



(51) International Patent Classification:

H01L 21/205 (2006.01) *H01L 21/31* (2006.01)
C23C 16/448 (2006.01)

(21) International Application Number:

PCT/IB2012/051094

(22) International Filing Date:

8 March 2012 (08.03.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2011-050431 8 March 2011 (08.03.2011) JP

(71) Applicant (for all designated States except US): **L'AIR LIQUIDE SOCIETE, ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE** [FR/FR]; 75 quai d'Orsay, F-75007 Paris (FR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **YANAGITA, Tomoko** [JP/JP]; Air Liquide Japan Ltd., Granpark Tower 3-4-1 Shibaura, Minato-ku, Tokyo (JP). **KOURA, Terumasa** [JP/JP]; Air Liquide Japan Ltd., Granpark Tower 3-4-1 Shibaura, Minato-ku, Tokyo (JP).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

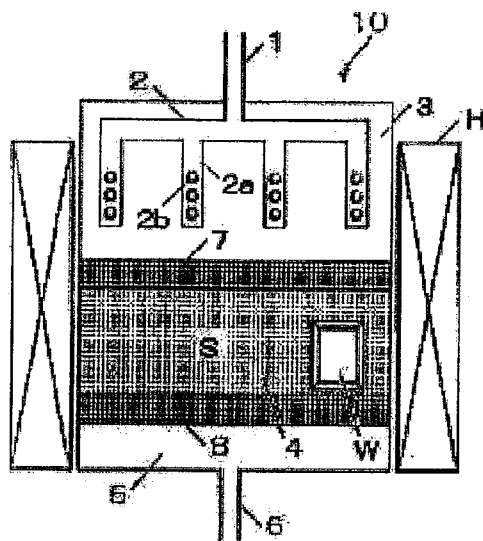
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

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

FIG 1



(57) Abstract: [Problem to Be Solved] To supply solid material gas at a stable concentration with a simple method and configuration, and precisely detect the remaining amount of solid material with a simple method. [Means for Solving the Problem] An apparatus and method characterized in that it aims at treating solid material S that can be sublimated and supplied at a specified rate by carrier gas C, and is equipped with carrier gas supply section 1, carrier gas dispersion means 2, dispersion chamber 3 that houses dispersion means 2 and disperses supplied carrier gas C, filling layer 4, supply-out chamber 5 that merges solid material gas G supplied from filling layer 4, supply-out section 6 of solid material gas G, first mesh section 7 that partitions dispersion chamber 3 and filling layer 4, and second mesh section 8 that partitions filling layer 4 and supply-out chamber 5.

SUPPLY APPARATUS AND METHOD OF SOLID MATERIAL GAS

Cross-Reference to Related Applications

[0001] This application claims the benefit of Japanese Patent Application No. 2011-050431, filed March 8, 2011, the entire contents of which are incorporated herein by reference.

Technological Field

[0002] The present invention relates to a gas supply apparatus for solid materials and method of supplying the same. The “solid materials” include 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 are widely used industrially, may be sublimated (vaporized) / supplied at a desired rate by a carrier gas, and 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 Art

[0003] Gas materials and liquid materials have been widely used in production devices that manufacture semiconductors and solar cells, at research facilities that develop new materials, and as materials (e.g. film-forming materials) for semiconductors that require high-purity products, but the use of sublimated solid materials as mentioned above, entrained by carrier gases, have recently been used more frequently. See, e.g., WO2009/087609 to L’Air Liquide. Such solid materials are sublimated and carried by low-reactive and highly stable inert gases, such as rare gases including helium and argon, and supplied to such facilities as the above-mentioned production devices and consumed.

[0004] For example, a configuration example of evaporator distribution system **110**, as shown in **FIG 7(A) and 7(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 US2004/016404 to Gregg et al.). Ampoule **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 ampoule. The vertically stacked containers can be mounted to and removed from the ampoule 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 ampoule, 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 US2004/016404). Here, **138** is a sealing O-ring and **140** is a gas outtake valve.

[0005] With the solid material gas supply apparatus (and its associated method of use) as described above, however, the following problems have occurred at times:

[0006] (i) With solid materials, in general, the supply components concentration (referred hereinafter as "Material Concentration") in the solid materials gas is easily affected by the contact area with the carrier gas, the Material Concentration can easily become unstable due to short-pass and localized irregularity in the flow rate of the carrier gas, and the Material Concentration in the carrier gas lowers with the reduction of the remaining solid material in the container.

[0007] (ii) Moreover, with the configuration of the above-mentioned evaporator distribution system **110**, the positioning of the material on the tray becomes uneven when the container is at an angle to pose the risk of the Material Concentration to become unstable, and the complex structure of the container makes it difficult to fill it with the material and purge the container.

[0008](iii) In general, as methods of detecting the remaining level of the filled material, pressure measurement for gaseous materials and a liquid level gauge for liquid materials are widely used as they can accurately detect the level since the uniformity of the material is high. For solid materials, on the other hand, weight measurement and a method of cumulatively calculating from the material concentration at the time it is supplied and the elapsed time while it is being used have been used, but it is at times necessary to secure time for the material to fill up to a specified capacity of space and to stabilize due to its diffusion to obtain a stable material concentration. Moreover, with the weight measurement method, change in the material concentration that accompanies local decrease of the solid material can not be detected, and its measurement error margin is great since the containers are connected to the piping and the containers in general are placed under a heated environment. Furthermore, measuring the material concentration requires such detection devices as the ultrasonic method, thermal-conductivity method, or infrared method. These detection devices are not only costly, but must be calibrated according to each solid material.

