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 (12) **Reissued Patent**  
**Härle**

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(54) **METHOD FOR PRODUCING NITRIDE MONOCRYSTALS**

5,905,276 A 5/1999 Manabe et al.

FOREIGN PATENT DOCUMENTS

(75) Inventor: **Volker Härle**, Waldetzenberg (DE)  
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 (21) Appl. No.: **11/069,936**  
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EP	62001874	1/1987
EP	0295467	12/1988
EP	02145773	6/1990
EP	0429272	5/1991
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§ 371 (c)(1),  
 (2), (4) Date: **Oct. 1, 2001**

(87) PCT Pub. No.: **WO00/46431**  
 PCT Pub. Date: **Aug. 10, 2000**

OTHER PUBLICATIONS

Nutt, Rodger W., "Synthesis and Characterization of (Trimethylsilyl)amino- and (Methyl(trimethylsilyl)amino) gallium Dichloride", American Chemical Society 1985, pp. 159-164.

Riedel, R., "Bis (dichlor-N-trimethylsilyl)cycloaminoalan Kristallstruktur und thermischer abbau zu Aluminiumnitrid", Z. anor. Allg. Chem. 603 (1991)p. 119-127, Stuttgart.

Nutt, Rodger W., "Synthesis and Characterization of (Trimethylsilyl)amino- and (Methyl(trimethylsilyl)amino) gallium Dichloride", American Chemical Society 1985, pp. 159-164.

Riedel, R., "Bis (dichlor-N-trimethylsilyl)cycloaminoalan Kristallstruktur und thermischer abbau zu Aluminiumnitrid", Z. anor. Allg. Chem. 603 (1991)p. 119-127, Stuttgart.

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(57) **ABSTRACT**

The inventive method exploits the fact that in solutions or melts which contain certain organic substances, small nitride crystallites consisting of GaN or AlN are formed by thermal reaction and decomposition. A vessel containing the melt is kept at a first temperature  $T_1$ . In the vessel is a substrate nucleus of be nitride to be formed, which is heated to second temperature  $T_2$  through the input of energy, where  $T_2 > T_1$ . Epitaxial growth from the melt then takes place on the surface of the substrate nucleus. The energy input can be carried out in different ways.

**Related U.S. Patent Documents**

Reissue of:

(64) Patent No.: **6,527,853**  
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 Filed: **Feb. 1, 2000**

(30) **Foreign Application Priority Data**

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(51) **Int. Cl.**  
**C30B 19/00** (2006.01)  
**C30B 19/08** (2006.01)

(52) **U.S. Cl.** ..... **117/54; 117/73; 117/952**

(58) **Field of Classification Search** ..... **117/54,**  
**117/73, 952**

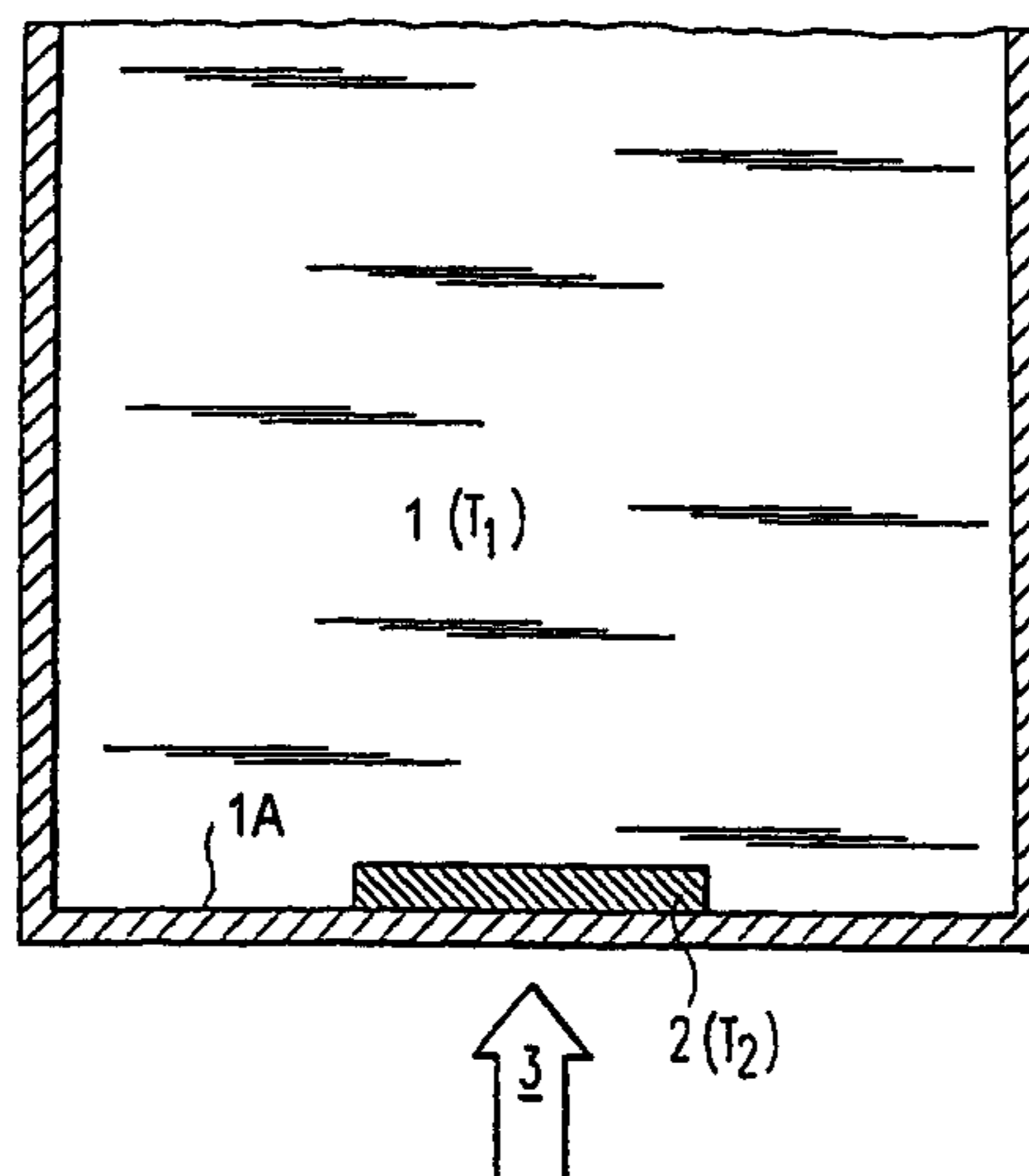
See application file for complete search history.

