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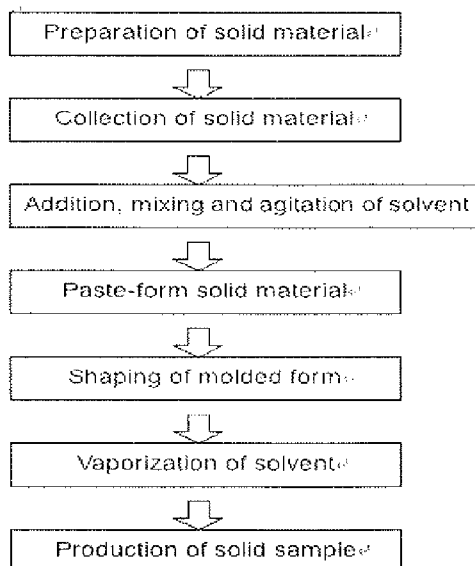
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(54) Title: SUPPLY APPARATUS AND METHOD OF SOLID MATERIAL GAS

Figure 2



(57) Abstract: A solid material gas supply apparatus and method in which solid material, which can be sublimated and supplied at a desired rate using carrier gas C, is processed into a paste or spray form by adding a solvent, and is equipped with a solid sample production means that produces solid sample S by vaporizing and removing said solvent, supply section 1 that supplies carrier gas C, dispersion section 2 that disperses the supplied carrier gas C, sample placement section 3 in which solid sample S is placed, and discharge section 4 that feeds out solid material gas G supplied from sample placement section 3.



SUPPLY APPARATUS AND METHOD OF SOLID MATERIAL GAS

Cross-Reference to Related Applications

This application claims the benefit under 35 U.S.C. § 119(a-d) to Japanese
5 patent application publication No. 2011-129312, filed June 9, 2011, the entire
contents of which are incorporated herein by reference.

Technical Field

The present invention relates to a supply apparatus and method of solid
10 material gas, such as solid organic compounds and solid organic metal
compounds, used, for example, in production devices and research facilities for
such items as semiconductors and solar cells. The "solid materials" referred to in
the present patent application are solid materials that are widely used industrially,
can be sublimated (vaporized) / supplied at a desired rate by a carrier gas, and
15 include, for example, such inorganic metal compounds as hafnium chloride, such
solid organic metal compounds as trimethyl indium, and such solid organic
compounds as phthalic acid.

Background

20 Gaseous materials and liquid materials have been used extensively in
production devices that manufacture semiconductors and solar cells (for example,
as film formation materials), research facilities for developing new materials, and
various processes in such facilities, but solid materials that have been sublimated
(vaporized) as described above have also been used often recently. See, e.g.,
25 WO2009/087609 to L'Air Liquide-Societe Anonyme Pour L'Etude et L'Exploitation
des Procédes Georges Claudes. Such solid materials are sublimated and carried
(referred hereinafter as "solid component gas") by highly stable inert gases with
low reactivity, such as rare gases including helium and argon, and are supplied to
and consumed at the above-mentioned production devices.

30 For example, a configuration example of evaporator distribution system **110**,
as shown in **Figure 6 (A) and (B)**, that has many containers to provide extensive
surface area for evaporating liquid and solid materials such as liquid and solid
source reagents used in such methods as the chemical vapor deposition method
(CVD), atomic layer chemical vapor deposition method (ALCVD), and ion

implantation method, can be cited (see for example JP 2006-503178). Ampule **112** comprises bottom section **114** and side walls **116** that form the inner chamber, and multiple containers **122** are stacked vertically inside the inner chamber of the ampule. The vertically stacked containers can be mounted to and removed from the ampule and can be separated individually from each other so that they can easily be purged and replaced. Internal carrier gas member **123** is located in the ampule, connected (welded) to carrier gas intake port **120**, and leads the carrier gas to below the container at the lower-most part of the containers stacked vertically at the bottom of the inner chamber. Internal carrier gas member **123** passes through cavity **127** in each container and container bottom **124**. Each individual container **122** is equipped with bottom **124** and side wall **126**, and has cavity **127** for placing a desired source material **128**. Each individual container has multiple protruded sections **130**, and each protruded section contains flow path **132** that allows the carrier gas to pass through the protruded section (see paragraphs 0018 ~ 0023 of JP 2006-503178). Here, **138** is a sealing O-ring and **140** is a gas outtake valve.

With the solid material gas supply apparatus and supply method as described above, however, the following problems have occurred at times:

(i) Solid materials in normal state are either in powder or granular form, and it is difficult to prevent them from scattering and distributing unevenly during their delivery to the supply devices and such work as installation, and thus their uniform sublimation and supply by carrier gas has been difficult.

(ii) Moreover, in cases the solid material is in powder form in particular, scattering and adhesion of the powder to the surrounding area due to generation of static electricity caused by their contact with the carrier gas that has been dried in a stored state has occurred. Adhered solid material not only obstruct further supply of the solid material to the supply device, but also makes it difficult to accurately measure the remaining amount of the solid material.

(iii) Furthermore, not only the remaining amount of the solid material greatly affects the material concentration, but also the form and format of the solid material greatly affects the material concentration. With powder or granular solid material in particular, it has been verified that sufficient material concentration can not be obtained due to such factors as the change in its state of contact with the carrier gas at the surface even if the remaining amount is at a desired level.

(iv) With the configuration of the above-mentioned evaporator distribution system **110**, there has been a problem of the distribution of the material on the tray becoming uneven when the container is tilted to possibly cause instability in the material concentration, and also the installation and purging of the container for the material are not easy due to the complex container structure.

(v) In general, weight measuring is used as a method to detect the remaining amount of the solid material, but it is impossible to detect the changes in the material concentration that accompanies local reduction of the solid material just by managing the weight.

WO2008/028170 to Advanced Technology Materials, Inc. discloses in paragraph 0103 many mechanisms to address these issues.

A need remains to provide a solid material gas supply apparatus and a supply method that supply solid material gas at a stable concentration, and can precisely and easily detect the remaining amount of the solid material with a simple method and configuration.

Summary

Disclosed are methods to supply a gas of a solid material to semiconductor or solar cell production devices. The solid material is introduced into one or more trays. A solvent is sprayed on a surface of the solid material in the trays. The one or more trays are introduced into the supply apparatus. The solvent is removed under an inert gas atmosphere. The solid material is sublimated to produce the gas of the solid material. The disclosed methods may further include one or more of the following aspects:

- approximately 1% w/w to approximately 10% w/w of solvent being sprayed on the surface of the solid material in the trays;
- approximately 5% w/w of solvent being sprayed on the surface of the solid material in the trays;
- the solid material being selected from the group consisting of hafnium chloride, zirconium chloride, trimethylindium, bis(cyclopentadienyl)magnesium, tetraethyl zinc, phthalic acid, naphthalene and anthracene;
- the solid precursor being selected from the group consisting of HfCl_4 , ZrCl_4 , and anthracene;

- the solvent being selected from the group consisting of n-hexane, n-octane, acetone, toluene, tetrahydrofuran, ethanol, ethylmethylketone, and 1,4-dioxane;
- the solid material being $ZrCl_4$ or $HfCl_4$ and the solvent being selected from the group consisting of n-hexane, n-octane, acetone, and toluene;
- the solid material being anthracene and the solvent being selected from the group consisting of n-hexane, n-octane, acetone, tetrahydrofuran, ethanol, ethylmethylketone, and 1,4-dioxane;
- weighing each of the one or more trays after introducing the solid material, weighing each of the one or more trays after spraying the solvent, and verifying removal of the solvent by weighing each of the one or more trays after removing the solvent;
- the solvent being removed prior to introducing the one or more trays into the supply apparatus; and
- supplying the gas of the solid material by a carrier gas from the supply apparatus to semiconductor or solar cell production devices.