Brief Explanation of Drawings

[0009] FIG 1 is a schematic illustration of the basic configuration example of the inventive solid material gas supply apparatus;

[0010] FIG 2a is a schematic illustration of the second configuration examples of the inventive solid material gas supply apparatus;

[0011] FIG 2b is a schematic illustration of the third configuration examples of the inventive solid material gas supply apparatus;

[0012] FIG 3a is an expanded schematic illustration of the fourth configuration example of the inventive solid material gas supply apparatus;

[0013] FIG 3b is a schematic illustration of the fourth configuration example of the inventive solid material gas supply apparatus;

[0014] FIGS 4a & 4b are explanatory drawings showing the results of verification using the inventive solid material gas supply apparatus;

[0015] FIG 5 is an explanatory drawing showing the results of verification using the inventive solid material gas supply apparatus;

[0016] FIG 6 is an explanatory drawing showing the results of verification using the inventive solid material gas supply apparatus;

[0017] FIG 7a is a schematic illustration of a prior art evaporator delivery system for vaporizing liquid and solid material based on conventional technologies; and

[0018] FIG 7b is a schematic illustration of the prior art tray of the evaporator delivery system for vaporizing liquid and solid material based on conventional technologies.

Detailed Description of Preferred Embodiments

[0019] The object of the present invention is 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.

[0020] In view of the above-described problems, the present inventors 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.

[0021] The present invention is a solid material gas supply apparatus characterized in that it is aimed at treating solid materials that can be sublimated and supplied at a specified rate using a carrier gas, and equipped with a carrier gas supply section, a dispersion means of said carrier gas, a dispersion chamber that houses said dispersion means and disperses the supplied carrier gas, a filling layer in which the aforementioned solid material is filled, a supply-out chamber that merges the solid material gas supplied from said filling layer, a supply-out section of said solid material gas, a first mesh section that partitions the aforementioned dispersion chamber and the aforementioned filling layer, and a second mesh section that partitions the aforementioned filling layer and the aforementioned supply-out chamber.

[0022] The present invention is also a solid material gas supply method using the above-mentioned supply apparatus, characterized in that solid material that can be sublimated and supplied at a specified rate by a carrier gas is filled inside the aforementioned filling layer, and then goes through primary

dispersion by multiple diverging flow paths; the carrier gas that has gone through secondary dispersion by the first mesh section located on the supply side to the aforementioned filling layer is supplied to the aforementioned filling layer; and the solid material gas supplied-out from the aforementioned filling layer, that has gone through third-order dispersion by the second mesh section located on the supply-out side to the aforementioned filling layer is supplied out.

[0023] As described above, there have been several problems in sublimating the solid material and supplying solid material gas with a stable material concentration. With the present invention, the inventors have discovered that it is possible to eliminate these problems by firstly dispersing the carrier gas that contacts the solid material and forming a uniform flow and a uniform thermal distribution to sublime the solid material uniformly, and by secondly dispersing and supplying out the solid material gas formed in the filling layer so that it has a uniform material concentration. In other words, it is possible to sublime the solid material uniformly and extract solid material gas with a uniform material concentration by applying the primary dispersion using a dispersion means, a dispersion chamber or divergent flow paths, the secondary dispersion by the first mesh section, and the third-order dispersion by the second mesh section. Moreover, by uniformly sublimating the solid material, it has become possible to uniformly reduce the amount of the solid material and maintain uniform sublimation of the solid material to provide a supply apparatus and supply method of solid material gas that can supply solid material gas at a stable concentration for a long period of time with a simple method and configuration.

[0024] The present invention is the above-mentioned solid material gas supply apparatus characterized in that either the aforementioned first mesh section or the second mesh section is installed in the upper section of the aforementioned filling layer, and, at the same time, can be movable vertically downwards by its own weight. In the event the part that partitions the filling layer (the first mesh section or the second mesh section in the present invention) is fixed, a space will be generated at the upper part of the filling layer as the volume of the solid material lowers. At this time, if there is a difference in the reduction of volume in the filling layer, the carrier gas tends to flow into areas with less load, and there

will be a possibility that such difference in the reduction of volume may expanded. The present invention makes it possible to supply out solid material gas with a stable concentration for a long period of time by ensuring a configuration in which carrier gas is introduced evenly to the filling layer from a location where the first mesh section or the second mesh section is constantly contacting the filling layer.

[0025] The present invention is the above-mentioned solid material gas supply apparatus characterized in that the aforementioned dispersion means is connected to the aforementioned supply section and is equipped with multiple divergent flow paths that diverges the carrier gas, and one or more spray nozzles installed in each of the divergent flow paths.

[0026] The primary dispersion function of the carrier gas introduced to the filling layer plays an important role in the formation of uniform solid material gas. The present invention has made it possible to form an excellent primary dispersion function, sublimate the solid material uniformly, and, at the same time, extract solid material gas with uniform material concentration.

[0027] The present invention is the above-mentioned solid material gas supply apparatus characterized in that the aforementioned dispersion means has one or more spray nozzles in each of the aforementioned dispersion chamber and the aforementioned filling layer.

[0028] With this configuration, it has become possible to introduce the carrier gas to the filling layer via the dispersion means and the dispersion chamber, and at the same time directly supply it from the dispersion means inserted into the filling layer to realize further uniform contact between the solid material and the carrier gas at the filling layer. At this time, by having a mesh section that partitions the dispersion means inserted into the filling layer and the filling layer, the carrier gas supplied directly to the filling layer merges the carrier gas from the dispersion chamber, making it possible to assure the secondary dispersion function by the primary dispersion and mesh section.