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**37 Claims, 2 Drawing Sheets**



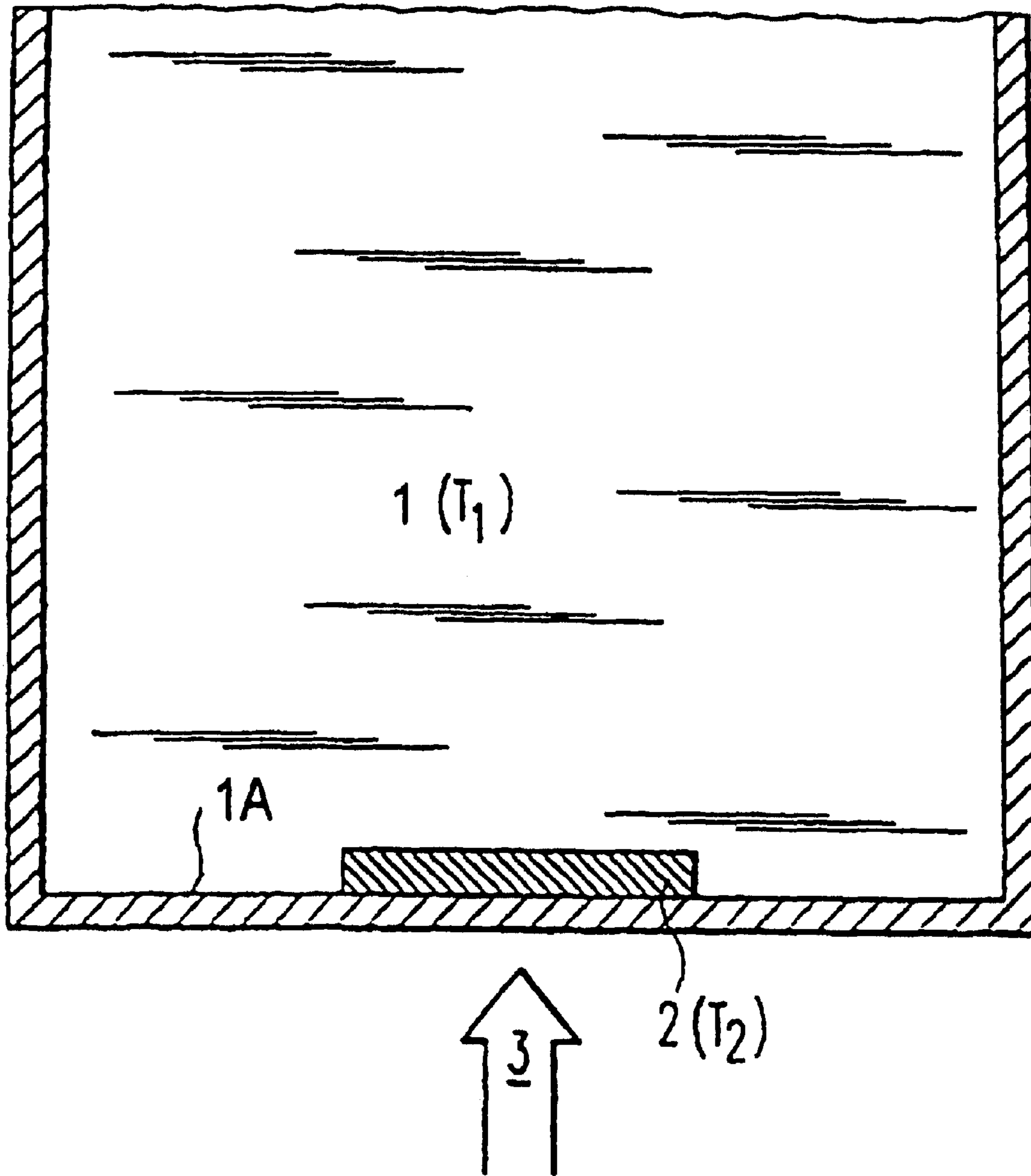


FIG. 1

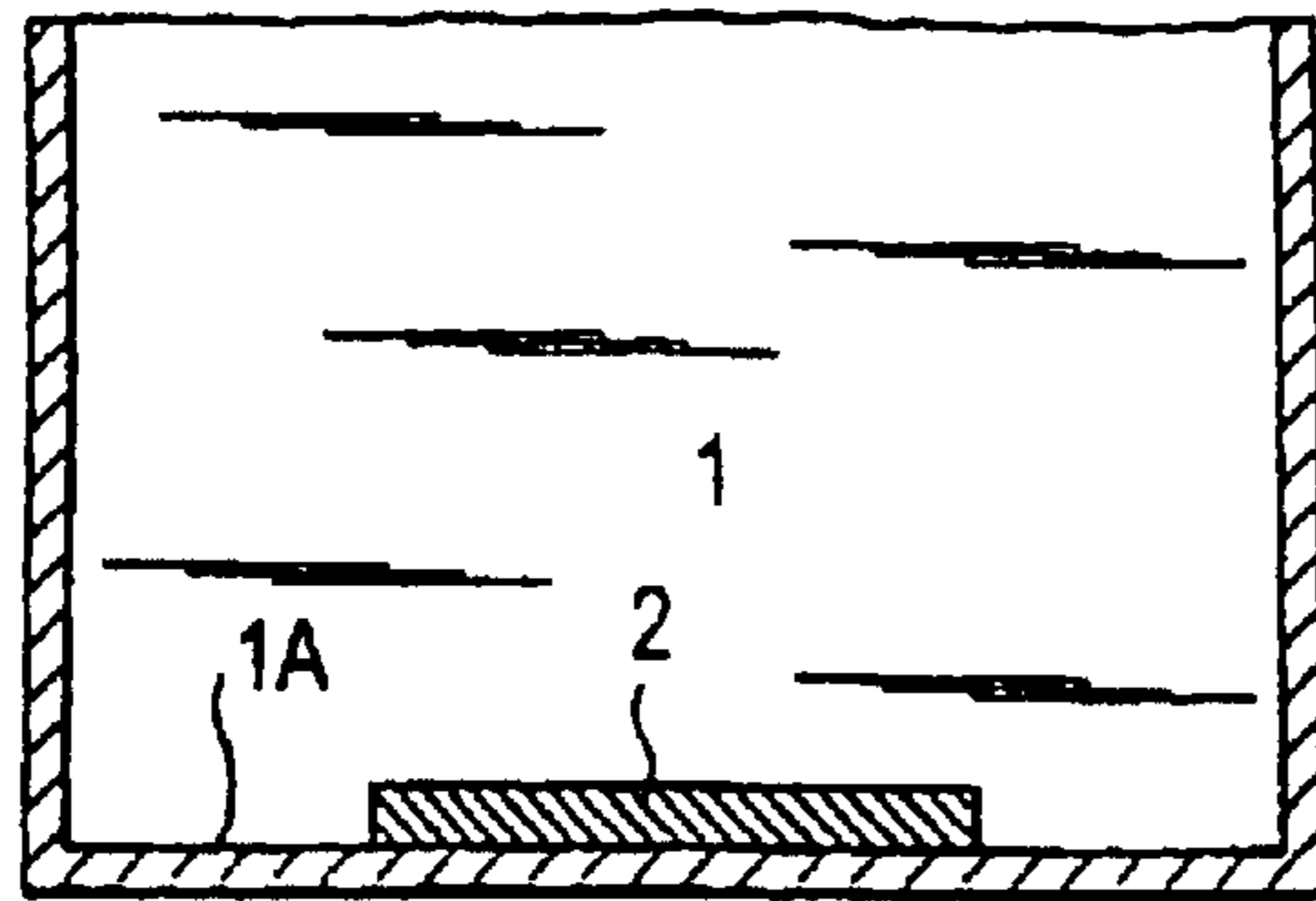


