

(19)



LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

(11)

N° de publication :

LU102344

(12)

BREVET D'INVENTION**B1**

(21)

N° de dépôt: LU102344

(51)

Int. Cl.:

H01L 21/02, C23C 16/27, C23C 16/455

(22)

Date de dépôt: 21/12/2020

(30)

Priorité:

(72)

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(43)

Date de mise à disposition du public: 21/06/2022

(47)

Date de délivrance: 21/06/2022

(73)

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(54)

A semiconductor having increased dopant concentration, a method of manufacturing thereof and a chemical reactor.

(57)

The present invention relates to a method for an extrinsic semiconductor manufacturing by chemical vapour deposition. A substrate is exposed by at least one semiconductor precursor and at least one dopant element. The method comprises steps of: injecting a hydrogen gas at constant flow; and injecting a gas containing the dopant element to a reaction chamber under constant flow rate, and injecting gas of the semiconductor precursor under pulsed flow rate; or injecting the dopant element and the semiconductor precursor under pulse flow rate, wherein pulse of the dopant element and the semiconductor precursor are alternating. In another aspect, product capable to be produced by the method is disclosed. The product is a layer of phosphorus doped diamond deposited on a substrate, characterized in the phosphorus dopant concentration is higher than 2×10^{20} phosphorous / cm^{-3} . In a third aspect, a reactor for carrying out the method is provided.

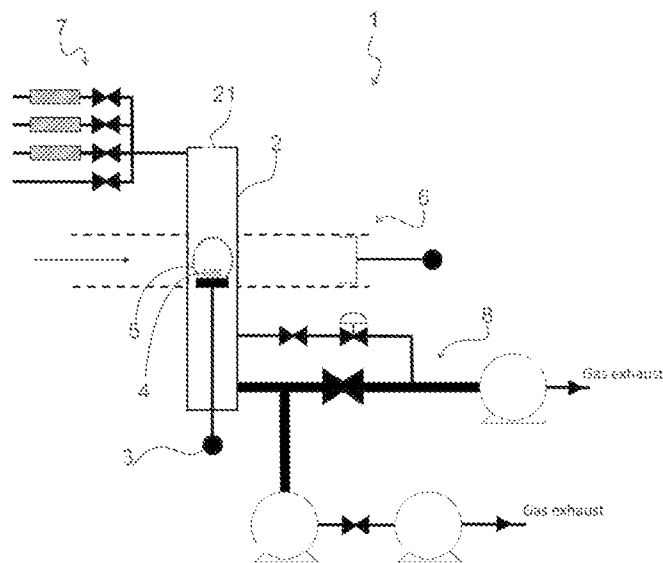


Fig. 9

A semiconductor having increased dopant concentration, a method of manufacturing thereof and a chemical reactor

Technical field

[001] The present invention pertains to material science, more particularly to semiconductor materials suitable for electronics and/or electrochemistry. In particular, the present invention relates to deposition of epitaxial layers or polycrystalline semiconductor layers with appropriate seeding pre-treatment, e.g. deposition of diamond seed, on a substrate.

[002] In a second aspect, the present invention relates to a method of doped semiconductor production, in particular via activated chemical vapour deposition, such as microwave plasma enhanced CVD or hot filament CVD methods.

[003] In yet another aspect, the present invention relates to a chemical reactor suitable for production such semiconductor suitable for electronics and/or electrochemical electrodes.

Background of the invention

[004] Diamond possesses physical and electrical properties such as high breakdown voltage, high thermal conductivity, small dielectric constant, wide band gap and excellent radiation hardness which qualifies its suitability for industrial application in high power electronics. Besides that, diamond is also chemically stable and is considered as a one of the bio-compatible material. It is known, e.g. from WO2019042484, that diamond can be used as a part of chemically stable electrochemical electrodes, heat spreaders with extreme thermal conductivity, radiation hard particle physics detectors, and high frequency surface acoustic wave filters.