[0029] The present invention is the above-mentioned solid material gas supply apparatus characterized in that a monitoring window or multiple photo-sensors are installed on the side wall of the aforementioned filling layer so that the filled

amount of the aforementioned solid material can be monitored visually by sight or through output from the photo-sensors.

[0030] As described above, the filled amount (remaining amount) of the solid material greatly affects the material concentration of the solid material gas, and with the conventional methods, precise detection of the remaining amount required considerably high cost. With the present invention having the configuration as described above, it has been verified that the filled amount and the state of unevenness of the remaining amount of the solid material in the filling layer between the first mesh section and the second mesh section can be directly detected precisely by installing a monitoring window or multiple photo-sensors. It has become possible to precisely detect the filled amount of the solid material precisely with a simple method and configuration.

[0031] The present invention is the above-mentioned solid material gas supply apparatus characterized in that the filled amount of the solid material is monitored at one or more parts of the aforementioned filling layer, and the carrier gas flow rates in the aforementioned divergent multiple flow paths are adjusted.

[0032] The remaining amount and the state of unevenness of the solid material in the filling layer greatly affects the material concentration of the solid material gas. The present invention aims at stabilizing the material concentration of the solid material gas by adjusting the carrier gas flow rate at the primary dispersion means based on the monitored remaining amount or the state of unevenness in the filling layer.

[0033] Configurations for implementing the inventive solid material gas supply apparatus (referred hereinafter as “the inventive apparatus”) and the solid material gas supply method using the inventive apparatus (referred hereinafter as “the inventive method”) are described on the basis of the drawings below. The inventive apparatus for processing solid materials that can be sublimated and supplied at a specified rate by a carrier gas, and is characterized in that the solid material is sublimated uniformly by applying the first (primary) dispersion with the dispersion means, dispersion chamber or divergent flow paths, second (secondary) dispersion with the first mesh section, and third dispersion with the

second mesh section to the carrier gas or the solid material gas, and at the same time extracting solid material gas with uniform material concentration. Moreover, a configuration that allows monitoring the filled amount of the solid material is desirable.

[0034] 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), zirconium chloride (ZrCl_4), such solid organic metal compounds as Trimethylindium ($(\text{CH}_3)_3\text{In}$) and bis-cyclopentadienyl magnesium ($\text{Mg}(\text{Cp})_2$) and tetraethyl zinc ($\text{Zn}(\text{C}_2\text{H}_5)_4$), and such solid 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 ~ 30 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 (°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

[0035] For the carrier gas, a low-reactivity and highly stable gas is desirable. Noble gases, for example, as helium, argon, and/or nitrogen gas may be used. Moreover, in order to stably sublime the solid material, a carrier gas with high heat capacity is desirable, and argon is most suitable.

Basic configuration example of solid material gas supply apparatus

[0036] FIG 1 is a schematic illustration of the basic configuration example (configuration example 1) of the inventive apparatus. Container 10 houses carrier gas C supply section 1, carrier gas C dispersion means 2, and is equipped with dispersion chamber 3 that disperses the supplied carrier gas C, filling layer 4 in which solid material S is filled, supply-out chamber 5 that merges solid material gas G supplied from filling layer 4, solid material gas G supply-out section 6, first mesh section 7 that partitions dispersion chamber 3 and filling layer 4, and second mesh section 8 that partitions filling layer 4 and supply-out chamber 5. Moreover, it is desirable that heater section H that heats filling layer 4 from outside container 10 is equipped. As shown in Table 1 above, by heating filling layer 4 to the set temperature corresponding to each solid material S, sublimation (vaporization) of solid material S is promoted to enable supply of solid material gas G with the specified material concentration. Here, in addition, monitoring window W is installed on the side wall of filling layer 4 of container 10 so that it is possible to detect the decreased amount of solid material S or the state of unevenness of the filled amount (decreased amount) inside filling layer 4.

[0037] Here, an example in which supply section 1, dispersion means 2 and dispersion chamber 3 are located in the upper section of container 10, and container 10 that supplies carrier gas C from the upper part of filling layer 4 is provided, but needless to say the configuration is not limited to this, and other configurations including a configuration in which these compositional units are placed in the lower section of container 10 are also possible. For example, as shown in FIG 2 (A), a configuration in which carrier gas C is supplied from the horizontal direction (second configuration example) can be sited. With this configuration, it is possible to set up a function to supplement the reduced solid material S from material supply valve 4a at the upper section, or a function to discharge unnecessary solid material S from material discharge valve 4b at the lower section.

[0038] A specified amount of solid material S to be processed is filled into supply section (not shown in figure) of container 10. The form of solid material S

is not limited in particular, but those that are molded into such forms as pellets or porous honeycomb with large contact area with carrier gas C and small flow resistance, or those carried in such carriers are preferable. The reduced amount of the sublimated solid material filled inside filling layer **4** is detected, and that amount is either supplemented or replaced after every specified duration of time.

Function of each part

[0039] It is desirable that dispersion means **2** of the inventive apparatus is equipped with multiple divergent flow paths **2a**, **2a...** (referred collectively hereinafter as “divergent flow paths **2a**”) that diverge carrier gas C, and one or more spray nozzles **2b**, **2b...** (referred collectively hereinafter as “spray nozzles **2b**”) installed in each divergent flow paths **2a**. This configuration makes it possible to disperse carrier gas C broadly inside dispersion chamber **3** by diverging the gas to each section inside dispersion chamber **3** at the horizontal cross section of dispersion chamber **3**, and spraying it from each section inside dispersion chamber **3** at the vertical cross section of dispersion chamber **3** as well. The number of divergent flow paths **2a** is preferably 1 to 20, and more preferably 2 to 10, but depending on the capacity of container **10** and the property of solid material **S**, the number is not limited to this range. The diameter of a tip of the spray nozzle **2b** is preferably 0.2 to 3 mm, but depending on the capacity of container **10**, property of solid material **S**, and diameter of divergent flow paths **2a**, it is not limited to this range. As to the location of the spray nozzle **2b**, it can be installed within a range of several centimeters on the upstream side from the end tip of divergent flow path **2a**. The number of spray nozzles tip **2b** is preferably 1 to several dozens for each divergent flow path **2a**. Moreover, the structure of the path from supply section **1** to the gas spray nozzle **2b** can be in a shower-head form.