FIG. 2A

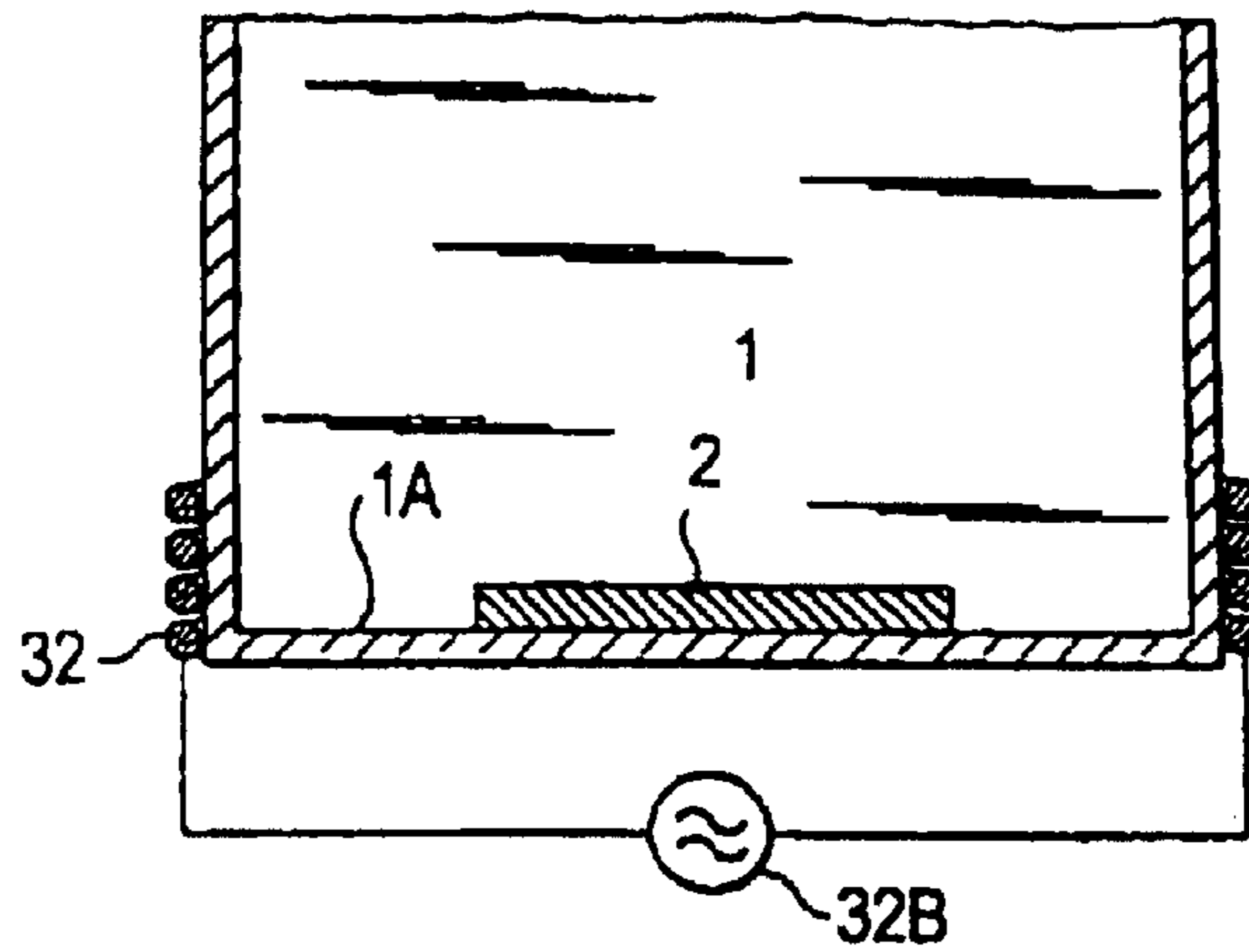
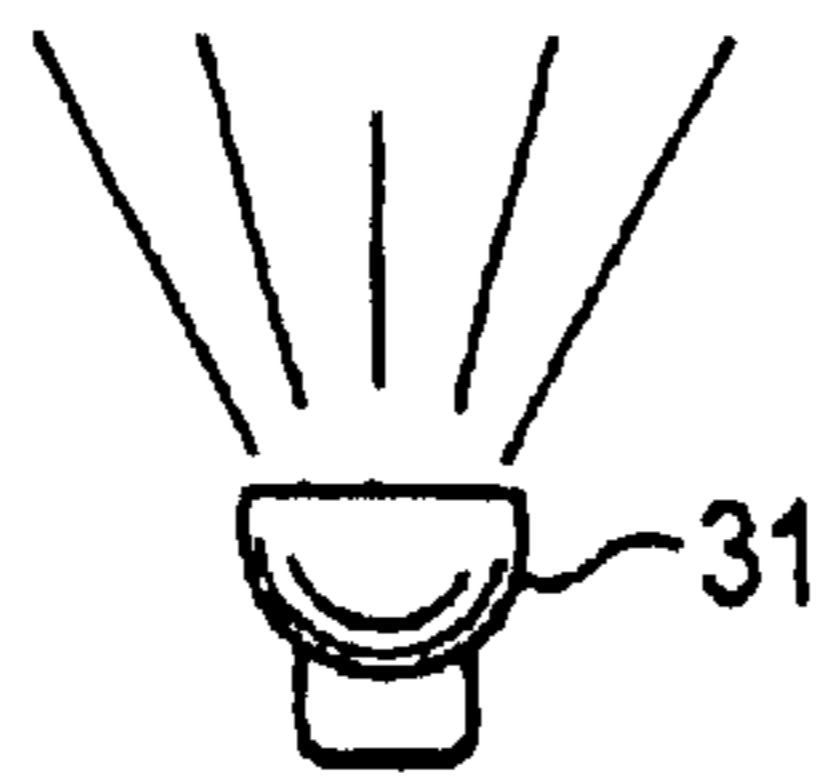