[005] Electrical properties of diamond are controlled by the addition of boron (p-type) and phosphorous (n-type) impurities. Diamond is also a unique material for quantum application with easily interrogable and controllable qubits at room temperature using the nitrogen vacancy or silicon vacancy defects. The key technology in the use of diamond for the fabrication of the next generation of quantum technologies and electronics is doping, i.e. the careful addition of impurities in diamond. Significant progresses have been achieved in the synthesis of doped diamond, yet the level of dopant incorporation remains limited depending on the substrate orientation, deposition conditions and the type of dopant (B, P,

N, Si, Ge, etc.). In particular, the incorporation efficiency of phosphorus and nitrogen in diamond are known to be very low compared to the relatively easy boron incorporation. Various approaches for increased doping efficiency have been studied, for instance, use of off-axis surfaces or different crystalline orientations, and microwave plasma pulsing [1]. However, these approaches have suffered from repeatability and reliability issues for phosphorus doping. Therefore, there is a need for new methods for increasing doping efficiency in diamond. LU102344

[006] Artificial diamonds can be produced by at least two methods: (i) high pressure and high temperature method that reproduces the natural formation process of diamond and (ii) chemical vapor deposition (CVD) method. The CVD method is carried out in the gas phase at low pressure and high temperature. The diamond growth process uses activated vapor or gas of organic compounds (generally methane) as carbon precursor for the diamond growth. The carbon precursor is generally (but not limited) diluted in hydrogen at different concentrations. The vapor (or gas) of the dopant elements' precursors are added in the gas mixture for the incorporation of the element during the growth process.

[007] There exists a large variety of CVD reactors for diamond deposition. They have in common a reaction cavity with different controlled precursor gas inputs, a pressure control system and a gas activation system. For the diamond growth to occur, the gas mixture needs to be activated to produce the chemicals at the origin of the diamond growth and the incorporation of dopants. The gases activation is carried out either electrically by creating an electrical discharge (i.e. a plasma) using generally microwave energy or thermal energy using hot filaments. The temperature of the substrate is generally above 600 °C, although diamond deposition at temperature as low as room temperature has been reported. The substrates are either diamond crystals for epitaxial growth or pre-treated materials that can withstand the process parameters (high temperature, reactive atomic hydrogen species, etc.), i.e. silicon, SiO₂, metals, etc. The diamond growth by CVD methods is directly related to the concentration of reactive species present in the gas phase. Although the exact process of diamond growth is not exactly known, it is acknowledged that atomic hydrogen (possibly halogen, e.g. chlorine) and CH_x radical (with $x \leq 3$) present in the activated process gas are essential for the diamond growth. Although the mechanism of dopant incorporation is not fully understood, the dopant (B, P, N, Si, etc.) incorporation also results from the activated species present in the gas phase.

- [008]** The latest results show, see Fig. 1, that atomic phosphorus and PH radical in the plasma of microwave plasma enhanced chemical vapor deposition systems are directly involved in the incorporation of phosphorus in diamond [2]. These results also show the drop of the atomic phosphorus and the PH radical concentration with the minute addition of methane. This effect is attributed to the unwanted crossed chemical reactions between the carbon and phosphorus precursors' radicals in the gas phase, which produce methinophosphide, which contributes to neither the phosphorus incorporation nor the diamond growth. LU102344
- [009]** The example, shown in Fig. 1, represents unwanted cross-reactions in the gas phase that can result of the addition of the dopant precursor in process gas used for the growth of undoped diamond. In the particular case of phosphorus doping, these unwanted reactions severely limit the incorporation of phosphorus in diamond and decrease the deposition rate at high concentration of the phosphorus precursor as illustrated below. The cross-reactions between the carbon precursor and the dopant precursor is not limited to phosphorus doping. Previous studies describes the complex chemical reactions between activated mixture of PH_3 or NH_3 and CH_4 for the understanding of the asthenosphere of Jovian planets [3]–[5] and report the formation of methylidyne phosphane (HCP) and hydrogen cyanide (HCN), respectively [3], [4]. Optical emission spectroscopy studies of plasmas used for diamond growth also report the presence of CN radical by the addition of nitrogen in the gas phase.
- [010]** US20170330746 discloses an apparatus and a method for manufacturing diamond electronic devices. The method comprises the step of positioning a substrate of diamond electronic device to a plasma enhanced chemical vapour deposition (PECVD) reactor, wherein the condition in the reactor is modulated, in particular controlling temperature of the substrate by manipulating microwave power, chamber pressure, and gas flow rates. In one embodiment, the modulation of temperature is above 600 °C and is pulsed. The pulsed variation of temperature is provided within 6 cycles in the range from 600 °C up to 1000 °C. According to the document, increase of dopant concentration in a diamond electronic device can be observed due to pulsed modulation of temperature. The flow rate of methane precursor, resp. phosphorus precursor is stable, i.e. there is a continues flow of both precursors.
- [011]** WO0000677 relates to a method for doping semiconductor materials. One of the semiconductor materials is diamond. In view of the WO0000677, an increased dopant concentration with nitrogen or boron can be observed according to a method disclosed