[0040] It is desirable that the material of first mesh section **7** and second mesh section **8** is a material that is highly heat conductive, corrosion resistant and porous. For example, it is possible to use a metal screen, metal plates or metal sintered body with fine holes, made of stainless steel or other materials, glass wool, or porous ceramic, with a specified thickness (e.g. several millimeters),

and with mesh diameters comprised between sizes 10 and 100 mesh (2 mm to 0.149 mm). First mesh section **7** partitions dispersion chamber **3** and filling layer **4**, and has a uniform secondary dispersion function of carrier gas C, and at the same time, can have a uniform heating function (heat diffusion function) of carrier gas C. Due to these functions, it is possible to realize uniform contact between solid material **S** in filling layer **4** with carrier gas C, and form uniform heat conductivity. Moreover, second mesh section **8** partitions filling layer **4** and supply-out chamber **5**, and at the same time, has a uniform tertiary dispersion function of solid material gas G, and can have a uniform heating function (heat diffusion function) of solid material gas G. Due to these functions, it is possible to form and supply solid material gas **S** with uniform material concentration.

[0041] Here, it is desirable that first mesh section **7** installed at the upper part of filling layer **4** is not fixed to container **10**, and is movable in the downward direction by its own weight. However, as described previously, in the case carrier gas C is supplied from the lower section of container **10**, it is desirable that second mesh section **8** is installed at the upper section of filling layer **4**, and has the same function. In addition to the function of partitioning filling layer **4**, it enables supplying out solid material gas G with stable concentration for a long period of time by filling the open space at upper section of filling layer **4** that is generated by the reduction of solid material **S**, and assuring a configuration with which carrier gas C is introduced uniformly to filling layer **4** from a position that constantly contacts filling layer **4**. With this configuration, it is possible to prevent short-passing of carrier gas C to areas with less load due to the reduction difference in solid material **S** inside filling layer **4**, and prevent further increase in the reduction difference in solid material **S**.

[0042] Monitoring window **W** is installed on the side wall of filling layer **4** to visually monitor the filled amount of solid material **S** between the first mesh section **7** and the second mesh section **8**. As demonstrated by the results of the verification experiment described later, the filled amount (remaining amount) of solid material **S** greatly affects the material concentration of solid material gas G. By visually checking the remaining amount and the uneven state of the remaining amount of solid material **S** in filling layer **4** directly, it is possible to

precisely detect the filled amount of the solid material with a simple method and configuration without the necessity of high cost as in conventional methods.

[0043] Monitoring of the filled amount of solid material **S** can further be used to adjust the flow rate of carrier gas **C** in each of divergent flow paths **2a**. That is, by adjusting the flow rate of carrier gas **C** at the stage of the first dispersion, it is possible to stabilize the material concentration in the solid material gas. More specifically, in the case the monitored remaining amount in filling layer **4** becomes lower than the set amount, and a specified time duration is necessary to supplement it, it is possible to assure the specified material concentration by reducing the overall flow rate of carrier gas **C**. In the case the remaining amount in filling layer **4** is uneven, it is possible to reduce the flow rate of carrier gas **C** in divergent flow path **2a** near the part where the remaining amount is low to eliminate the state of unevenness. The flow rate of carrier gas **C** can be adjusted with a throttle valve, on-off valve or damper (not shown in figure) installed in divergent flow path **2a**.

[0044] Instead of the visual detection through monitoring window **W**, a configuration (third configuration example) for monitoring the filled amount of solid material **S** with the output from photo-sensors **P** by installing multiple photo-sensors at the side wall of filling layer **4**, as shown in **FIG 2(B)**, is also preferable. The configuration of photo-sensor **P** can either be multiple single sensors or a sensor array that possesses multiple sensors. The method of photo-sensor can be the reflection type installed on one of the side walls of filling layer and detects light reflected by filling layer **4**, or the transmission type sensor installed on the other side of filling layer **4** and detects light that passes through filling layer **4**.

Solid material gas supply method using the inventive apparatus

[0045] In the inventive apparatus having the configuration as shown in **FIG 1**, the processes (1) ~ (6) in which the specified amount of solid material **S** is filled into filling layer **4**, carrier gas **C** is introduced to filling layer **4** that is heated to the specified temperature, and solid material gas **G** with the specified material concentration is extracted, are explained in detail below.

[0046](1) Supply of carrier gas

Carrier gas C is supplied from supply section **1** to container **10**. The pressure and flow rate of the carrier gas to be supplied are adjusted in advance according to specifications to specified values. The adjustment of the pressure and flow rate conditions is not limited to either before its supply to container **10** or after its supply-out from container **10**.

[0047](2) Primary dispersion of carrier gas

Carrier gas C supplied into container **10** is first introduced to dispersion chamber **3** in a state dispersed by dispersion means **2** connected to supply section **1**. At this time, carrier gas C is diverged at the horizontal cross section of dispersion chamber **3** by divergent flow path **2a**, and distributed also at the vertical cross section of dispersion chamber **3** by spray nozzle **2b**, and can be dispersed widely inside dispersion chamber **3** as it is sprayed out from various locations inside dispersion chamber **3**. This highly dispersed state obtained by the primary dispersion will result in more effective functioning of the secondary and tertiary dispersion treatments that will be discussed later.