FIG. 2B

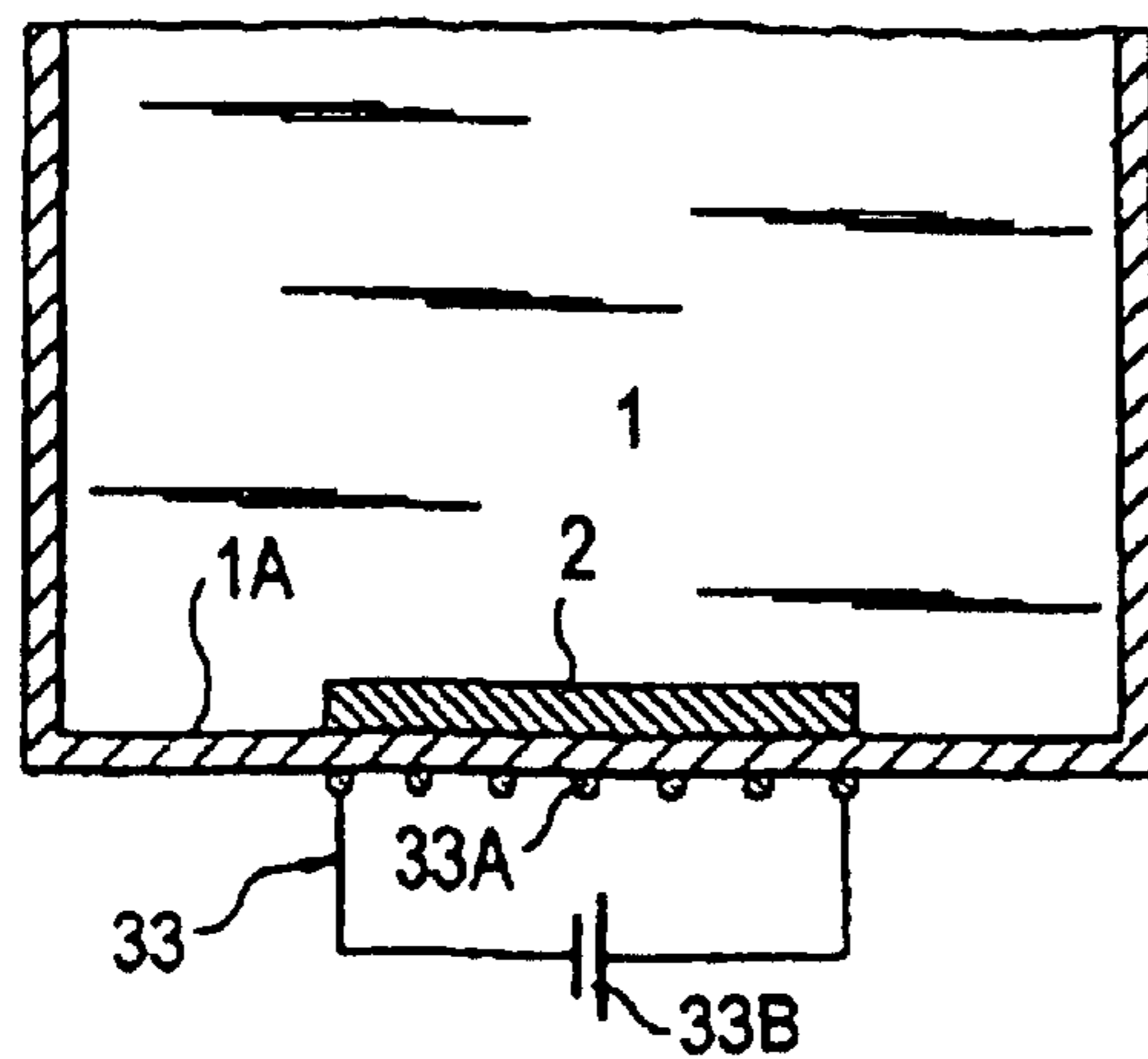


FIG. 2C

## METHOD FOR PRODUCING NITRIDE MONOCRYSTALS

**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.**

This invention relates to a method for producing nitride monocrystals [pursuant to Patent claim 1].

The production of high-efficiency structural elements such as semiconductor lasers and light-emitting diodes requires substrate crystals with maximized crystal perfection. Especially structural elements based on nitride semiconductors, for example such as Ga(In,Al)N, with which the ultraviolet to blue-green spectral region of the visible spectrum has very recently been opened up, can meet this requirement only conditionally, since the necessary semiconductor layer sequences are deposited on so-called foreign substrates (sapphire; SiC; Si; GaAs; etc.). However, perfect crystals require the use of "homosubstrates," or substrates of the same or closely related material, to realize the low dislocation densities required for the structural elements.

Nitride crystals have very high bond energies. To produce corresponding substrate crystals, therefore, extremely high pressure and temperatures of about 1000° C. and higher are necessary. The existing methods are based either on methods that enable the formation of crystals from the melt at high pressure, or on a sublimation method in which crystal growth occurs essentially from the gas phase. Quasi-crystals also lead to reduction of dislocation densities, but because of the lattice misfits physically present, they contain prestresses that can be eliminated only by the interfering dislocations. Such quasi-crystals are produced by deposition of thick nitride films on foreign substrates (like sapphire; SiC; Si; GaAs; etc.). Examples of methods used are organometallic gas phase epitaxy and hydride gas phase epitaxy.

The methods described here, on the one hand, are very costly and tedious, and on the other hand they do not provide the desired crystal perfection.

The underlying objective of this invention is thus to describe a method for producing nitrides, especially [(Ga, Al)Ni [sic]], (*Ga, Al nitride*), that on the one hand is as economical as possible, and on the other hand permits the most perfect possible monocrystalline structure.

The method pursuant to the invention for solving this problem is based on the thermal reaction and decomposition (pyrolysis) of an organic substance that contains the atomic constituents of the nitride monocrystal to be formed. This organic substance is contained in a solution or in a melt that is held at a first temperature. In the solution of the melt there is a substrate nucleus consisting of the nitride material to be grown or of a related type of nitride material. This substrate nucleus is supplied with thermal energy so that a second temperature is reached, at least on its surface in contact with the melt, that is higher than the first temperature. Because of this, nitride molecules are formed and deposited on the heated surface, and the nitride monocrystal thus grows.

In papers by R. Riedel et al. (*Z. anorg. allg. Chem.* 603 (1991), 119–127) and W. Rodger Nutt et al. (*Inorg. Chem.* 1985, 24, 159–164), it was shown, for example, that AlN and GaN "microcrystals" can be produced from the thermal reaction of various organic substances (bis(dichloro-N-trimethylsilyl)cycloaminoalane; (trimethylsilyl)amino- and methyl(trimethylsilyl)aminogallium dichloride). The objective of the method described here is selective thermal

decomposition on a crystal surface. For this purpose, the desired material or a related type of material is made available as a "crystal nucleus." The selective heating of just this surface leads to the decomposition of the organic compounds that are either in a melt or in a solution. Nitride molecules are formed that contain all of the atoms necessary for crystal construction. Heating the surface of the nucleus leads to the molecules formed also being able to be deposited only there, which leads to crystal growth. Such a method, moreover, is economical and requires only small expenditures for apparatus.

It is preferred for the solution or melt containing the organic substance to be in a container, and for the crystal nucleus to be positioned along a section of the container wall, with the thermal energy being fed to the substrate nucleus through this section of the container wall.