therein. The method comprises steps of controlling of a dopant concentration introduced LU102344 into an epitaxial film during CVD by controlling energy of dopant atoms impinged on the film. In an embodiment, the energy of dopant can be modulated via flow condition which can be continues or pulsed. However, when pulse regime was used, both precursors in a gas sources were introduced in pulsed regime simultaneously.

[012] US8017182 discloses a method for an epitaxy layer formation. The layers comprise metal and semi-metal oxides and nitrides deposited on a wafer substrate. The layers are deposited on the substrate using atomic layer deposition (ALD) method and chemical vapour deposition (CVD) method. Document further discloses combination of ALD and CVD in pulse regime.

Citation of non-patent literature

- [1] F. A. Koeck, S. Chowdhury, and R. J. Nemanich, "Phosphorus incorporation for n-type doping of diamond with (100) and related surface orientation," US 2017/0330746 A1, Nov. 16, 2017.
- [2] M. A. Lobaev, D. B. Radishev, A. M. Gorbachev, A. L. Vikharev, and M. N. Drozdov, "Investigation of Microwave Plasma during Diamond Doping by Phosphorus Using Optical Emission Spectroscopy," Phys. Status Solidi A, vol. 216, no. 21, p. 1900234, Nov. 2019, doi: 10.1002/pssa.201900234.
- [3] J. P. Ferris, J. Y. Morimoto, R. Benson, and A. Bossard, "Photochemistry of NH₃, CH₄ and PH₃. Possible applications to the Jovian planets," Origins of Life, vol. 12, no. 3, pp. 261–265, Sep. 1982, doi: 10.1007/BF00926895.
- [4] A. R. Bossard, R. Kamga, and F. Raulin, "Gas phase synthesis of organophosphorus compounds and the atmosphere of the giant planets," Icarus, vol. 67, no. 2, pp. 305–324, Aug. 1986, doi: 10.1016/0019-1035(86)90111-9.
- [5] A. Bossard, R. Kamga, and F. Raulin, "Quantitative gas chromatographic analysis of low-molecular-weight alkylphosphines in the presence of phosphine and hydrocarbons," Journal of Chromatography A, vol. 330, pp. 400–402, Jan. 1985, doi: 10.1016/S0021-9673(01)82003-3.

Summary of the invention

- [013]** In view of the prior art drawbacks, there is a need for a method for increasing dopant concentration in whole bulk of the semiconductor and thus increase doping efficiency of the CVD process in semiconductor materials such as silicon and more preferably diamond. LU102344
- [014]** In a first aspect, the present invention relates to a method of production an extrinsic semiconductor by chemical vapour deposition. In semiconductor production, doping is the intentional introduction of impurities into an intrinsic semiconductor for modulating its electrical, optical and structural properties. The doped material is referred to as an extrinsic semiconductor.
- [015]** The method according to the present invention comprises the step of exposure of a substrate to chemical vapour of at least one semiconductor precursor and at least one dopant element. The substrate is further exposed to a hydrogen gas under constant flow in a reactor chamber. In a first alternative, the substrate is further exposed to the semiconductor precursor under pulse flow and exposed to the dopant element under constant flow. Alternatively, dopant element and semiconductor precursor are both introduced under pulse flow, however the pulses of injection are alternating.
- [016]** The method according to the present invention increases incorporation of dopant in semiconductor via controlling the flow of precursors in time to limit the unwanted cross reaction in the gas phase between the different precursors by the separation in time. The precursors' gas injection (i.e. to pulse the injection of the precursors) maximizes the concentration of active dopant precursor in the gas phase.
- [017]** An alternative technical effect of the method according to present invention is reduction of non-diamond (i.e. sp^2 -carbon) in deposited diamond layer by pulsing the carbon precursor gas. It is further provided increasing the active hydrogen species in the gas phase responsible for the etching of sp^2 -carbon, or by pulsing the injection of oxygen gas that is also known to etch sp^2 -carbon.
- [018]** Flow is the volume of fluid that passes in a unit of time. Flow is often measured in units of standard cubic centimeters per minute (sccm) in standard conditions for temperature and pressure of a given fluid. A skilled person knows the method how to measure the flow of the gas being introduced into the reaction chamber.