Also disclosed is a supply apparatus of solid material gas characterized in that the solid material, which can be sublimated and supplied at a desired rate using a carrier gas, is processed into a paste or spray form by adding a solvent, and has a solid sample production means that produces a solid sample by vaporizing and removing said solvent, a supply section that supplies the carrier gas, a dispersion section that disperses the supplied carrier gas, a sample placement section in which the aforementioned sample is placed, and a discharge section that feeds out the solid material gas supplied from said sample placement section. The supply apparatus may include one or more of the following aspects:

- the aforementioned solid sample production means being equipped with an inert gas inlet section and a tray to place the solid sample, and that the solid material processed into a paste or spray form is placed statically in said inert gas atmosphere under atmospheric pressure to vaporize and remove the aforementioned solvent to produce the solid sample placed on the aforementioned tray; and
- the aforementioned dispersion section being connected to the aforementioned supply section, it is equipped with multiple divergent flow

paths that diverge the carrier gas, and one or more spray nozzles installed in each of the divergent flow paths, that spray the carrier gas onto the solid sample placed on the aforementioned placement section.

Also disclosed are solid material gas supply methods using the solid material gas supply apparatus described above, characterized in that the solid sample produced in accordance with the following pre-processes is placed, and a prescribed amount of the solid material is sublimated and supplied by the carrier gas.

(1) A process of preparing powder or granular solid material.

(2) A process of collecting a prescribed amount of the aforementioned solid material in the container with a prescribed capacity.

(3) A process of adding a prescribed amount of solvent to the aforementioned container, mixing and agitating it with the aforementioned solid material, and producing solid material in paste form.

(4) A process of shaping the aforementioned paste-form solid material into a form with a flat surface.

(5) A process of statically placing the aforementioned solid sample in a prescribed sealed container, and producing the solid sample by vaporizing and removing the solvent under an inert gas atmosphere. The disclosed solid material gas supply methods may include one or more of the following aspects:

- a tray for placing the aforementioned solid sample is located in the sample placement section, dispersed carrier gas is supplied to said sample placement section, the carrier gas is discharged from the aforementioned sample placement section, and the carrier gas accompanying the solid material is dispersed and mixed, and discharged as the solid material gas; and
- the concentration of the solid material in the aforementioned solid material gas and the flow rate of the aforementioned carrier gas are monitored, and the remaining amount of the solid material in the aforementioned solid sample is controlled based on the remaining amount of the aforementioned solid sample and the concentration of the solid material in the aforementioned solid material gas acquired in advance.

Brief Description of Drawings

For a further understanding of the nature and objects of the present invention, reference should be made to the following detailed description, taken in conjunction with the accompanying graphs, in which like elements are given
5 the same or analogous reference numbers, and wherein:

Figure 1 is a schematic illustration of the basic configuration example of the solid material gas supply apparatus;

Figure 2 is an explanatory drawing showing an example of a paste production process of the solid sample of the solid material gas supply
10 apparatus;

Figure 3 is a schematic illustration of the second configuration example of the solid material gas supply apparatus;

Figure 4 is an explanatory drawing showing an example of a degree of reliance of the solid material components concentration in the solid material gas
15 on the remaining amount of the solid material;

Figure 5 is an explanatory drawing showing an example of a degree of reliance of the solid material components concentration in the solid material gas on the remaining amount of the solid material; and

Figure 6 is a schematic illustration of a prior art example of an evaporator
20 delivery system for vaporizing liquid and solid material based on conventional technologies.

Detailed Description of Preferred Embodiments

In view of the above-described problems, the present inventors
25 conducted intensive research and discovered that the aim can be reached by means of the solid material gas supply apparatus and supply method described below.

Disclosed is a supply apparatus of solid material gas, which is characterized in that the solid material, which can be sublimated and supplied at
30 a desired rate using a carrier gas, is processed into a paste or spray form by adding a solvent, and has a solid sample production means that produces a solid sample by vaporizing and removing said solvent, a supply section that supplies the carrier gas, a dispersion section that disperses the supplied carrier gas, a sample placement section in which the aforementioned sample is placed,

and a discharge section that feeds out the solid material gas supplied from said sample placement section. The disclosed supply apparatus provides only one embodiment in which the sublimated solid material gas may be utilized. One of ordinary skill in the art will recognize that the disclosed methods may also be used to supply the gas of a solid material without a carrier gas, for example, in ion implant devices.

As described above, there have been several problems in sublimating the solid material and supplying it at a stable material concentration. The disclosed apparatus and methods solve these problems by first dispersing the carrier gas that contacts the solid material to create a uniform flow and uniformly sublime the solid material, processing the solid material into a paste or spray form by adding a solvent and producing a solid sample by vaporizing and removing said solvent. In other words, it is possible to uniformly sublime the solid material and extract solid material gas with uniform material concentration by exposing it to the dispersed carrier gas without scattering or unevenness due to the processing or static electricity with the solid sample produced in this manner. Moreover, by uniformly sublimating the solid material, it is possible to uniformly reduce the amount of the solid material and maintain uniform sublimation of the solid material to provide a solid material gas supply apparatus that can supply solid material gas with stable concentration for an extended period of time with a simple method and configuration.

The above-described supply apparatus of solid material gas is characterized in that the aforementioned solid sample production means is equipped with a inert gas gas inlet section and a tray to place the solid sample, and that the solid material processed into a paste or spray form is placed statically in said inert gas atmosphere under atmospheric pressure to vaporize and remove the aforementioned solvent to produce the solid sample placed on the aforementioned tray.

The form of the solid sample and the condition of its fine pores that contact the carrier gas greatly affect the supply of solid material gas with stable concentration. The disclosed apparatus and methods make it possible to produce solid sample with even distribution even to its finely porous interior and with a large surface area, without scattering and unevenness due to processing

or static electricity, by vaporizing and removing solvent from the solid sample processed into a paste or spray form and in which the solid material is evenly dispersed. Moreover, it is possible to extract solid material gas with uniform material concentration by uniformly sublimating the solid material components from the solid sample produced by these methods.

The above-described supply apparatus of solid material gas is characterized in that the aforementioned dispersion section is connected to the aforementioned supply section, it is equipped with multiple divergent flow paths that diverge the carrier gas, and one or more spray nozzles installed in each of the divergent flow paths, that spray the carrier gas onto the solid sample placed on the aforementioned placement section.

The dispersion function of the carrier gas introduced to the sample placement section plays an important role in forming homogeneous solid material gas. The present invention has made it possible to form an excellent dispersion function to sublime the solid material uniformly, and extract solid material gas with uniform material concentration by diverging the carrier gas and supplying the carrier gas dispersed from one or more spray nozzles installed in the divergent flow paths onto the solid sample placed on the tray.

The disclosed solid material gas supply methods may supply a gas of a solid material from the above-described supply apparatus using a carrier gas. However, one of ordinary skill in the art will recognize that the disclosed solid material gas supply methods may also be used in an apparatus that supplies the gas of a solid material without a carrier gas, for example, to ion implant devices.

One of the disclosed solid material gas supply methods is characterized in that the solid sample produced in accordance with the following pre-processes is placed, and a prescribed amount of the solid material is sublimated and supplied by the carrier gas.

(1) A process of preparing powder or granular solid material.

(2) A process of collecting a prescribed amount of the aforementioned solid material in the container with a prescribed capacity.