[0048](3) Secondary dispersion of carrier gas

Carrier gas introduced into dispersion chamber **3** is then introduced to filling layer **4** via first mesh section **7**. At this time, carrier gas C dispersed inside dispersion chamber **3** is further finely dispersed by the fine pores at first mesh section **7**, and absorbs the heat of first mesh section **7** to maintain the set temperature or be heated. Carrier gas C supplied out from first mesh section **7** can form a state with almost uniform temperature and flow rate at any location in first mesh section **7**.

[0049](4) Production of solid material gas

Carrier gas C that passed through first mesh section **7** is then introduced to filling layer **4**, and by contact with solid material **S** inside filling layer **4**, solid material gas G having the specified vapor pressure of the vaporized solid material **S** is produced. It is possible to ensure sufficient contact time and obtain solid material gas G with stable material concentration by setting the flow rate of carrier gas C and capacity of filling layer **4** so that the space velocity will be as specified in advance. As solid material gas G is produced, the amount of solid

material **S** decreases from the upper layers of filling layer **4**. Decrease in solid material **S** can be monitored through monitoring window **W** visually or detected by photo-sensor output described later. The decrease in the material concentration that accompanies reduction of solid material **S** can be prevented by maintaining the thickness of filling layer **4** to above the specified thickness. Moreover, unevenness, if any, in the reduction amount of solid material **S** in filling layer **4** can also be monitored and can be corrected by supplementing or replacing solid material **S**.

[0050] (5) Tertiary dispersion of solid material gas

Solid material gas **G** produced at filling layer **4** is then introduced to supply-out chamber **5** via second mesh section **8**. At this time, while solid material gas **G** produced at filling layer **4** has the specified uniformity, strictly speaking, there is unevenness in its flow rate in the planar direction and in its material concentration (in fact, there is possibility of unevenness in its temperature due to absorption of sublimation heat). Solid material gas **G** introduced to second mesh section **8** is further finely dispersed by the pores at second mesh section **8** (tertiary dispersion) and at the same absorbs the heat of first mesh section **8** to maintain the set temperature or be heated. Solid material gas supplied out from second mesh section **8** can form a state with almost uniform temperature and flow rate at any location in second mesh section **8**.

[0051] (6) Supplying out solid material gas

Solid material gas **G** that passed second mesh section **8** merges in supply-out chamber **5** where it is mixed and homogenized to produce solid material gas **G** with the specified material concentration. Produced solid material gas **G** is then supplied out from supply-out section **6**.

Another configuration example of solid material gas supply apparatus

[0052] FIG 3 is a schematic illustration of another configuration example (fourth configuration example) of the inventive solid material gas supply apparatus. In the first to third configuration examples provided above, the reduction amount of solid material **S** at areas near first mesh section **7** that partitions dispersion chamber **3** and filling layer **4** is large since carrier gas **C** is supplied to filling

layer **4** from dispersion chamber **2**. With the fourth configuration example, it is possible to directly supply carrier gas C from divergent flow path **2** also to filling layer **4** so that it merges with carrier gas C from dispersion chamber **3** to perform further uniform contact between solid material **S** and carrier gas C in filling layer **4** by adopting a configuration having one or more spray nozzles each in dispersion chamber **2** and filling layer **4** as secondary dispersion means **2**. Here, divergent flow path **2** has spray nozzles **2b** inside dispersion chamber **3**, and spray nozzles **2c**, **2c**... (referred collectively hereinafter as “spray nozzle **2c**”) in filling layer **4**, as shown in **FIG 3(B)**.

[0053] More specifically, pore sections **7a**, **7a**... (referred collectively hereinafter as “pore sections **7a**”) into which divergent flow path **2a** can be inserted are set up at first mesh section **7**, open spaces **4c**, **4c**... (referred collectively hereinafter as “open spaces **4c**”) into which divergent flow path **2a** can be inserted are formed inside filling layer **4**, and divergent flow path **2a** is inserted into each open space **4c** through each pore section **7a**. At this time, it is desirable that the peripheral area of open space **4c** is partitioned from filling layer **4** with the same member (referred hereinafter as “third mesh section **9**”) as first mesh section **7**. At the same carrier gas C that has been uniformly dispersed through primary dispersion function by spray nozzle **2b** at dispersion chamber **3** and secondary dispersion function by first mesh section **7** is introduced to filling layer **4**, carrier gas C that has been uniformly dispersed through primary dispersion function by spray nozzle **2c** inside filling layer **4** and secondary dispersion function by third mesh section **9** is introduced to filling layer **4**. Here, by being connected to first mesh section **7**, third mesh section **9** can disperse carrier gas C to both.

Verification of functions of the inventive apparatus and method

[0054] The functions of the inventive apparatus and method are verified as below using the first configuration example of the inventive apparatus with hafnium chloride (HfCl_4) as the solid material.

[0055] (i) Verification conditions

4 divergent flow paths, and dispersion means equipped with 20 gas spray nozzles at each divergent flow path were used. 100-mesh stainless steel flat-woven metal screens were used as the first and second mesh sections, and the first mesh section was mounted at the upper part of the filling layer. The filling layer filled with 350g of hafnium chloride was heated by a heater to 150°C. The concentration of HfCl_4 in the supplied solid material gas was measured by a TCD sensor (Valco Model TCD2-NIFE-110) installed in the rear tier of the container.