[019] In a preferred embodiment, the semiconductor precursor is selected from the group of: LU102344
methane, ethane, silane, Si_2H_6 , GeH_4 .

[020] In another preferred embodiment, the dopant element is selected from the group of:

- acceptor atoms such as boron, aluminium, gallium, indium; or
- donor atoms such as phosphorus, arsenic, antimony, bismuth; or
- or others elements as germanium, silicon, chromium, nickel, tin, cobalt, sulphur, gold and platinum.

[021] In another preferred embodiment, shape of the pulse of semiconductor precursor is squared, harmonics or sawtooth wave shapes.

[022] In another preferred embodiment, the total gas flow is preferably between 200 and 2000 sccm.

[023] In yet another embodiment, time period of the process is up to 30 min depending on the gas flow dynamic of the reactor, typically few minutes. The duration of the gas injection is from 1% - 50% of the time period of the process (duty cycle).

[024] The second aspect of the present invention concerns a reactor for production of an extrinsic semiconductor. The reactor is especially suitable for carrying out the method in accordance with the present invention.

[025] The reactor comprises:

- a vacuum chamber;
- a substrate holder inside the vacuum chamber, the holder is capable to hold a sample, wherein
the sample is configured to receive plasma from a chemical vapour deposition system;
- at least one gas injecting system capable to inject hydrogen gas, semiconductor precursor and dopant element into the vacuum chamber, wherein the gas injecting system is capable to inject the hydrogen gas at constant flow; and
 - inject the dopant element to the reactor under constant flow, and the semiconductor precursor under pulsed flow;

or

– inject both, the dopant element and the semiconductor precursor under pulse flow rate, wherein pulse injection of the dopant element and the semiconductor precursor are alternating; and wherein the reactor further comprises:

- a pumping system capable to evacuate the gases from the reaction chamber; and
- gas activation system configured to activate the gases introduced by the gas introducing system to form reactive species for the doped semiconductor growth.

[026] In a preferred embodiment, the gas activation system is microwave plasma enhanced chemical vapour deposition reactor. Microwave plasma enhanced CVD reactor is more convenient to use compared to hot filament. Filaments need to be replaced regularly, the element of the filament can also contaminate the diamond layer. Yet, microwave plasma is limited in size, which is not the case for hot filament gas activation.

[027] In another preferred embodiment, the gas activation system is hot filament chemical vapour deposition reactor.

[028] In a third aspect of the present invention, a product obtainable by the method according to the present invention is disclosed. The product is a layer of phosphorus doped diamond obtainable by the method according to the invention, wherein the phosphorus dopant concentration is higher than 2×10^{20} phosphorus atoms / cm^{-3} . The layer can have thickness from 10 nm to 100 μm .

[029] In another aspect of the present invention, the product can be used as a semiconductor used for electronics as source, drain in a transistor, or interlayer to form a low resistive ohmic contact in diamond-based diodes or transistors.

[030] In another aspect, the product obtainable by the method according to the present invention can be used as working electrode, preferably working electrode in electrochemistry.

Brief description of drawings

Fig. 1a represents optical emission spectra of PH and the variation of the intensity of the maximum line of the PH spectrum as a function of the added methane flow in hydrogen plasma.

Fig. 1b represents optical emission spectra of PH and the variation of the intensity of the maximum line of the CH line as a function of the methane concentration in the gas phase.

Fig. 1c represents normalized intensity of the atomic phosphorus emission lines (213 nm and 253 nm), the PH line and the CH line as a function of the methane concentration in hydrogen plasma in a log-log scale. LU102344

Fig. 2a is time dependent variation of the H, at. P, PH and CH species light emission in pulsed injection of methane (1 min) over one period of time (5 min) at a concentration of phosphine in hydrogen of 6×10^{-6} .