(3) A process of adding a prescribed amount of solvent to the aforementioned container, mixing and agitating it with the aforementioned solid material, and producing solid material in paste form.

(4) A process of shaping the aforementioned paste-form solid material into a form with a flat surface.

(5) A process of statically placing the aforementioned solid sample in a prescribed sealed container, and producing the solid sample by vaporizing and removing the solvent under an inert gas atmosphere.

In an alternate embodiment, the disclosed solid material gas supply method is characterized in that the solid sample is produced in accordance with the following pre-processes, and a prescribed amount of the solid material is sublimated and supplied by the carrier gas.

(1) A process of preparing powder or granular solid material.

(2) A process of introducing a prescribed amount of the aforementioned solid material in the tray.

(3) A process of spraying a prescribed amount of solvent on a surface of the aforementioned solid material in the tray.

(4) A process of statically placing the aforementioned trays in a prescribed sealed container, and producing the solid sample by vaporizing and removing the solvent under an inert gas atmosphere.

In order to assure stability in the material concentration, stable sublimation of the solid material components from the solid sample becomes an important factor. The disclosed methods make it possible to supply solid material gas with a stable concentration by forming paste- or spray-form solid material using a solvent, thereafter vaporizing and removing the solvent, and uniformly sublimating the solid material from the surface of the solid sample without causing scattering or unevenness due to the processing or static electricity.

The disclosed solid material gas supply methods are characterized in that a tray for placing the aforementioned solid sample is located in the sample placement section, dispersed carrier gas is supplied to said sample placement section, and the carrier gas accompanying the solid material is dispersed and mixed and discharged from the aforementioned sample placement section as the solid material gas.

As described above, the solid sample produced in the pre-processes makes it possible to uniformly sublimate the solid material from the surface of the solid sample, and by making it accompany uniformly dispersed carrier gas in a

state the sample is placed on the dedicated tray it is possible to produce and supply solid material gas with stable concentration of solid material components.

The disclosed solid material gas supply methods are characterized in that the concentration of the solid material in the aforementioned solid material gas and the flow rate of the aforementioned carrier gas are monitored, and the remaining amount of the solid material in the aforementioned solid sample is controlled based on the remaining amount of the aforementioned solid sample and the concentration of the solid material in the aforementioned solid material gas acquired in advance.

The remaining amount of the solid material inside the sample placement section greatly affects the material concentration in the solid material gas. That is, it has been found that when the remaining amount of the solid material becomes smaller than a specified level, lowering of the material concentration is caused not only according to the total amount of the sublimated solid material, but also according to the remaining amount itself as well as such factors as the form and format (properties) of the solid material. The disclosed methods are aimed at stabilizing the material concentration of the solid material gas by monitoring the concentration of the solid material in the solid material gas and the flow rate of the carrier gas to grasp the total amount of solid material sublimated, and by controlling the remaining amount of the solid material in the solid sample based on the relationship between the pre-acquired remaining amount of the aforementioned solid sample and the concentration of the solid material in the aforementioned solid material gas.

Configurations for implementing the solid material gas supply apparatus and the solid material gas supply methods using the apparatus are described on the basis of the drawings below. However, one of ordinary skill in the art will recognize that the disclosed solid material gas supply methods may also be used in an apparatus that supplies the gas of a solid material without a carrier gas, for example, to ion implant devices.

The solid material gas supply apparatus is equipped with a solid material production means that produces the solid material, a supply section that supplies the carrier gas, a dispersion section that disperses the supplied carrier gas, a sample placement section where the solid sample is placed, and a

discharge section that discharges the solid material gas discharged from the sample placement section. By processing the solid material into paste- or spray-form by adding solvent, and then having the dispersed carrier gas contact the solid sample made by vaporizing and removing the solvent, it is possible to uniformly sublime the solid material and extract solid material gas with uniform material concentration without causing scattering or unevenness due to processing or static electricity.

The "solid materials" referred to herein are solid materials that are widely used industrially and can be sublimated (vaporized) at a specified temperature.

Those solid materials include, for example, such inorganic metal compounds as hafnium chloride (HfCl_4) and zirconium chloride (ZrCl_4), such organic metal compounds as trimethylindium ($(\text{CH}_3)_3\text{In}$), bis-cyclopentadienyl magnesium ($\text{Mg}(\text{Cp})_2$), and tetraethyl zinc ($\text{Zn}(\text{C}_2\text{H}_5)_4$), and such organic compounds as phthalic acid ($\text{C}_6\text{H}_4(\text{COOH})_2$), naphthalene (C_{10}H_8), and anthracene ($\text{C}_{14}\text{H}_{10}$). In addition to materials that are solid under ambient temperatures ($20 \sim 30^\circ\text{C}$) and ambient pressure (approximately 0.1MPa) in general, materials that are solid under pressured condition or low-temperature condition are also broadly included. **Table 1** below shows examples of solid materials, their set temperatures, and their vapor pressures under those set temperatures. Needless to say the solid materials and set conditions are not limited to those provided in **Table 1**.

Table 1

Compound	Solid material example	Set temperature ($^\circ\text{C}$)	Vapor pressure (kPa)
Inorganic metal compound	Hafnium chloride	150	0.037
	Zirconium chloride	190	0.132
Organic metal compound	Trimethylindium	20	0.0227
Organic compound	Naphthalene	25	0.011
	Anthracene	145	0.132

For the solvents, any solvent having suitable vapor pressure and that does not react with the solid material may be used. Exemplary solvents include n-hexane, n-octane, acetone, toluene, tetrahydrofuran, ethanol, ethylmethylketone, or 1,4-dioxane. For HfCl_4 and ZrCl_4 , the solvent is preferably n-hexane, n-octane, acetone or toluene. For anthracene, the solvent is preferably n-hexane, n-octane, acetone, tetrahydrofuran, ethanol, ethylmethylketone, or 1,4-dioxane.

For the carrier gas, low-reactive and highly stable gas is desirable, and noble gases, for example, as helium and argon, or nitrogen gas may be used. Moreover, in order to stably sublime the solid material, carrier gas with high heat capacity is desirable, and argon is most suitable.

Figure 1 is a schematic illustration of the main supply apparatus body of the basic configuration example of the apparatus. The apparatus includes a solid sample production means (not shown in the Figure, and its details are provided later) that is the pre-processing means, and is composed of supply section **1** for carrier gas **C**, dispersion section **2** for carrier gas **C**, sample placement section **3** where solid sample **S** is placed, and discharge chamber **4** where solid material gas **G** that is discharged from sample placement section **3** is merged. It is desirable that heating section **5** that heats sample placement section **3** from outside container **10** is also installed. As shown in **Table 1** above, it is possible to promote sublimation (vaporization) of solid sample **S** and supply solid material gas **G** with the desired material concentration by heating to a set temperature corresponding to each solid sample **S**.

Carrier gas **C** supplied from supply section **1** is sprayed out in a radial fashion throughout the entire interior of sample placement section **3** by dispersion means **2** installed at the center of sample placement section **3**. It is desirable that the direction of spraying carrier gas **C** is horizontal to sample placement section **3** so that it sweeps through the surface of solid sample **S** placed on tray **3a**. Carrier gas **C** that is uniformly dispersed inside sample placement section **3** contacts solid sample **S**, accompany the solid material components sublimated, and then discharged from sample placement section **3** while being mixed and agitated via discharge chamber **4** as solid material gas **G**.