[0056] (ii) Verification items

The following items were verified:

- (ii-1) While the function of the monitoring window was being verified,
- (ii-2) the change in concentration of HfCl_4 when the carrier gas flow rate was changed from 50 to 200 and 500 SCCM, was measured.
- (ii-3) Next, HfCl_4 was supplied out from its maximum amount at the time it was filled (the remaining amount of HfCl_4 at this stage is considered 100%) until its remaining amount became 10%, and the concentration of HfCl_4 between that duration was measured.

[0057] (iii) Verification results

[0058] (iii-1) Verification of monitoring window function

As shown in **FIG 4(A)**, HfCl_4 was visible throughout the entire surface of monitoring window **W** at the initial stage when the container was filled to the upper section. At a stage the amount has been reduced, the surface of the upper part of filling layer **4** and first mesh section **7** were visible through monitoring window **W**, as shown in **FIG 4(B)**. As described above, it has been verified that the state of HfCl_4 filled inside the container can be inspected visibly through monitoring window **W**.

[0059] (iii-2) Verification of the influence of carrier gas flow rate on material concentration

As shown in **FIG 5**, HfCl_4 concentration was stable at approximately 370 ppm within the range of carrier gas flow rate of 50 ~ 500 SCCM, and it was verified that HfCl_4 at saturated vapor pressure was carried and supplied out.

[0060] (iii-3) verification of the influence of the remaining amount of the solid material on material concentration

As shown in **FIG 6**, HfCl_4 of approximately 370 ppm that is the saturated amount, was carried by the carrier gas until the remaining amount was 20%, and high concentration stability was verified. Therefore, for HfCl_4 , it was verified that the monitoring window is necessary within the range its remaining amount is 20% or more.

[0061] It will be understood that many additional changes in the details, materials, steps, and arrangement of parts, which have been herein described 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.

We claim:

1. A solid material gas supply apparatus characterized in that it is aimed at treating solid materials that can be sublimated and supplied at a specified rate using a carrier gas, and equipped with a carrier gas supply section, a dispersion means of said carrier gas, a dispersion chamber that houses said dispersion means and disperses the supplied carrier gas, a filling layer in which the aforementioned solid material is filled, a supply-out chamber that merges the solid material gas supplied from said filling layer, a supply-out section of said solid material gas, a first mesh section that partitions the aforementioned dispersion chamber and the aforementioned filling layer, and a second mesh section that partitions the aforementioned filling layer and the aforementioned supply-out chamber.
2. A solid material gas supply apparatus in accordance with Claim 1, characterized in that either the aforementioned first mesh section or the second mesh section is installed in the upper section of the aforementioned filling layer, and, at the same time, can be movable vertically downwards by its own weight.
3. A solid material gas supply apparatus in accordance with Claim 1 or Claim 2, characterized in that the aforementioned dispersion means is connected to the aforementioned supply section and is equipped with multiple divergent flow paths that diverges the carrier gas, and one or more spray nozzles installed in each of the divergent flow paths.
4. A solid material gas supply apparatus in accordance with Claim 3, characterized in that the aforementioned dispersion means has one or more spray nozzles in each of the aforementioned dispersion chamber and the aforementioned filling layer.
5. A solid material gas supply apparatus in accordance with either Claim 1, Claim 2, Claim 3 or Claim 4, characterized in that a monitoring window or multiple photo-sensors are installed on the side wall of the aforementioned

filling layer so that the filled amount of the aforementioned solid material can be monitored visually by sight or through output from said photo-sensors.

6. A solid material gas supply method using the supply apparatus in accordance with Claim 1 through Claim 5, characterized in that solid material that can be sublimated and supplied at a specified rate by a carrier gas is filled inside the aforementioned filling layer, and then goes through primary dispersion by multiple diverging flow paths;

the carrier gas that has gone through secondary dispersion by the first mesh section located on the supply side to the aforementioned filling layer is supplied to the aforementioned filling layer,

and the solid material gas supplied-out from the aforementioned filling layer, that has gone through third-order dispersion by the second mesh section located on the supply-out side to the aforementioned filling layer is supplied out.

7. A solid material gas supply method in accordance with Claim 6, characterized in that the filled amount of the solid material is monitored at one or more locations in the aforementioned filling layer, and the flow rate of the carrier gas in the aforementioned multiple divergent flow paths is adjusted.

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FIG 1

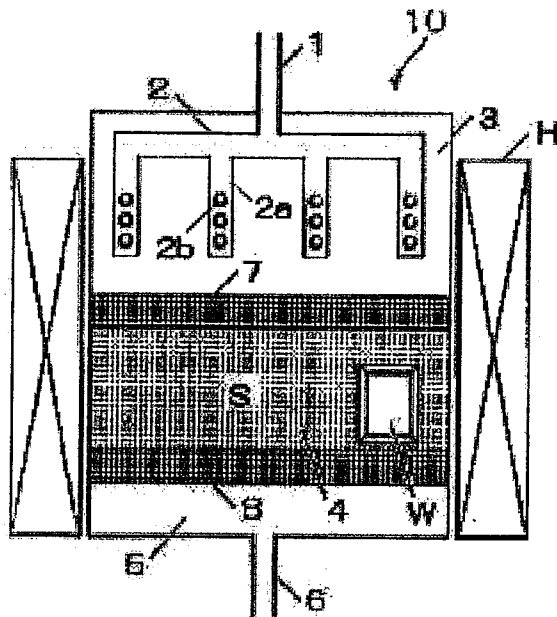
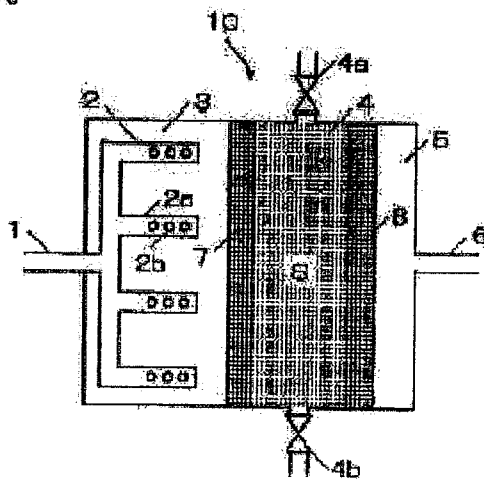
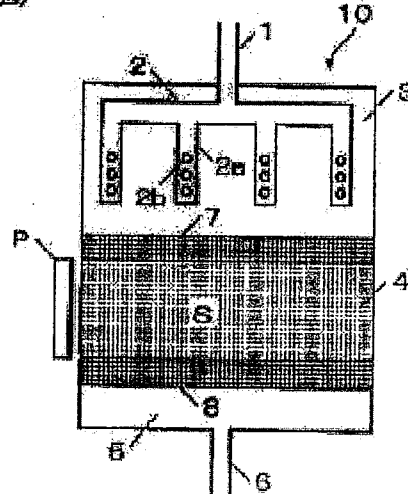