Fig. 2b Time dependent variation of the H, at. P, PH and CH species light emission in pulsed injection of methane (1 min) over one period of time (5 min) at concentration of phosphine in hydrogen of 1.2×10^{-3} .

Fig. 2c schematically represents an embodiment, wherein the dopant element and semiconductor precursors are alternating in time periods.

Fig. 3a shows phosphorus concentration in diamond as function of the depth as measured by secondary ion mass spectroscopy depending on the flow of phosphine (continuous) in the reactor and the methane (pulse) injection mode.

Fig. 3b shows increase in the incorporation efficiency of the pulsed injection compared to the continuous injection of CH_4 methods and the phosphorus concentration in diamond as a function of the nominal ratio of PH_3 and CH_4 flow rate and the methane injection mode: continuous (black squares) or pulsed (red dots).

Fig. 4 shows comparison of the deposition rate of phosphorus doped diamond for continuous and pulsed methane injection.

Fig. 5 schematically represents a reactor for carrying out a method in accordance with the present invention.

Fig. 6 schematically represents a preferred embodiment of the reactor according to present invention having enhanced pumping system.

Fig. 7 schematically represents a preferred embodiment of the reactor according to the present invention having injected system.

Fig. 8 schematically represents a preferred embodiment of the reactor according to the present invention having enhanced gas activation system.

Fig. 9 schematically represents a preferred embodiment of the reactor according to the present invention comprising all of the above-mentioned enhanced systems. LU102344

Detailed description of the preferred embodiments

[031] Fig. 1a represents the decreasing PH radical emission line intensity at constant concentration of phosphine gas with the increasing concentration of methane in the hydrogen plasma in a NIRIM type microwave plasma enhanced chemical vapour deposition system. Simultaneously, the CH radical emission line increases consistently with the methane concentration as shown in Fig. 1b. The disappearing of the PH radical and atomic phosphorus and the increasing CH concentrations in the plasma are summarized in Fig. 1c where are reported their respective emission line intensity with the increasing concentration of methane in the plasma. Fig. 1a – 1c represents prior art solution for constant flow injection.

[032] Figure 2a and 2b represents the time dependent evolution of the normalized light intensity of the emission wavelengths of the atomic hydrogen, CH radical, PH radical and atomic phosphorus (at. P) from an H_2 - CH_4 - PH_4 plasma in a NIRIM type microwave plasma enhanced chemical vapor deposition system over one period of time (5 mins) and a pulsed injection of methane of 1 min also illustrate the variation of the chemical species in the reactor due to chemical reaction between precursors. While the intensity of the hydrogen line remains nearly constant over the period of time, one can observe a clear simultaneous drop of the intensity of the PH and at. P emission lines to their background level with the addition of methane in the gas phase and the rise of the intensity of the CH radical emission line. Once the flow of the methane is stopped, one can observe the simultaneous exponential 1- drop of the intensity of the CH radical emission line and 2- increase of the intensity of the PH and at. phosphorous emission lines. These exponential increase and decreases are function of the gas flow dynamic of the CVD reactor and dependent of the total gas flow and the reactor's volume. One can also observe the lower amplitude of the CH line intensity due to these reactions in the gas phase at equivalent concentration of methane and phosphine. These figures show the possibility to control the concentration of the carbon and phosphorus radical in the reactor in time. This method has been used to test the incorporation of phosphorus in diamond depending on the continuous or pulsed flow of methane. The difference between examples of the method shown in Fig. 2a and 2b

is concentration of precursors. In a first example, Fig. 2a, the concentration of precursor in hydrogen was $6 \text{ E-}6$. In an example according to Fig. 2b was $1.6 \text{ E-}3$. LU102344

[033] In an example, increase of the dopant in an extrinsic semiconductor can be provided by the exposure of a substrate by hydrogen gas at constant flow. The pulses of the dopant element and semiconductor can be alternating, i.e. in a first time period t_1 a pulse of the dopant element is injected into a reaction chamber while the semiconductor precursor gas is not injected therein. At the time period t_2 , the step of injection is opposite, i.e. the dopant element is not injected into the reaction chamber while the semiconductor precursor is injected therein. The alternation of the pulses is schematically shown in Fig. 2c. In some example, the time periods t_1 and t_2 can be 60 s.