The thermal energy can be introduced in different ways. For example the substrate nucleus can be impacted by radiation emitted by a radiation source, particularly an infrared radiation source. However, the thermal energy can also be supplied inductively. Another possibility consists of introducing the thermal energy through a resistance heater. This can contain resistance wires that run in the section of the container wall and can be supplied with electrical current.

The invention will be described in detail below with reference to examples of embodiments in the drawings. The drawings show:

FIG. 1 a schematic arrangement for implementing the method of the invention;

FIGS. 2A to C forms of embodiment with respect to supplying the thermal energy to the substrate nucleus.

FIG. 1 shows a schematic arrangement for implementing the method of the invention.

This arrangement includes a container 1 to hold a liquid solution or melt that contains an organic compound that contains the atomic constituents of the nitride monocrystal to be formed. The solution or melt is held at a first temperature  $T_1$ , for example by storing the container 1 in a furnace and adjusting the temperature of the furnace to the temperature  $T_1$ . At the bottom of the container 1 is placed a substrate nucleus 2 that consists of the nitride to be grown or a related type of nitride. This substrate nucleus 2 is heated by means of an energy source that is symbolized by the arrow 3, so that at least its surface in contact with the melt reaches a temperature  $T_2$  that is higher than  $T_1$ . This makes possible the thermal decomposition of the organic substance and the formation and deposition of nitride molecules on the substrate nucleus 2.

When gallium nitride (GaN), for example, is to be grown, as described in the publication by Nutt et al. cited above, (trimethylsilyl)aminogallium dichloride or methyl(trimethylsilyl)aminogallium dichloride can be used as the organic substance.

On the other hand, if aluminum nitride (AlN) is to be grown, as described in the publication by Riedel et al. cited above, bis(dichloro-N-trimethylsilyl)cycloaminoalane can be used as the organic substance.

FIGS. 2A to 2C illustrate three different types of embodiment for the energy supply. The arrow 3 in FIG. 1 is thus replaced in these figures by corresponding conceivable structures.

According to FIG. 2A, for purposes of radiant heating there is a light source 31, preferably an infrared light source, below the container 1, whose emitted radiation is pointed at the section of the container wall at which the substrate nucleus 2 is located. It is also theoretically conceivable for the substrate nucleus 2 to be at any position in the melt

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whatsoever, and for the radiation of an external light source to be focused on it by suitable optics.

In the arrangement of FIG. 2B, the heat energy is introduced by inductive coupling. To this end, the lower section of the container 1 is surrounded by a coil winding 32 that is powered with alternating current from a source of alternating voltage 32B. Here also there is spatial freedom inasmuch as the coil 32 and thus the substrate nucleus 2 can be positioned at any longitudinal position on the container 1.

In the arrangement of FIG. 2C, the thermal energy is supplied by a resistance heater 33. The resistance heater 33 has a resistance wire 33A that is in contact with the container wall and can be powered by a direct-voltage source 33B with direct current. This produces Joule heat that can penetrate through the container wall into the substrate nucleus 2. The resistance wire 33A preferably follows a looped or spiral-shaped path and thus covers a certain area, in order to impact it as homogeneously as possible with thermal energy. It can be embedded permanently in the container wall with connecting wires fed to the outside. However, it is also conceivable for it to be inserted into recesses provided for it on the outside of the container wall when needed.

Heat can be supplied very selectively to the substrate nucleus 2 by this method, but the substrate nucleus 2 has to be produced on the container wall.

A fourth possibility for energy supply, not illustrated, consists of introducing microwave energy. For this purpose, a microwave energy source, for example, a magnetron, can be placed beneath the container 1. The microwave radiation emitted by it can be fed to the section of the container wall on which the substrate nucleus 2 is positioned, with or without the use of a microwave guide.

Supplying the energy by means of electromagnetic radiation or inductively has the advantage over the resistance heater that the substrate nucleus 2 in principle can be located anywhere in the melt. In the case of the resistance heater, on the other hand, the substrate nucleus 2 has to be in contact with a wall of the container.

In addition to the temperature control of the growth process described and pursuant to the invention, other measures can be resorted to for homogenizing the growth process. For example, the melt can be agitated constantly during growth by a mechanical mixer. The substrate nucleus 2 can also be rotated around its cylindrical axis during growth, and/or it can be pulled through the solution at a low velocity. To control crystal growth, a static or likewise rotating electric field or magnetic field can also be applied. Finally, laminar flow can be produced in the solution, for example by having the solution flow to the substrate nucleus in a tube pointed at the substrate nucleus. All of the measures mentioned can arbitrarily be combined with one another to provide optimal growth conditions.

What is claimed is:

1. Method for producing a substrate of a nitride monocrystal suitable for semiconductor manufacture, characterized by the process steps

preparation of a solution or melt containing an organic compound at a first temperature  $T_1$ , wherein the organic compound contains the atomic constituents of the nitride monocrystal to be formed, and wherein there is a substrate nucleus of the nitride to be grown or of a related nitride in the melt, supplying thermal energy to the substrate nucleus so that a temperature  $T_2$  is reached at least by its surface in contact with the melt, wherein  $T_2 > T_1$ .

2. Method pursuant to claim 1, characterized by the fact that

the melt is in a container, and

the substrate nucleus is positioned along at least one section of the container wall, and

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the thermal energy is supplied to the substrate nucleus through this section of the container wall.

3. Method pursuant to claim 2, characterized by the fact that

the thermal energy is supplied by the radiation of a radiation source, particularly of an infrared radiation source.

4. Method pursuant to claim 2, characterized by the fact that

the thermal energy is supplied by inductive coupling.