A prescribed amount of solid sample **S** that is the object of processing is placed on tray **3a** in sample placement section **3** without scattering and unevenness due to processing or static electricity. The form of solid sample **S** when produced by the paste method is not limited in particular, but it is preferable to be molded into a pellet, porous or honeycomb form that has a large contact area with carrier gas **C**. The form of the solid sample **S** when produced by the spray method remains the same or similar to the powder or granular form of the solid. The sublimated and reduced amount of solid sample **S** placed in sample placement section **3** is grasped and is replenished or replaced after every specified duration.

Dispersion means **2** of the apparatus for carrier gas **C** can disperse carrier gas **C** widely inside dispersion chamber **3** by having a configuration in which carrier gas **C** is sprayed from various locations along the vertical cross section inside sample placement section **3**. It is preferable that dispersion means **2** is connected to supply section **1** and has a configuration in which a component that has a dispersion function is located at its border with sample placement section **3**. The component with a dispersion function can, for example, be a metal screen made of stainless steel or other material, a metal plate with fine pores, a sintered metal body, glass wool, or porous ceramics, with a prescribed thickness (several mm for example) with pores of several tens to several hundreds mesh pore diameter. This configuration can partition the flow path of carrier gas **C** and sample placement section **3**, and provide uniform dispersion function of carrier gas **C** and at the same time uniform heating function (heat dispersion function) of carrier gas **C**. Owing to these functions, it is possible to assure uniform contact between solid sample **S** placed in sample placement section **3** and carrier gas **C**, form uniform heat conductivity, and form and supply solid material gas **G** with uniform material concentration and temperature property.

It is preferable that tray **3a** has a configuration with which it is possible to place multiple solid samples **S** in the horizontal direction and at the same time in a radial form, from the center to the circumference of sample placement section **3**. This configuration allows uniform contact with the uniformly dispersed carrier gas **C** and form solid material gas **G** with uniform material concentration. It is

also preferable that tray **3a** has a configuration with which it is possible to install multiple tiers of tray **3a** in the vertical direction in sample placement section **3**. This configuration assures uniform contact with carrier gas **C** while efficiently housing multiple solid samples in the container with a specified capacity, and
5 allows formation of solid material gas with uniform material concentration.

The remaining amount of solid sample **S** can be monitored by using the Verification results provided later. That is, from the finding that lowering of the sublimated material concentration is caused not only due to the total amount of sublimated solid material, but also depending on the remaining amount itself and
10 the form and format (properties) of the solid material when the remaining amount of the solid material becomes smaller than the prescribed amount, it is possible to control the remaining amount of the solid material in solid sample **S** by monitoring the material concentration in solid material gas **G** and the flow rate of carrier gas **C**, and based on the relationship between the pre-acquired remaining
15 amount of solid sample **S** and the material concentration in solid material gas **G**. Details on the specific method of calculating the remaining amount and the control method will be provided later. It is also possible to supply solid material gas **G** with stable material concentration by adjusting the flow rate of carrier gas **C** using the acquired information on the remaining amount of solid sample **S**.
20 That is, in cases the monitored remaining amount in sample placement section **3** becomes smaller than the set amount, and a prescribed amount of time is necessary to replenish it, the desired material concentration can be assured by reducing the overall flow rate of carrier gas **C**. The flow rate of carrier gas **C** can be adjusted using such devices as a throttle valve, on-off valve or a damper (not
25 shown in Figure) installed in dispersion means **2**.

Solid sample **S** is produced at the solid sample production means (not shown in Figure) that has an inert gas introduction section and tray **3a** for placing the solid sample. The solid material processed into a paste or spray form by adding solvents is statically placed in an inert gas atmosphere under
30 atmospheric pressure, and solid sample **S** placed on tray **3a** is produced by vaporizing and removing the solvent. By vaporizing and removing the solvent from the solid sample in which the solid material processed into a paste or spray form is evenly dispersed, it is possible to produce solid sample **S** with uniformly

distributed fine pores even to its interior and with a large surface area without causing scattering or unevenness due to processing or static electricity.

The process of producing solid sample **S** and the process of extracting solid material gas **G** having the prescribed solid material concentration at a state
5 in which prescribed amount of solid sample **S** is placed in sample placement section **3**, and sample placement section **3** is heated to the prescribed temperature, is provided below in detail.

Solid sample **S** is produced according to the following processes in the supply process of solid material gas **G**. By forming the solid material into a paste
10 or spray form using a solvent, and then vaporizing and removing the solvent, it is possible to produce solid sample **S** that allows uniform sublimation of the solid material from its surface.

Detailed explanation is provided below in accordance with the paste method procedure shown in **Figure 2**.

15 (1) A process of preparing the solid material

A prescribed amount of solid material in powder or granular form under normal condition is prepared. In case the solid material is in granular form with varying sizes of granules, it is desirable to crush it into powder or evenly sized granular form. Moreover, in the event the solid material is reactive, the above
20 process is done under an inert gas atmosphere.

(2) A process of collecting solid material

A container with a specified capacity is prepared and a prescribed amount of the solid material is collected and placed inside the container. In the event a binder (binding agent) is necessary, a specified amount of the binder is prepared
25 in advance and added to the container to be mixed with the solid material.

(3) A process of adding the solvent and mixing and agitating it with the solid material

A specified amount of solvent is added to the container and mixed and agitated with the solid material. In the event the solid material is a type that heats
30 up during the mixing and agitation, the speed of adding, mixing and agitating is controlled. The amount of solvent added will be sufficient to form a paste material (a paste is a suspension of material in a background fluid, which behaves as a solid until a sufficiently large load or stress is applied).

(4) A process of producing the paste-form solid material

The solid material is mixed and agitated with the solvent inside the container to produce paste-form solid material.

(5) A process of shaping a molded form

5 A molded form with a flat surface is formed using the paste-form solid material. Such methods as pouring the paste-form solid material into a specified mold or using the container as the mold can be used.

(6) A process of vaporizing and removing the solvent

10 The solid sample is placed statically in a specified sealed container, and the solvent is vaporized and removed under an inert gas atmosphere. Such methods as feeding in the inert gas or depressurizing the sealed container can be used. In the apparatus, the solvent is vaporized and removed in a state the molded paste-form solid material is placed on the tray for filling the solid sample.

(7) A process of producing the solid sample

15 Solid sample **S** is produced by vaporizing and removing the solvent. By having the solid material components sublimated from the flat surface that constitutes the molded form accompany the carrier gas, it is possible to supply solid material gas with a stable concentration.

20 In an alternate embodiment, a detailed explanation is provided below in accordance with the spray method procedure.

(1) A process of preparing the solid material

25 A prescribed amount of solid material in powder or granular form under normal condition is prepared. In case the solid material is in granular form with varying sizes of granules, it is desirable to crush it into powder or evenly sized granular form. Moreover, in the event the solid material is reactive, the above process is done under an inert gas atmosphere.

(2) A process of introducing a prescribed amount of the aforementioned solid material in the tray.

30 A tray with a specified capacity is prepared and a prescribed amount of the solid material is collected and placed inside the tray. The amount of solid material placed inside the tray will depend upon the size of the tray.

(3) A process of spraying a prescribed amount of solvent on a surface of the aforementioned solid material in the tray.

A specified amount of solvent is uniformly sprayed on a surface of the solid material in the tray. Preferably, between approximately 1% w/w and approximately 10% w/w of solvent is sprayed on the surface of the solid material in the trays.

5 (4) A process of vaporizing and removing the solvent

The trays containing the solid material are placed statically in a specified sealed container, and the solvent is vaporized and removed under an inert gas atmosphere. Such methods as feeding in the inert gas or depressurizing the sealed container can be used. The vaporizing process may take place in the
10 apparatus or prior to introducing the trays into the apparatus.