[034] Fig. 3a shows the in-depth chemical phosphorus concentration in a multilayer diamond sample prepared with different phosphorus concentrations/flows using either continuous or pulsed injection of methane in the reactor as measured by secondary ion mass spectroscopy. One can observe the higher concentration of phosphorus in domains of pulsed methane injection in each interval of constant flow/concentration of phosphine.

[035] Fig. 3b shows the higher incorporation of phosphorus in diamond using the pulsed injection of methane compared to the continuous injection. The increase of phosphorus incorporation varies with the increasing ratio of the flow of PH_3 and CH_4 (setting point for the methane when the flow is on).

[036] In some embodiment, the semiconductor precursor can be silicon or diamond, such as CVD diamond. Example of dopant element can be boron, phosphorus or any other element from III B or V B column of periodic table of elements.

[037] Fig. 4 represents a result of phosphorus dopant increase incorporated in diamond semiconductor precursor. The results show (i) the logical lower deposition rate using the pulsed method due to the lower used amount of carbon precursor (1/5) and (ii) the faster drop of the growth rate in continuous injection mode compared to the pulsed injection mode. These results obtained by a simple control of only the injection of methane in the gas phase illustrate the technical effect of the method according to the present invention increasing the incorporation of dopant in diamond.

[038] The use of the pulse gas injection is not limited to the increase of dopant concentration, but LU102344

it can be used for the reduction of non-diamond (i.e. sp^2 -carbon) in deposited diamond layer by pulsing the carbon precursor gas, i.e. that is equivalent to increasing the active hydrogen species in the gas phase responsible for the etching of sp^2 carbon, or by pulsing the injection of oxygen gas that is also known to etch sp^2 carbon.

[039] Referring to FIG. 5, a gas activation system **6**, a gas injecting system **7** and a pumping system **8** employed in a reactor **1** according to the invention is shown. A vacuum chamber **2** is further employed in the reactor **1** in accordance with the present invention. The vacuum chamber **2** contains a substrate holder **3** therein and a sample **4** positioned on the holder **3** as a skilled person in the art would normally use it. The vacuum chamber **2** can communicate with other systems **6**, **7**, **8** as described in the present disclosure through gate valves. Between the gas injecting system **7** and pumping system **8**, a reaction space can be surrounded by collars made of stainless steel and/or an insulator so that excited reactant gas does not spread out to the inside of the structure and does not accumulate the product which can cause flakes to be present therein. Gas injecting system **7** is configured to inject a semiconductor precursor and dopant gas in accordance with the present invention. The gas activation system **6** is capable to activate gasses to form a plasma **5** therefrom. The gas activation system **6** is further configured to activate the gasses near to the sample **4** so that, desired chemical reactions are triggered nearby a resonance space. In some embodiment, the gas activation system **6** can be a microwave chemical vapour deposition system (MCVD) or plasma enhanced chemical vapour deposition system (PECVD). Besides the others, the gas injecting system **7** is introducing the hydrogen gas into the reactor **1** at constant flow. The gas injecting system **7** can introduce the gases of dopant element and semiconductor precursor in two regimes. In a first regime, the dopant element is introduced at constant flow and semiconductor is introduced at pulsed flow, such as shown in Fig. 3a. In a second regime, the gas injecting system **7** is configured to introduced the dopant element and semiconductor precursor in alternating pulses, such as shown in Fig. 2c. In both regime, the gas activation system **6** is configured to active the gasses and form plasma **5** from the gasses being presented at vacuum chamber **2** near to the sample **4** in the particular time. The pump system **8** can be a turbomolecular pump used for pumping cycles. The pumping system **8** is used in order to minimize the system background gases, in particular the gasses that were present in the vacuum chamber in previous loop of the cycle.

[040] As above suggested, non-reactive gas can be introduced into the reaction space into the vacuum chamber **2** through conduit a pipe. In some embodiments, the non-reactive gas can be activated via microwaves radiated into the resonance space from a microwave oscillator comprised in the gas activation system **6** through a window made of synthetic quartz.