5. Method pursuant to claim 2, characterized by the fact that

the thermal energy is supplied by a resistance heater, that contains resistance wires powered with an electrical current, which are in contact with the container wall.

6. Method pursuant to claim 2, characterized by the fact that

the resistance wires are embedded in the container wall.

7. Method pursuant to claim 2, characterized by the fact that

the thermal energy is supplied by microwave radiation.

8. Method pursuant to claim 1, characterized by the fact that

the thermal energy is supplied by the radiation of a radiation source, particularly of an infrared radiation source.

9. Method pursuant to claim 1, characterized by the fact that

the thermal energy is supplied by inductive coupling.

[10. Method pursuant to claim 1, characterized by the fact that

the thermal energy is supplied by a resistance heater, that contains resistance wires powered with an electrical current, which are in contact with the container wall.]

[11. Method pursuant to claim 10, characterized by the fact that

the resistance wires are embedded in the container wall.]

12. Method pursuant to claim 1, characterized by the fact that

the thermal energy is supplied by microwave radiation.

13. Method pursuant to claim 1, characterized by the fact that

the nitride is AlN, and

the organic compound is bis(dichloro-N-trimethylsilyl)cycloaminoalane.

14. Method pursuant to claim 1, characterized by the fact that

the nitride is GaN, and

the organic compound is (trimethylsilyl)aminogallium dichloride or methyl(trimethylsilyl)aminogallium dichloride.

15. A method for producing a substrate of a nitride monocrystal suitable for semiconductor manufacture, characterized by the process steps:

preparing a solution or melt containing an organic compound at a first temperature  $T_1$ , wherein the organic compound contains the atomic constituents of the nitride monocrystal to be formed, and wherein there is a substrate nucleus of the nitride to be grown or of a related nitride in the solution or melt; and

supplying thermal energy to the substrate nucleus so that a temperature  $T_2$  is reached at least by its surface in contact with the melt, wherein  $T_2 > T_1$ .

16. The method of claim 15, wherein the solution or melt is in a container, the substrate nucleus positioned along at least one section of the container wall, and the thermal energy is supplied to the substrate nucleus through this section of the container wall.

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17. The method of claim 16, wherein the thermal energy is supplied by a resistance heater comprising resistance wires powered with an electrical current, wherein the resistance wires are in contact with the container wall.

18. The method of claim 17, wherein the resistance wires are embedded in the container wall.

19. The method of claim 15, wherein the thermal energy is supplied by the radiation of an infrared radiation source.

20. The method of claim 15, wherein the thermal energy is supplied by inductive coupling.

21. The method of claim 15, wherein the thermal energy is supplied by microwave radiation.

22. The method of claim 15, wherein the nitride to be grown is AlN.

23. The method of claim 22, wherein the organic compound is bis(dichloro-N-trimethylsilyl)cycloaminoalane.

24. The method of claim 15, wherein the nitride to be grown is GaN.

25. The method of claim 24, wherein the organic compound is (trimethylsilyl)aminogallium dichloride or methyl (trimethylsilyl)aminogallium dichloride.

26. A method for producing a substrate of a nitride monocrystal suitable for semiconductor manufacture, characterized by the process steps:

preparing a solution or melt containing an organic compound at a first temperature  $T_1$ , wherein the organic compound contains the atomic constituents of the nitride monocrystal to be formed, and wherein there is a substrate nucleus in the solution or melt; and

supplying thermal energy to the substrate nucleus so that a temperature  $T_2$  is reached at least by its surface in contact with the melt, wherein  $T_2 > T_1$ .

27. The method of claim 26, wherein the substrate nucleus comprises a material selected to realize low dislocation densities in the nitride to be grown.

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28. The method of claim 27, wherein the substrate nucleus material is the nitride to be grown or a related nitride.

29. The method of claim 28, wherein the substrate nucleus material is the nitride to be grown.

30. The method of claim 26, wherein the solution or melt is in a container, the substrate nucleus is positioned along at least one section of the container wall, and the thermal energy is supplied to the substrate nucleus through this section of the container wall.

31. The method of claim 30, wherein the thermal energy is supplied by a resistance heater comprising resistance wires powered with an electrical current, wherein the resistance wires are in contact with the container wall.

32. The method of claim 31, wherein the resistance wires are embedded in the container wall.

33. The method of claim 26, wherein the thermal energy is supplied by the radiation of an infrared radiation source.

34. The method of claim 26, wherein the thermal energy is supplied by inductive coupling.

35. The method of claim 26, wherein the thermal energy is supplied by microwave radiation.

36. The method of claim 26, wherein the nitride to be grown is AlN.

37. The method of claim 36, wherein the organic compound is bis(dichloro-N-trimethylsilyl)cycloaminoalane.

38. The method of claim 26, wherein the nitride is GaN.

39. The method of claim 38, wherein the organic compound is (trimethylsilyl)aminogallium dichloride or methyl (trimethylsilyl)aminogallium dichloride.

