 ppm and the variation of the water content of B₂O₃ is controlled to fall within a range from +20% to -20%. With CO₂ gas replaced with CO gas, a similar result has also been obtained in a similar manner.

Thus, the present invention can provide a method of preparing a compound semiconductor crystal in a sealed system (a system incapable of supplying a gas from outside an airtight vessel) using a gas-impermeable airtight vessel to allow the compound semiconductor crystal to be doped with carbon in high reproducibility.

Furthermore, carbon oxide gas of a predetermined partial pressure sealed in the gas-impermeable airtight vessel together with compound semiconductor provided as a raw material allows a compound semiconductor crystal with a desired carbon concentration and hence with a desired electrical characteristic to be prepared in high reproducibility, since the electrical characteristic of the compound semiconductor crystal depends on the carbon concentration of the crystal.

Thus the present invention can provide satisfactory crystal yield.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

What is claimed is:

1. A method of preparing a compound semiconductor crystal containing carbon, comprising the following steps:

- a) selecting a partial pressure of a carbon oxide gas;
- b) sealing said carbon oxide gas having said partial pressure, and a semiconductor raw material, in a gas-impermeable airtight vessel;
- c) after said step b), increasing a temperature of said airtight vessel to melt said raw material in said airtight vessel and thereby form a melted material from said raw material; and
- d) after said step c), decreasing said temperature of said airtight vessel to solidify said melted material and thereby grow said compound semiconductor crystal containing a resultant content of said carbon, wherein said resultant content of said carbon is dependent on said partial pressure of said carbon oxide gas selected in said step a).

2. The method according to claim 1, wherein said carbon oxide gas includes at least one of CO gas and CO₂ gas.

3. The method according to claim 1, wherein said steps a) and b) are carried out so that said partial pressure of said carbon oxide gas is in a range from 0.1 to 100 Torr at 25° C.

4. The method according to claim 1, further comprising a preliminary step of selecting a carbon content value, wherein said step a) comprises selecting said partial pressure of said carbon oxide gas dependent on said carbon content value, and wherein said resultant content of said carbon in said compound semiconductor crystal is equal to said carbon content value.

5. The method according to claim 1,

wherein said steps b) and c) are carried out so that said melted material is located on a first side of a plane extending along a melt interface of said melted material in said airtight vessel, and a gas-filled space containing at least a portion of said carbon oxide gas is provided within said airtight vessel on a second side of said plane opposite said first side, and

further comprising, during said step d), controlling said temperature of said airtight vessel, on said second side of said plane, so that a hottest portion of said gas-filled space and a coolest portion of said gas-filled space have a temperature difference of no more than 300° C. therebetween.

6. The method according to claim 1, wherein said resultant content of said carbon in said compound semiconductor crystal is a resultant local content of carbon at a location in said compound semiconductor crystal defined by a fraction solidified (g) of 0.1.

7. The method of claim 1, further comprising a preliminary step of selecting a carbon content value, and wherein said step a) comprises selecting said partial pressure dependent on said carbon content value.

8. The method according to claim 1, wherein said step a) comprises selecting said partial pressure according to a formula:

$$C_{CARBON} = \alpha \times P^{0.5},$$

wherein C_{CARBON} represents a value of said resultant content of said carbon per cm³ of said compound semiconductor crystal to be achieved in said step d).

9. The method of preparing a compound semiconductor crystal according to claim 1, wherein said carbon oxide gas is sealed in said airtight vessel according to an expression:

$$C_{CARBON} = \alpha \times P^{0.5},$$

wherein C_{CARBON} represents a carbon concentration in said compound semiconductor crystal, P (Torr) represents a partial pressure of said carbon oxide gas represented in, and α represents any coefficient.

10. The method according to claim 1, further comprising a step of subjecting said airtight vessel to a vacuum heat treatment before said step of sealing said carbon oxide gas in said airtight vessel.

11. The method according to claim 10, wherein said vacuum heat treatment is carried out at an elevated temperature no more than 350° C.

12. The method according to claim 1, further comprising providing said airtight vessel to have at least an internal vessel wall formed of a material excluding carbon, and further ensuring that no additional carbon is introduced into said carbon oxide gas during at least one of said steps c) and d).

13. The method according to claim 12, wherein said material excluding carbon includes at least one material selected

from the group consisting of quartz, silicon nitride, boron nitride, pyrolytic boron nitride and alumina.

14. The method according to claim 1, further comprising a preliminary step of providing said semiconductor raw material so that said compound semiconductor crystal contains GaAs.