(5) A process of producing the solid sample

Solid sample **S** is produced by vaporizing and removing the solvent. By having the solid material components sublimated from the surface, it is possible to supply solid material gas with a stable concentration.

15 One of ordinary skill in the art will recognize that the paste method may be suitable for certain formulations whereas the spray method may be suitable for other formulations. For example and as illustrated in the following examples, it took a long time to remove n-hexane from a paste of HfCl_4 and n-hexane. However, the paste material is easier to prepare and handle than the material
20 prepared by the spray method at least because the paste sample may be produced in bulk quantities and added to the tray, whereas each tray has to be individually prepared by the spray method. The specific solvent, solid material, and form of the solid material will dictate which solid sample preparation method should be employed. For example, even different grain sizes of the same solid
25 material and same solvent may result in the utilization of different solid sample preparation methods.

A process of placing the solid sample and supplying the solid material gas:

(1) Placing the solid sample

30 Solid sample **S** produced by either method is placed in sample placement section **3** of the main body of the supply apparatus in a state the flat surface is facing up on tray **3a**. This allows efficient contact with carrier gas **C**. At this time, it is desirable that multiple tiers of tray **3a** are placed in the vertical direction and

multiple solid samples **S** are placed evenly spread out in a radial manner from the center to the outer circumference in the horizontal direction of sample placement section **3**.

(2) Supply of carrier gas

5 Carrier gas **C** is supplied from supply section **1** in a state solid sample **S** is placed. The pressure and flow rate of carrier gas **C** supplied are adjusted to the desired set values. The adjustment of the pressure and flow rate conditions is not limited to either before and after it is supplied to the supply apparatus.

(3) Dispersion of carrier gas

10 The supplied carrier gas **C** is first introduced to sample placement section **3** in a state it is dispersed by dispersion means **2** connected to supply section **1**. At this time, carrier gas **C** is dispersed widely throughout inside sample placement section **3** as it is sprayed out while being dispersed over the horizontal cross section of sample placement section **3**, and at the same time it
15 is also distributed over the vertical cross section of sample placement section **3** and sprayed inside sample placement section **3**.

(4) Production of solid material gas

Under a condition in which carrier gas **C** is widely dispersed in sample placement section **3** and heated to the set temperature corresponding to each
20 solid sample, solid material gas **G** that has vapor pressure of the desired sublimated solid material concentration is produced by carrier gas **C** contacting solid sample **S** on tray **3a**. By setting the flow rate of carrier gas **C** and the capacity of sample placement section **3** in advance so that the space velocity will be as desired, it is possible to assure ample contact time, and obtain solid
25 material gas **G** with stable material concentration. As solid material gas **G** is being produced, the amount of solid sample **S** reduces from the upper surface of solid sample **S**. The reduction in the amount of solid sample **S** may be monitored visually through a monitoring window (not shown) or by optical sensor output (not shown) that is explained later. Lowering of the material concentration that
30 accompanies reduction in solid sample **S** can be prevented by placing more tray **3a** (solid sample **S**) than prescribed.

(5) Supply of solid material gas

Solid material gas **G** produced in sample placement section **3** merges at the upper open space of sample placement section **3**, and it is mixed and homogenized to produce solid material **G** with the desired material concentration. The solid material gas **G** produced is then discharged from
5 discharge section **4**.

Figure 3 is a schematic illustration of the second configuration example of the apparatus. The apparatus has multiple divergent flow paths **6** that connect dispersion section **2** with supply section **1** and divert carrier gas **C** inside sample placement section **3**, and one or more spray nozzles **6a** installed in each
10 divergent flow path **6**, that spray carrier gas **C** to solid sample **S** placed on tray **3a** in sample placement section **3**. Due to the contact by carrier gas **C** dispersed at dispersion section **2** from the horizontal direction as well as the contact by diverted and dispersed carrier gas **C** from spray nozzles **6a** from the vertical direction to solid sample **S** placed on tray **3a**, it is possible to form excellent
15 dispersion function to uniformly sublime the solid material, and extract solid material gas **G** with uniform material concentration. Improvement in the efficiency of sublimating each solid sample **S** eliminates variability in the sublimation rate of the solid material in each solid sample **S** placed inside sample placement section **3**, and allows formation of more homogeneous solid
20 magterial gas **G**.

The number of divergent flow paths is preferably 1 to 20, but it is not limited to this range depending on the capacity of sample placement section **3** and the properties of solid sample **S**. The diameter of spray nozzle **6a** is preferably 2mm to 3mm, but it is not limited to this range depending on the
25 capacity of sample placement section **3**, the properties of solid sample **S**, and the pipe diameter of divergent flow path **6**. The location of spray nozzle **6a** can be within a several centimeter range on the upstream side from divergent flow path **6**. The number of spray nozzles **6a** is preferably one to several tens for each divergent flow path **6**. The structure from supply section **1** to gas spray
30 nozzle **6a** can be in a shower-head form. It is also possible to place a highly heat-conductive and corrosion-resistant porous component at spray nozzle **6a**. This further improves uniformity of carrier gas **C** that contacts solid sample **S** by

further dispersing carrier gas **C** sprayed from the vertical direction towards solid sample **S**.

Examples

The following non-limiting examples are provided to further illustrate embodiments of the invention. However, the examples are not intended to be all inclusive and are not intended to limit the scope of the inventions described herein.

10 Example 1

The functions of solid sample **S** produced by the paste method were verified as follows using hafnium tetrachloride (HfCl_4) as the solid material.

(i) Verification conditions

750g each of HfCl_4 that is in solid, granular form under normal conditions (referred hereinafter as "powder sample") and solid sample produced using the disclosed paste method were collected, divided onto 8 stainless steel trays (correspond to tray **3a**), and inserted into a special stainless steel container (referred hereinafter as "container").

(ii) Production of solid sample **S**

For solid sample **S**, 750g of HfCl_4 in powder form as the solid material was collected in the stainless steel container in a glove box in a nitrogen atmosphere, and 100g of n-hexane as the solvent was added. The HfCl_4 / n-hexane mixture was agitated using a Teflon™ spatula to make it into a paste form. The resulting paste was divided onto 8 stainless steel trays and the upper surface of each piece was flattened using a (smaller) Teflon™ spatula. These trays were placed statically in the glove box for 3 days to vaporize the n-hexane. The completion of evaporation was confirmed by measuring the weight before and after the evaporation (the paste weighing 850g before evaporation weighed 750g after the evaporation of n-hexane).

30 (iii) Verification items

The "reliance of the remaining amount of HfCl_4 on HfCl_4 concentration" was verified using solid sample **S** and the powder sample. More specifically, containers in which both samples were placed were tipped over 90 degrees

sideways, left in that state for 10 minutes, then both containers were returned to their original upright position, and the solid material concentration discharged from the containers was measured. The changes in the solid material concentration were tracked when heated to 150°C using an incubator and 0.1SLM of N₂ carrier gas was introduced. A TCD detector (Valco Microvolume TCD TCD2-NIFE-110) was used to measure the solid material concentration.

(iv) Verification results

Under the verification conditions described above, the verification results regarding the "reliance of the remaining amount of HfCl₄ on HfCl₄ concentration" as shown in **Figure 4** were obtained.

(iv-1) In the case of solid sample **S**, a certain concentration of vaporization from remaining amount of 100% (initial stage of placement) to 10% (after 90% of consumption) was confirmed since the HfCl₄ was arranged evenly within the tray. HfCl₄ sublimates in the container and discharged accompanying the carrier gas, but since the carrier gas passes over the surface of solid sample **S** made of homogeneous solid material HfCl₄, the concentration also maintained stable.