\* \* \* \* \*

UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : RE 40,718 E  
APPLICATION NO. : 11/069936  
DATED : June 9, 2009  
INVENTOR(S) : Volker Härle

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

Column 2, Other Publications, Rodger W. Nutt Reference, third line, replace  
“Society” with --Society--

Column 2, Other Publications, delete second occurrence of Rodger W. Nutt and  
R. Riedel references

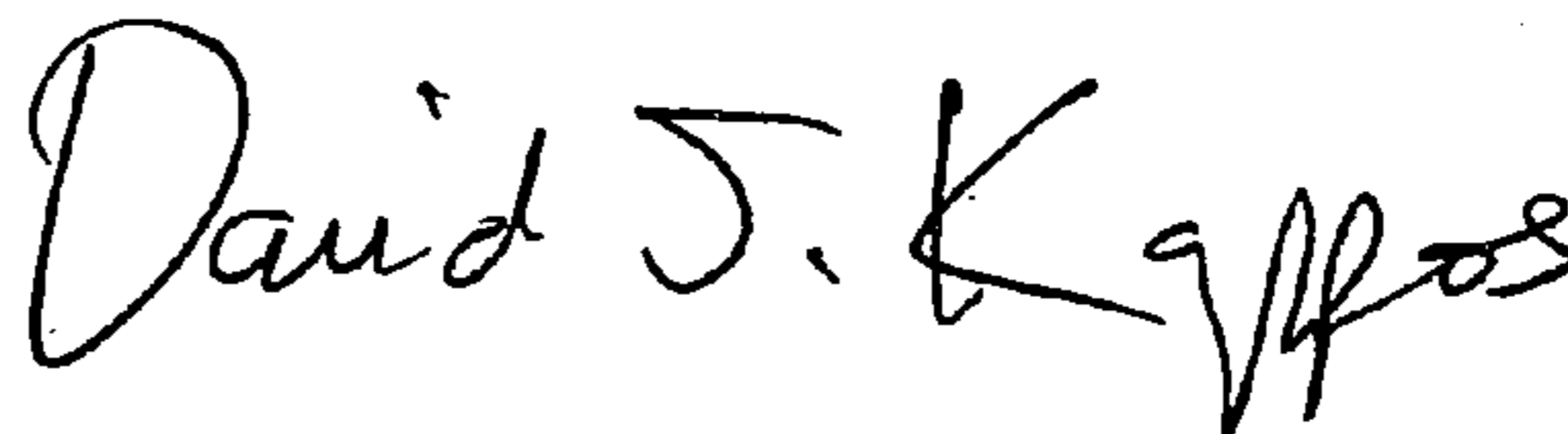
Column 4, Line 15, claim 6, replace “claim 2” with --[claim 2] *claim 5*--

Column 4, Line 64, claim 15, replace “*nucleus positioned*” with --*nucleus is  
positioned*--

Column 5, Line 28, claim 26, replace “*nucleus in*” with --*nucleus of the nitride to be  
grown or of a related material in*--

Signed and Sealed this

Eighteenth Day of August, 2009



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

UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : RE 40,718 E  
APPLICATION NO. : 11/069936  
DATED : June 9, 2009  
INVENTOR(S) : Volker Härle

Page 1 of 1

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Title Page

Column 2, Foreign Patent Documents replace “EP 62001874 1/1987” with  
--JP 62001874 1/1987--

Column 2, Foreign Patent Documents replace “EP 02145773 6/1990” with  
--JP 02145773 6/1990--

Column 2, Abstract, line 6, replace “be nitride” with --the nitride--

Signed and Sealed this

Fourth Day of May, 2010

A handwritten signature in black ink that reads "David J. Kappos". The signature is written in a cursive, flowing style.

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



UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : RE 40,718 E  
APPLICATION NO. : 11/069936  
DATED : June 9, 2009  
INVENTOR(S) : Volker Härle

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:

Column 4

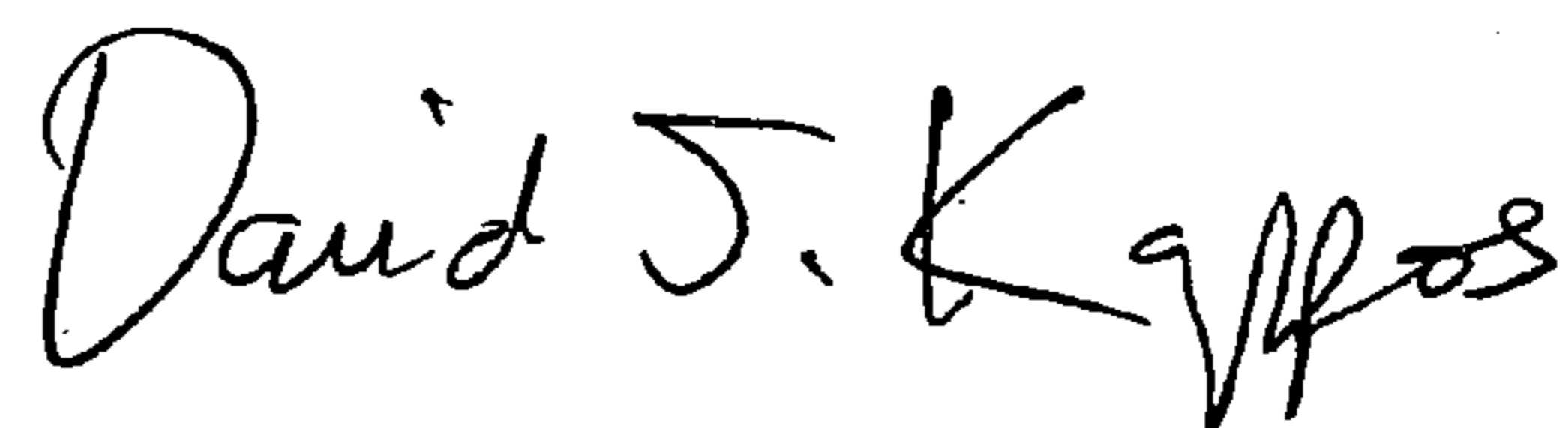
Line 61, insert the words --solution or-- before the words --melt, wherein--

Column 5

Line 32, insert the words --solution or-- before the words --melt, wherein--

Signed and Sealed this

Thirteenth Day of July, 2010

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*