FIG 2

(A)



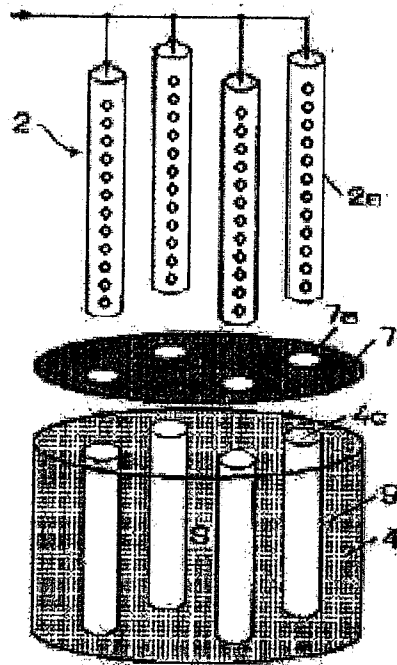
(B)



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FIG 3

(A)



(B)

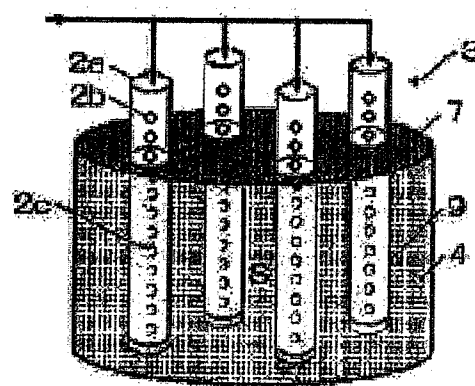
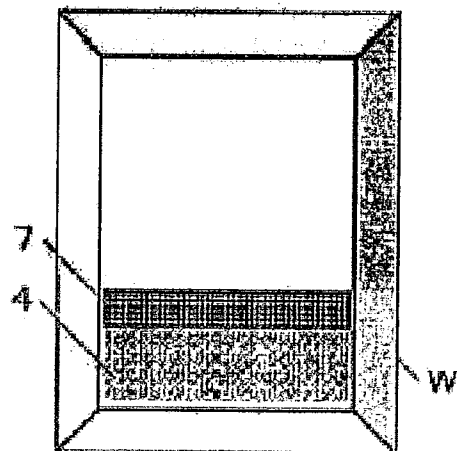
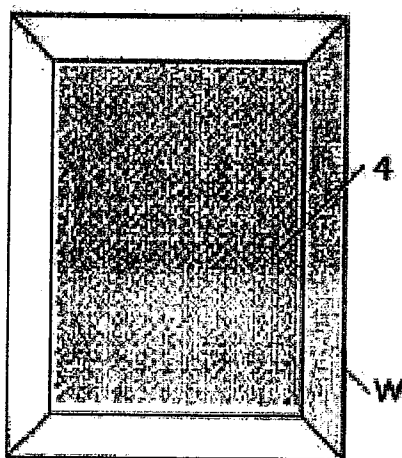