(iv-2) In the case of the powder sample, the overall concentration lowered as the carrier gas tends to flow through flow paths with relatively small amount of HfCl₄ due to unevenness in the distribution of HfCl₄ on the tray as the container was tipped, and due to the fact HfCl₄ fell from the tray. The concentration also lowered due to the fact the number of flow paths that do not contact HfCl₄ increases (passes through parts of the tray where HfCl₄ is not present) when the remaining amount become 40% and lower.

(v) Summary

As stated above, it was confirmed that it is possible to supply solid material gas **G** with stable material concentration as a result of using paste-form solid sample **S** to prevent affects from tilting during transportation, and at the same time assuring stable sublimation of the solid components due to uniform contact with carrier gas **C**. However, it took a long time to evaporate the solvent from the paste. Additionally, for HfCl₄ and n-hexane, the surface of the solid after removal of the solvent was irregular. The irregular surface makes it

difficult to stack the trays in the apparatus. Furthermore, the irregular surface interrupts the carrier gas **C** flow, which may result in unstable gas concentration.

With the apparatus, it is possible to manage the remaining amount of the solid material in solid sample **S** by grasping the relationship between the remaining amount of solid sample **S** and the material concentration in solid material gas **G** for the solid material to be the object of supply in advance as described in the verification results above.

The decreased amount ΔS of the solid material sublimated from solid sample **S** can be calculated by monitoring material concentration M of solid material gas **G** and flow rate F of carrier gas **C**. That is, as shown in Equation 1 below, the decreased amount per unit hour is calculated from the material concentration and the flow rate, and by integrating (Σ) it the decreased amount ΔS is calculated.

$$\Delta S = \Sigma (M \times F) \text{ --- Equation 1}$$

Therefore, it is possible to calculate the remaining amount of solid sample **S** (it is generally equal in value to the remaining amount of the solid material in solid sample **S**) by subtracting the decreased amount ΔS from the initially set value of the solid material S_0 . Moreover, in cases the decreased amount is within the range that requires addition or replacement of solid sample **S**, it is possible to obtain the remaining amount of the solid material in the solid sample based on the "relationship between the remaining amount of the solid material and the material concentration in the solid material gas" that has been obtained in advance since the progress in the decreased amount of solid sample **S** accompanies lowering of the material concentration in solid material gas **G** (in case calculation is possible from the relational equation, the remaining amount can be calculated).

As stated above, being able to accurately grasp (calculate) the remaining amount of the solid material in solid sample **S** makes it possible with the apparatus to supply solid material gas **G** with stable material concentration for an extended period of time. That is, by monitoring the remaining amount of solid material, it is possible to accurately predict and manage the material concentration based on the "relationship between the remaining amount of the solid material and the material concentration in the solid material gas."

Moreover, it is possible to conduct maintenance and management work including preparation of solid sample **S** since the time when adding or replacing solid sample **S** is necessary or since it is possible to estimate the amount of the solid material based on the remaining amount of the solid material in solid sample **S**.

Example 2

The functions of spray sample **S** were verified as follows using hafnium tetrachloride (HfCl_4) as the solid material.

(i) Verification conditions

750g of HfCl_4 that is in powder form under normal conditions (referred hereinafter as "powder sample") was collected, divided onto 8 stainless steel trays (correspond to tray **3a**), and inserted into a special stainless steel container (referred hereinafter as "container"). A solid sample was also produced using the disclosed method (referred hereinafter as "spray sample **S**").

(ii) Production of spray sample **S**

For spray sample **S**, 100g of HfCl_4 in solid, granular form as the solid material was added into a stainless steel tray. 5g of acetone as the solvent was uniformly sprayed on the HfCl_4 surface using a spray nozzle. Each step was repeated until a total of 8 stainless steel trays were prepared. These processes were performed in a glove box in a nitrogen atmosphere. These trays remained in the glove box for 12 hours to vaporize the acetone. The completion of evaporation was confirmed by measuring the weight before and after the evaporation (the stainless steel tray weighing 426g before evaporation, weighed 421g after the evaporation of acetone).

(iii) Verification items

The "reliance of the remaining amount of HfCl_4 on HfCl_4 concentration" was verified using spray sample **S** and the powder sample. More specifically, containers in which both samples were placed were tipped over 90 degrees sideways, left in that state for 10 minutes, then both containers were returned to their original upright position, and the solid material concentration discharged from the containers was measured. The changes in the solid material concentration were tracked when heated to 150°C using an incubator and

0.1SLM of N₂ carrier gas was introduced. A TCD detector (Valco Microvolume TCD TCD2-NIFE-110) was used to measure the solid material concentration.

(iv) Verification results

Under the verification conditions described above, the verification results regarding the "reliance of the remaining amount of HfCl₄ on HfCl₄ concentration" as shown in **Figure 5** were obtained.

(iv-1) In the case of spray sample **S**, a certain concentration of vaporization from remaining amount of 100% (initial stage of placement) to 10% (after 90% of consumption) was confirmed since the HfCl₄ was arranged evenly within the tray. HfCl₄ sublimates in the container and discharged accompanying the carrier gas, but since the carrier gas passes over the surface of solid sample **S** made of homogeneous solid material HfCl₄, the concentration also maintained stable.

(iv-2) In the case of the powder sample, the overall concentration lowered as the carrier gas tends to flow through flow paths with relatively small amount of HfCl₄ due to unevenness in the distribution of HfCl₄ on the tray as the container was tipped, and due to the fact HfCl₄ fell from the tray. The concentration also lowered due to the fact the number of flow paths that do not contact HfCl₄ increases (passes through parts of the tray where HfCl₄ is not present) when the remaining amount become 40% and lower.

(v) Summary

As stated above, it was confirmed that it is possible to supply solid material gas **G** with stable material concentration as a result of using spray-form solid sample **S** to prevent affects from tilting during transportation, and at the same time assuring stable sublimation of the solid components due to uniform contact with carrier gas **C**. The solvent evaporated from the solid material prepared by the spray method more quickly than from the solid material prepared by the paste method. Furthermore, the surface of the solid after removal of the solvent was flat. The flat surface makes it easier to stack the trays in the apparatus. Furthermore, the flat surface does not interrupt the carrier gas **C** flow, producing a more stable gas concentration.

As in Example 1, with the disclosed spray method, it is possible to manage the remaining amount of the solid material in solid sample **S** by

grasping the relationship between the remaining amount of solid sample **S** and the material concentration in solid material gas **G** for the solid material to be the object of supply in advance as described in the verification results above.

Finally, it takes less time to evaporate acetone from the spray method
5 than it takes to evaporate n-hexane from the paste method, resulting in a more efficient delivery method.

It will be understood that many additional changes in the details, materials, steps, and arrangement of parts, which have been herein described
10 and illustrated in order to explain the nature of the invention, may be made by those skilled in the art within the principle and scope of the invention as expressed in the appended claims. Thus, the present invention is not intended to be limited to the specific embodiments in the examples given above and/or the attached drawings.

15

Explanation of codes

	1	Supply section
	2	Dispersion section
	3	Sample placement section
5	3a	Tray
	4	Discharge section
	5	Heater section
	6	Divergent flow path
	6a	Spray nozzle
10	C	Carrier gas
	G	Solid material gas
	S	Solid sample

We claim:

1. A method to supply a gas of a solid material to semiconductor or solar cell production devices, the method comprising:

- 5 Introducing the solid material into one or more trays;
 Spraying a solvent on a surface of the solid material in the trays;
 Introducing the one or more trays into the supply apparatus;
 Removing the solvent under an inert gas atmosphere; and
 Sublimating the solid material to produce the gas of the solid material.