15. The method according to claim 14, wherein said steps are carried out so that said resultant content of said carbon in said compound semiconductor crystal is in a range from $0.1 \times 10^{15} \text{ cm}^{-3}$ to $20 \times 10^{15} \text{ cm}^{-3}$.

16. The method according to claim 1, wherein in said step c), said melted material occupies a melt volume that is bounded along one plane by a melt interface of said melted material in said airtight vessel, said melt volume is located on a first side of said plane extending along said melt interface in said airtight vessel, said carbon oxide gas occupies a first gas-filled volume within said airtight vessel on said first side of said plane and a second gas-filled volume within said airtight vessel on a second side of said plane opposite said first side, and said second gas-filled volume is larger than said first gas-filled volume.

17. The method according to claim 16, wherein said second gas-filled volume is at least twice as large as said first gas-filled volume.

18. The method according to claim 1, further comprising a preliminary step of selecting a carbon content value, and wherein said step a) comprises selecting said partial pressure according to a formula:

$$C_{CARBON} = \alpha \times P^{0.5},$$

wherein C_{CARBON} represents said carbon content value in atoms of carbon per cm³ of said compound semiconductor crystal, P represents said partial pressure in Torr, and α represents a dependence coefficient.

19. The method according to claim 18, wherein said dependence coefficient α is in a range from $0.25 \times 10^{15} \text{ cm}^{-3} / \text{Torr}^{0.5}$ to $4 \times 10^{15} \text{ cm}^{-3} / \text{Torr}^{0.5}$.

20. The method according to claim 18, wherein said dependence coefficient α is in a range from $0.5 \times 10^{15} \text{ cm}^{-3} / \text{Torr}^{0.5}$ to $2 \times 10^{15} \text{ cm}^{-3} / \text{Torr}^{0.5}$.

21. The method according to claim 1, further comprising providing said airtight vessel to have at least a portion thereof formed of quartz.

22. The method according to claim 21, wherein said airtight vessel is provided to have a wall thickness of said portion formed of quartz being at least 1.5 mm.

23. The method according to claim 21, further comprising controlling said temperature during said steps c) and d) so that said portion formed of quartz never exceeds 1270° C.

24. The method according to claim 1, wherein said step b) further comprises sealing a boron oxide based substance together with said carbon oxide gas and said raw material in said airtight vessel, said step c) further comprises melting said boron oxide based substance to form a melted boron oxide based substance, and said melted material is at least partially in contact with said melted boron oxide based substance during said step d).

25. The method according to claim 24, wherein said melted boron oxide based substance forms a continuous layer entirely along an interface of said melted material on a plane between said melted material and said melted boron oxide based substance.

26. The method according to claim 24, further comprising selecting said boron oxide based substance to comprise boron oxide and a water content of not more than 300 ppm of water.

27. The method according to claim 24, further comprising selecting said boron oxide based substance to comprise boron oxide and a water content of not more than 100 ppm of water.

28. The method according to claim 24, further comprising selecting said boron oxide based substance to comprise boron oxide and a water content of water, wherein said water content has a variation in a range from -20% to +20% relative to an average of said water content.

29. The method according to claim 1, further comprising providing said airtight vessel to have at least an internal vessel wall thereof formed of a first material excluding carbon, and further providing that at least one content of said airtight vessel has at least an outer surface formed of a second material excluding carbon.

30. The method according to claim 29, wherein said step b) further comprises placing said raw material in a crucible and sealing said crucible in said airtight vessel, wherein said step b) additionally comprises sealing a boron oxide based substance in said airtight vessel, and wherein said content includes said raw material, said crucible, and said boron oxide based substance.

31. The method according to claim 29, wherein each one of said first material and said second material respectively comprises at least one respective material selected from the group consisting of quartz, silicon nitride, boron nitride, pyrolytic boron nitride and alumina.

32. The method according to claim 29, wherein said first material and said second material both consist of the same material.

33. The method according to claim 29, wherein said first material and said second material consist respectively of two different materials.

34. The method according claim 1, further comprising:
a first preliminary step of providing a correlation between partial pressure values for said carbon oxide gas and carbon content values for said compound semiconductor crystal; and
a second preliminary step of selecting a carbon content value;
wherein said step a) comprises selecting said partial pressure to have a partial pressure value correlated to said carbon content value by said correlation.

35. The method according to claim 34, wherein said resultant content of said carbon in said compound semiconductor crystal is equal to said carbon content value that has been selected in said second preliminary step.

36. The method according to claim 34, wherein said correlation is defined by a formula:

$$C_{CARBON} = \alpha \times P^{0.5},$$

wherein C_{CARBON} represents said carbon content value, P represents said partial pressure value, and α represents a dependence coefficient.