FIG 4

(A) When remaining amount is large (B) When remaining amount is small



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FIG 5

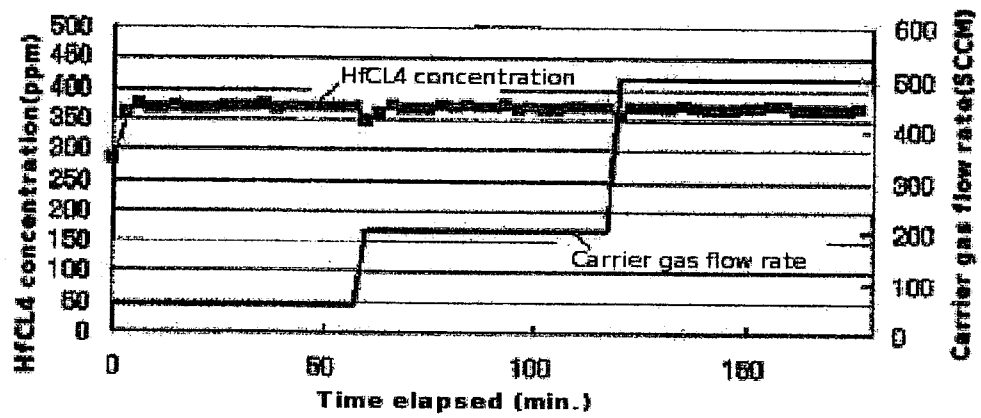
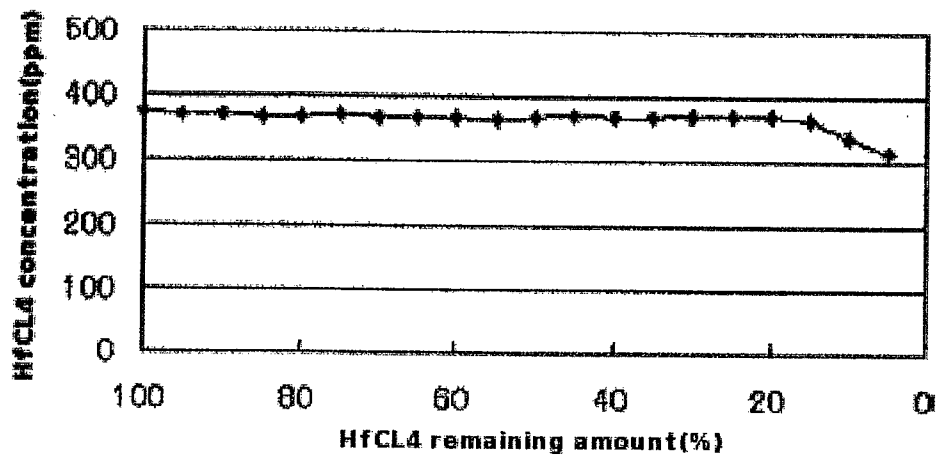
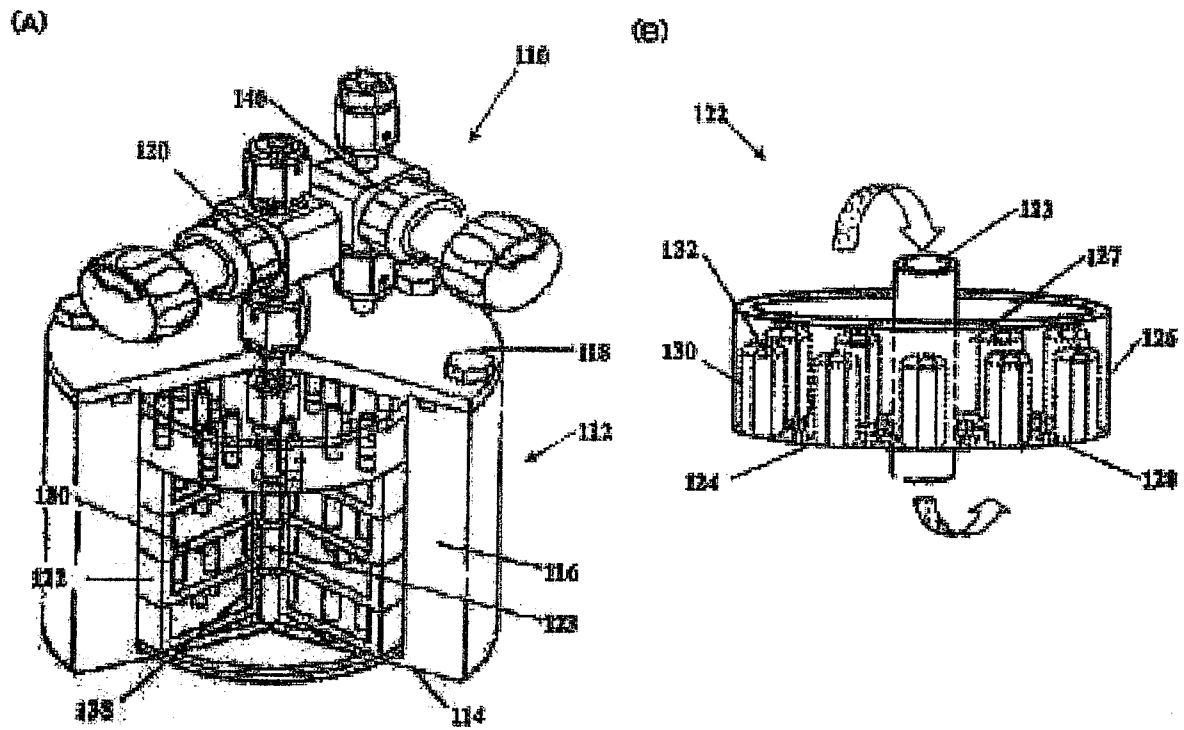


FIG 6



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FIG 7



INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2012/051094

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. H01L21/205 (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. H01L21/205, C23C16/448, H01L21/31

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.
X Y A	Microfilm of the specification and drawings annexed to the written application of Japanese Utility Model Application No.73658/1989 (Laid-open No.14166/1991) (NIPPON SANSO CORPORATION) 1991.02.13, page4,line8 to page11,line2 ,Figs.1-3 (No Family)	1-2, 6 2-3, 5, 7 4
X Y A	JP 07-278818 A (MURATA MANUFACTURING CO., LTD.) 1995.10.24, [0022]-[0025], Fig.1 (No Family)	1, 3, 6 2-3, 5, 7 4



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

15.05.2012

Date of mailing of the international search report

29.05.2012

Name and mailing address of the ISA/JP

Japan Patent Office

3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan

Authorized officer

Yuichi Yamamoto

Telephone No. +81-3-3581-1101 Ext. 3471

4R 3123

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2012/051094

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2006/101767 A2 (ADVANCED TECHNOLOGY MATERIALS, INC.) 2006.09.28, [0072], [0186] & JP 2008-538158 A & US 2008/0191153 A1 & EP 1866074 A & CN 101495190 A & SG 160401 A & KR 10-2007-0113290 A	5, 7