[041] Fig. 6 discloses a preferred embodiment of the reactor **1**, wherein the pumping system **8** comprises at least three pumps, in particular a rotary oil pump **81**, a turbo-molecular pump **82** and a membrane pump **83**. The rotary oil pump **81** is connected to the vacuum chamber **2** through a first pipe wherein the first pipe comprises a valve **841** and throttle valve **842** serving for the selection of the pumping configuration valve **841** and the control of the pumping speed and therefor the pressure in the reactor. The rotary oil pump **81** is also connected to the vacuum chamber **2** through a second pipe comprising a second valve **851**. Gas is exhausted through the rotary oil pump **81**. The turbo molecular pump **82** is connected to the membrane pump **83** through a pipe comprising valve **862**. The turbomolecular pump **82** is connected to the second pipe connected to the vacuum chamber **2** through a valve **861**. Gases can also be exhausted through a system of the turbomolecular pump **82** and the membrane pump **83**. The pumping system **8** as described above provides three pumping configurations to evacuate the system to a base pressure below 1E-6 mbar via a first pumping using the rotary pump followed by the turbomolecular pumping to control the pressure in the reactor through the Throttle valve **842**. The embodiment may further comprise an optical window for optical scanning of the sample **4** positioned on the substrate holder **3** in close proximity of the plasma **5** created by a gas activation system **6**.

[042] Fig. 7 discloses a preferred embodiment of the reactor **1**, wherein the gas injecting system **7** further comprises mass flow controllers **711** and valves **712** connected to gas sources **71**, **72**, **73** and **74**. The gas source **74** is directly connected to a gas valve **741** without a mass controller. Gas source **71** contains hydrogen and through mass flow controller **711**, which is used to control the flow rate of the gas from the gas source **71**, the gas to the vacuum chamber. Any of the herewith disclosed mass flow controller **711** can advantageously maintain the flow rate of the gases at a setpoint value for a period of time before the flow rate begins to drop. Gas source **72** contains the semiconductor gas precursor (usually methane for diamond deposition, silane for silicon). Gas source **73** contains the dopant gas precursor. Gas source **74** contains nitrogen, argon or air. The gas source **74** is used to vent the reactor. All of the herewith described sources **71 72 73 74** are connected to the vacuum chamber **2** via gas valves **712**, **741** which serves for isolation of the gas lines during the

evacuation of the reactor and its base pressure prior to the semiconductor deposition. The present embodiment of the reactor further comprises an optical window **21** for optical scanning a sample **4**. The reactor further comprises a vacuum chamber **2** which can be a quartz tube. A substrate holder **3** is further provided to hold the sample **4** and in proximity of plasma **5** created by the gas activation system **6**. The pumping system **8** enables to evacuate gasses which are not desired to be present in the vacuum chamber.

[043] Fig. 8 discloses a preferred embodiment of the reactor **1**, wherein the gas activation system **6** is microwave plasma enhanced CVD system. The microwave CVD activation system, microwave electric discharge power **61** is directly introduced into the vacuum chamber **2** thereby causing glow discharge plasmas **5** in close proximity of the sample **4**. The waveguide **62** serves for the microwave controlled propagation. The waveguide **62** is connected to sliding microwave short circuit **63** which serves for the adjustment of the plasma position in the reactor (quartz tube). The embodiment further comprises a pumping system **8**.

[044] Fig. 9 discloses a preferred embodiment of the reactor **1** comprising all of the above-mentioned preferred embodiments according to Fig. 6, 7 and 8.

Industrial applicability

[045] The present invention can be used in the fabrication of diamond (silicon) unipolar and bipolar electronic devices in the formation of low contact resistivity ohmic contacts in diodes and transistor, or as drain and source in metal-oxide-semiconductor field effect transistor (MOSFET) for layers with atomic phosphorus concentration in diamond above $2 \times 10^{20} \text{ cm}^{-3}$. They can be used also in the fabrication of electrochemical electrodes and electrochemical sensors.