10

2. The method of claim 1, wherein approximately 1% w/w to approximately 10% w/w of solvent is sprayed on the surface of the solid material in the trays.

15 3. The method of either of claim 1 or 2, wherein the solid material is selected from the group consisting of hafnium chloride, zirconium chloride, trimethylindium, bis(cyclopentadienyl)magnesium, tetraethyl zinc, phthalic acid, naphthalene and anthracene.

20 4. The method of claim 3, wherein the solid precursor is selected from the group consisting of HfCl_4 , ZrCl_4 , and anthracene.

 5. The method of any one of claims 1 to 4, wherein the solvent is selected from the group consisting of n-hexane, n-octane, acetone, toluene,
25 tetrahydrofuran, ethanol, ethylmethylketone, and 1,4-dioxane.

 6. The method of either of claim 1 or 2, wherein the solid material is ZrCl_4 or HfCl_4 and the solvent is selected from the group consisting of n-hexane, n-octane, acetone, and toluene.

30

7. The method of either of claim 1 or 2, wherein the solid material is anthracene and the solvent is selected from the group consisting of n-hexane, n-octane, acetone, tetrahydrofuran, ethanol, ethylmethylketone, and 1,4-dioxane.

8. The method of any one of claims 1 to 7, further comprising weighing each of the one or more trays after introducing the solid material, weighing each of the one or more trays after spraying the solvent, and verifying removal of the solvent by weighing each of the one or more trays after removing the solvent.

5

9. The method of any one of claims 1 to 8, wherein the solvent is removed prior to introducing the one or more trays into the supply apparatus.

10. The method of any one of claims 1 to 9, further comprising supplying the gas of the solid material by a carrier gas from the supply apparatus to semiconductor or solar cell production devices.

10

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Figure 1

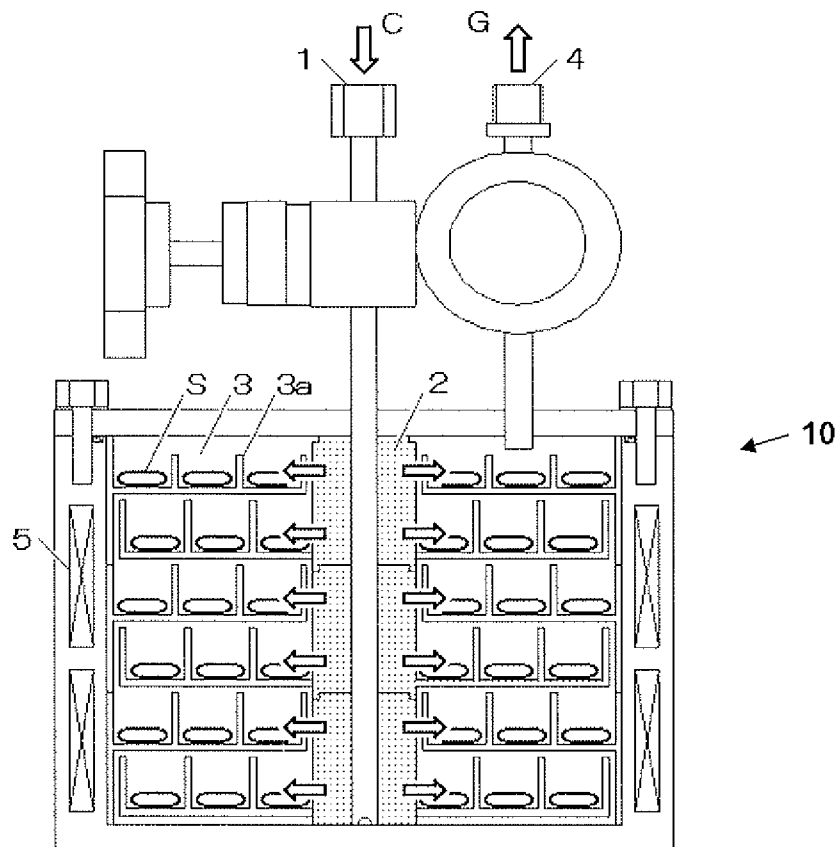
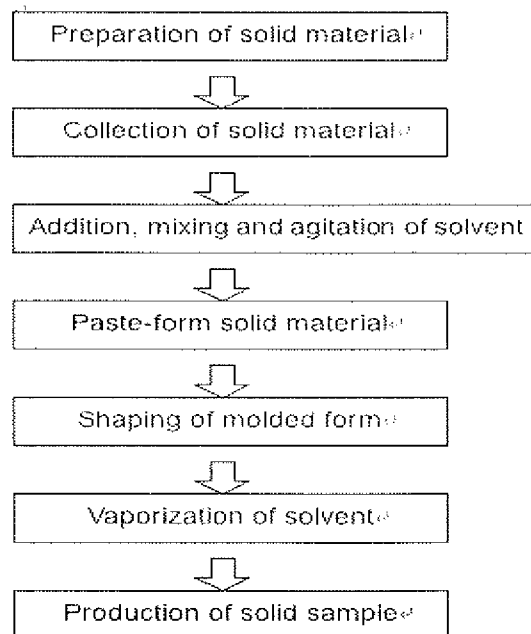