37. The method according to claim 36, wherein said dependence coefficient α is in a range from $0.25 \times 10^{15} \text{ cm}^{-3} / \text{Torr}^{0.5}$ to $4 \times 10^{15} \text{ cm}^{-3} / \text{Torr}^{0.5}$ for C_{CARBON} being in terms of atoms of carbon per cm^3 and P being in terms of Torr.

38. The method according to claim 1, wherein said steps are carried out so that said resultant content of said carbon in said compound semiconductor crystal is in a range from $0.1 \times 10^{15} \text{ cm}^{-3}$ to $20 \times 10^{15} \text{ cm}^{-3}$.

39. The method according to claim 38, wherein said resultant content of said carbon in said compound semiconductor crystal is a resultant local content of carbon at a location in said compound semiconductor crystal defined by a fraction solidified (g) of 0.1.

40. The method according to claim 38, wherein said resultant content of said carbon in said compound semiconductor crystal is a resultant local content of carbon at a location in said compound semiconductor crystal.

41. The method according to claim 40, wherein said location is at a shoulder of said compound semiconductor crystal.

42. The method according to claim 40, wherein said location is a location defined by a fraction solidified (g) of 0.1 in said compound semiconductor crystal.

43. *A method of preparing a compound semiconductor crystal containing carbon, comprising: sealing a semiconductor raw material and a boron oxide based substance in a gas-impermeable airtight vessel and increasing a temperature of said airtight vessel to melt said raw material and said boron oxide based substance in said airtight vessel and thereby form a melted material from said raw material; and decreasing said temperature of said airtight vessel to solidify said melted material and thereby grow said compound semiconductor crystal containing a resultant content of said carbon, characterized by selecting a partial pressure of a carbon oxide gas, and making said carbon oxide gas having said selected partial pressure coexistent with said semiconductor raw material and boron oxide based substance prior to sealing said vessel, so that said resultant content of said carbon is dependent on said selected partial pressure of said carbon oxide gas.*

44. *The method according to claim 43, wherein said partial pressure selecting step is carried out so that said resultant content of said carbon in said compound semiconductor crystal is in a range from $0.1 \times 10^{15} \text{ cm}^{-3}$ to $20 \times 10^{15} \text{ cm}^{-3}$.*

45. *A method of preparing a compound semiconductor crystal containing carbon, comprising*

making a selected partial pressure of a carbon oxide gas coexistent with a melted material of a compound semiconductor raw material and a melted boron oxide base substance in a gas-impermeable airtight vessel, and then

decreasing a temperature of said airtight vessel to solidify said melted material and thereby grow said compound semiconductor crystal containing a controlled amount of carbon.

46. *The method according to claim 45, wherein said steps are carried out so that said controlled amount of carbon in said compound semiconductor crystal is in a range from $0.1 \times 10^{15} \text{ cm}^{-3}$ to $20 \times 10^{15} \text{ cm}^{-3}$.*

47. *A method of preparing a compound semiconductor crystal containing carbon, comprising:*

sealing a semiconductor raw material (2) and a boron oxide based substance (4) in a gas-impermeable airtight vessel, heating said raw material and said boron oxide based substance in said airtight vessel to melt them and thereby forming a melted material from said raw material; and

decreasing said temperature of said airtight vessel to solidify said melted material and thereby grow said compound semiconductor crystal containing a resultant content of said carbon,

characterized by

selecting a partial pressure of a carbon oxide gas (7) and making said carbon oxide gas coexistent with said semiconductor raw material and boron oxide based substance prior to sealing said vessel, so that said resultant content of said carbon is dependent on said selected partial pressure of said carbon oxide gas.

48. *The method according to claim 47, wherein said carbon oxide gas (7) includes at least one type of gas selected from the group consisting CO gas and CO₂ gas.*

49. *The method of preparing a compound semiconductor crystal according to claim 47, wherein said carbon oxide*

gas (7) is sealed in said airtight vessel (8) having a partial pressure of 13.3 to 13333 Pa (0.1 to 100 Torr) at 25° C.

50. The method of preparing a compound semiconductor crystal according to claim 47, wherein growing said compound semiconductor crystal, a space behind a raw-material melt (2) formed from said melted semiconductor material has a most heated portion and a least heated portion with a temperature difference of no more than 300° C. therebetween.

51. The method of preparing a compound semiconductor crystal according to claim 47, wherein said semiconductor raw material (2) comprises a compound semiconductor material.

52. The method of preparing a compound semiconductor crystal according to claim 47, wherein said semiconductor raw material (2) comprises GaAs.

53. The method according to claim 47, wherein said melted semiconductor material (2) is at least partially kept in contact with said boron oxide based substance (4) in growing said compound semiconductor crystal.

54. The method according to claim 53, wherein said melted semiconductor material (2) has an upper surface entirely covered with said boron oxide based substance (4) in growing said compound semiconductor crystal.

55. The method according to claim 53, further comprising selecting said boron oxide based substance (4) to comprise boron oxide and a water content of water, wherein said water content has a variation in a range from -20% to +20% relative to an average of said water content.

56. The method according to claim 53, wherein said boron oxide based substance (4) has a water content of no more than a first upper limit value of 300 ppm.

57. The method according to claim 56, wherein said boron oxide based substance (4) has a water content of no more than a second upper limit value of 100 ppm.

58. The method of preparing a compound semiconductor crystal according to claim 47, wherein said carbon oxide gas (7) is sealed in said airtight vessel (8) according to an expression:

$$C_{\text{carbon}} = a \times P^{0.5}$$

wherein C_{carbon} (cm^{-3}) represents a carbon concentration in said compound semiconductor crystal, P (Pa) represents a partial pressure of said carbon oxide gas (7), and "a" represents any coefficient.

59. The method of preparing a compound semiconductor crystal according to claim 58, wherein said coefficient a ranges from 0.217×10^{14} to $3.46 \times 10^{14} \text{ cm}^{-3}/\text{Pa}^{0.5}$ (0.25×10^{15} to $4 \times 10^{15} \text{ cm}^{-3}/\text{Torr}^{0.5}$).

60. The method of preparing a compound semiconductor crystal according to claim 59, wherein said coefficient a ranges from 0.433×10^{14} to $1.73 \times 10^{14} \text{ cm}^{-3}/\text{Pa}^{0.5}$ (0.5×10^{15} to $2 \times 10^{15} \text{ cm}^{-3}/\text{Torr}^{0.5}$).

61. The method of preparing a compound semiconductor crystal according to claim 47, wherein a step of subjecting

said airtight vessel (8) to a vacuum heat treatment is provided before the step of sealing said airtight vessel (8).

62. The method of preparing a compound semiconductor crystal according to claim 61, wherein said vacuum heat treatment is performed at no more than 350° C.

63. The method of preparing a compound semiconductor crystal according to claim 47, wherein at least an internal wall of said airtight vessel (8) and at least an outer surface of the content of said airtight vessel (8) other than said compound semiconductor material and said boron oxide based substance (4) are formed from a material excluding carbon.

64. The method of preparing a compound semiconductor crystal according to claim 63, wherein said material excluding carbon includes at least one material selected from the group consisting of quartz, silicon nitride, boron nitride, pyrolytic boron nitride and alumina.

65. The method of preparing a compound semiconductor crystal according to claim 47, wherein said gas-impermeable airtight vessel (8) at least has a portion formed from quartz.

66. The method of preparing a compound semiconductor crystal according to claim 65, wherein said portion formed from quartz has a thickness of no less than 1.5 mm.

67. The method of preparing a compound semiconductor crystal according to claim 65, wherein said portion formed from quartz is controlled to have a temperature of at most 1270° C. in growing said compound crystal.

68. The method of preparing a compound semiconductor crystal according to claim 47, wherein a space behind a raw-material melt (2) formed from said melted semiconductor material is larger in volume than a space on the side of said raw-material melt.

69. The method of preparing a compound semiconductor crystal according to claim 68, wherein a space behind said raw-material melt (2) is no less than twice larger in volume than said space on the side of said raw-material melt.

70. The method of claim 47, wherein said compound semiconductor crystal has a carbon concentration of $0.1 \times 10^{15} \text{ cm}^{-3}$ to $20 \times 10^{15} \text{ cm}^{-3}$.

71. The method of claim 70, wherein said compound semiconductor contains GaAs.

72. A method of preparing a compound semiconductor crystal containing carbon, comprising

making a selected partial pressure of a carbon oxide gas coexistent with a melted material of a compound semiconductor raw material and a melted boron oxide base substance in a crucible in a gas-impermeable airtight vessel, and then

decreasing a temperature of said airtight vessel to solidify said melted material in the crucible and thereby grow said compound semiconductor crystal containing a controlled amount of carbon.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : RE 40,662 E
APPLICATION NO. : 10/640430
DATED : March 17, 2009
INVENTOR(S) : Tomohiro Kawase

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title Page item 56 Other Publications, page 2, line 28, "Kawasw" should be --Kawase--

Signed and Sealed this

Tenth Day of November, 2009

A handwritten signature in black ink that reads "David J. Kappos". The signature is written in a cursive style with a large initial 'D' and 'K'.

David J. Kappos
Director of the United States Patent and Trademark Office