Figure 2



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Figure 3

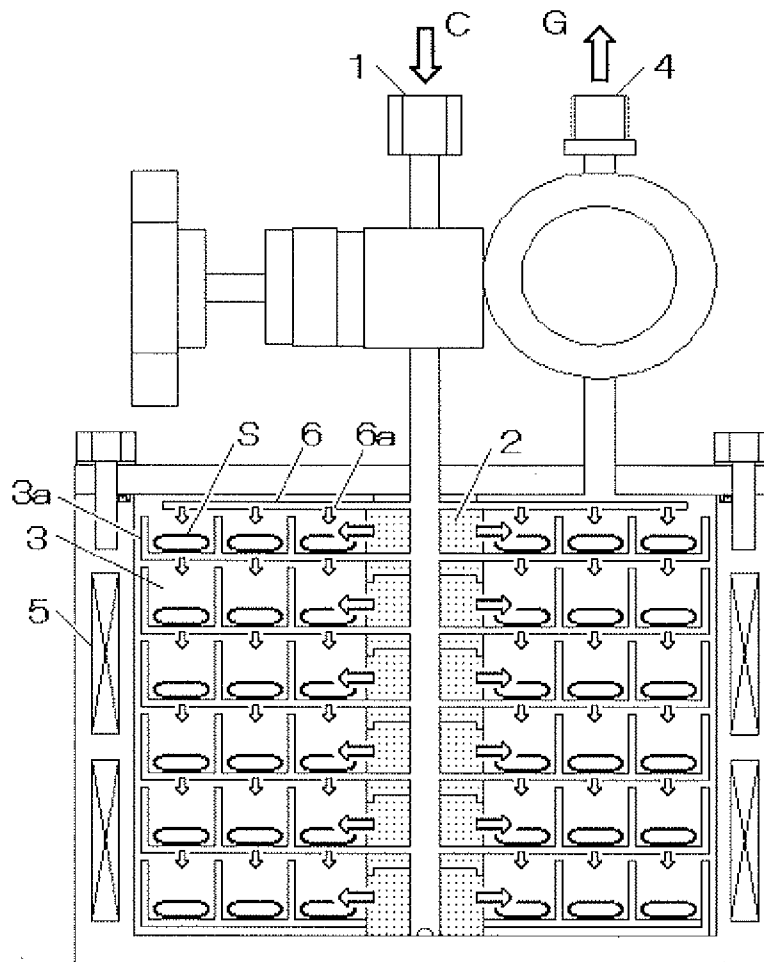


Figure 4

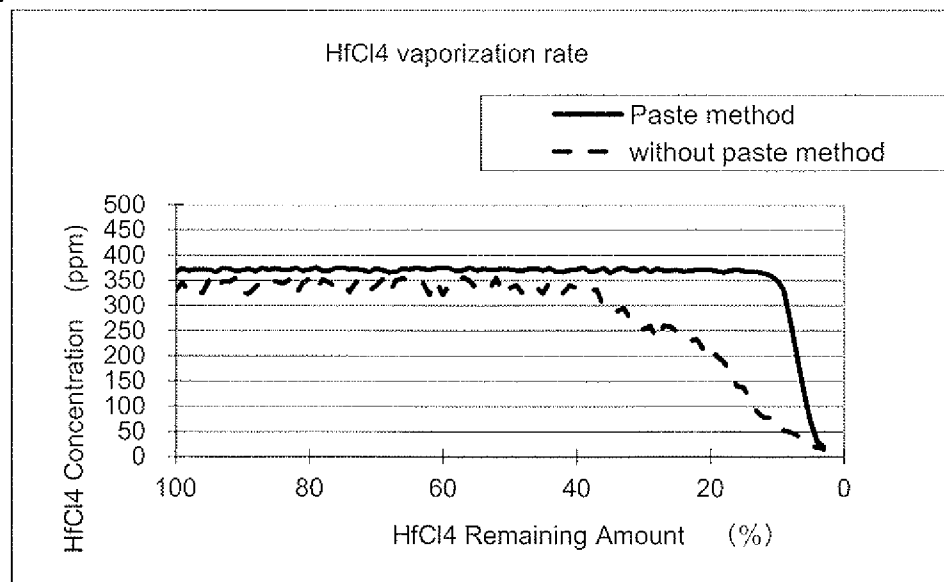
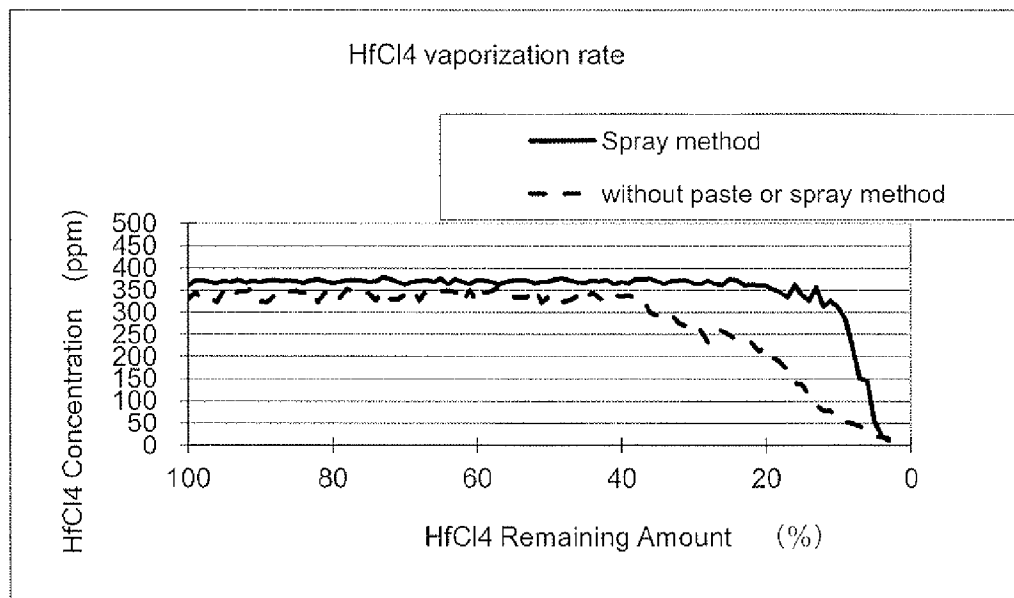
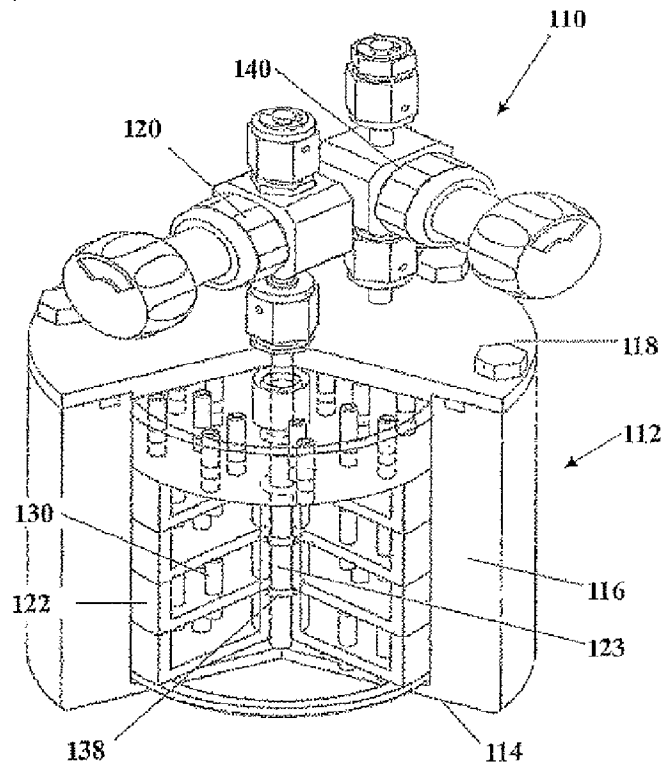


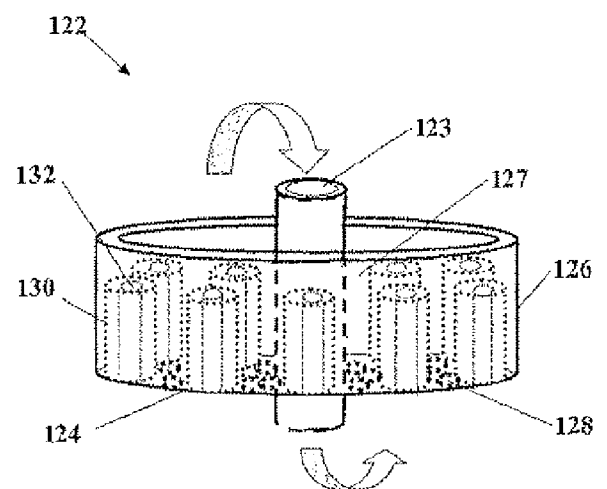
Figure 5



(A) Figure 6 PRIOR ART



(B)



INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2012/052922

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. B01J7/00 (2006.01) i, C23C14/48 (2006.01) i, C23C16/448 (2006.01) i,
H01L21/31 (2006.01) i

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)

Int.Cl. B01J7/00, C23C14/00, C23C16/00, H01L21/00

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2012
Registered utility model specifications of Japan 1996-2012
Published registered utility model applications of Japan 1994-2012

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2010-502833 A (ADVANCED TECHNOLOGY MATERIALS, INC.) 2010.01.28, whole document	1-10
A	JP 2006-503178 A (ADVANCED TECHNOLOGY MATERIALS, INC.) 2006.01.26, whole document	1-10

☐ Further documents are listed in the continuation of Box C.

☒ 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

"E" earlier application or patent but published on or after the international filing date

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"&" document member of the same patent family

Date of the actual completion of the international search

29.10.2012

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

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