Claims

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1. A method of a doped diamond layer manufacturing by chemical vapour deposition, wherein a substrate is exposed to a semiconductor precursor and a dopant element, wherein the method is characterized in that, it further comprising:
 - injecting hydrogen gas into a reactor chamber at constant flow; and
 - injecting of the semiconductor precursor is pulsed flow injecting and injecting the dopant element under is constant flow injecting;or
 - injecting of both, the dopant element and the semiconductor precursor are pulse flow, wherein pulse of the dopant element and the semiconductor precursor are alternating.
2. The method according to claim 1, wherein the semiconductor precursor is selected from the group of: methane, ethane....
3. The method according to anyone of the preceding claims, wherein the dopant element is selected from the group of:
 - acceptor atoms such as boron, aluminium, gallium, indium; or
 - donor atoms such as phosphorus, arsenic, antimony, bismuth or lithium; or
 - germanium, silicon, chromium, nickel, tin, cobalt, sulphur, gold and platinum.
4. The method according to anyone of the preceding claims, wherein shape of the pulse injection of the semiconductor precursor is harmonics or sawtooth wave shape.
5. The method according to anyone of the preceding claims, wherein total gas flow is below 2000 sccm, preferably between 200 – 2000 sccm.
6. The method according to anyone of the preceding claims, wherein the duration of the semiconductor and/or dopant precursor gas(es) injection is 1% – 50% of the time period.
7. The method according to anyone of the preceding claims, the time period of the semiconductor and/or dopant precursor gas(es) injection is below 30 min, preferably between 1 – 5 min.
8. A chemical vapour deposition reactor (1) for production of an extrinsic semiconductor wherein the reactor (1) comprises:

- a vacuum chamber (2);
 - a substrate holder (3) inside the vacuum chamber (2), the substrate holder (3) is capable to hold a sample (4), wherein
 - the sample (4) is configured to receive plasma (5) from a chemical vapour deposition system;
 - at least one gas injecting system (7) capable to inject hydrogen gas, semiconductor precursor and dopant element into the vacuum chamber, wherein the gas injecting system (7) is capable to inject the hydrogen gas at constant flow; and
 - inject the dopant element to the reactor (1) under constant flow, and the semiconductor precursor under pulsed flow;
 - or
 - inject both, the dopant element and the semiconductor precursor under pulse flow rate, wherein pulse injection of the dopant element and the semiconductor precursor are alternating; and wherein the reactor further comprises:
 - a pumping system (8) capable to evacuate the gases from the reaction chamber (2); and
 - gas activation system (6) configured to activate the gases introduced by the gas injecting system (7) to form reactive species for the doped semiconductor growth.
9. The reactor (1) according to claim 8, wherein the gas activation system (6) is microwave plasma enhanced chemical vapour deposition reactor.
10. The reactor (1) according to claim 8, wherein the gas activation system (6) is hot filament chemical vapour deposition reactor.
11. A layer of phosphorus doped diamond obtainable by the method according to anyone of the claims 1 – 6, wherein the phosphorus dopant concentration is higher than $2 \cdot 10^{20}$ dopant elements / cm^{-3} .
12. Use of the layer according to claim 11 as a source or drain in a transistor or an interlayer to form an ohmic contact in a diamond-based diode or a transistor.
13. An electrode comprising the layer according to claim 11.

1. Verfahren zur Herstellung eines extrinsischen Halbleiters durch chemische Gasphasenabscheidung, wobei ein Substrat einem Halbleitervorläufer und einem Dotierelement ausgesetzt wird, wobei das Verfahren dadurch gekennzeichnet ist, dass es ferner umfasst:

Einspritzen von Wasserstoffgas in eine Reaktorkammer bei konstantem Durchfluss; und

Das Injizieren des Halbleitervorläufers ist ein Impulsinjektionsinjektion, und das Injizieren des Dotierstoffelements unter einer Konstantflussinjektion ist;

oder

Das Einspritzen von sowohl dem Dotierstoffelement als auch dem Halbleitervorläufer ist ein Impulsfluss, wobei sich der Impuls des Dotierstoffelements und des Halbleitervorläufers abwechselt.

2. Verfahren nach Anspruch 1, wobei der Halbleitervorläufer ausgewählt ist aus der Gruppe von: Methan, Ethan, Silan, Si_2H_6 , GeH_4 .

3. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Dotierstoffelement ausgewählt ist aus der Gruppe von:

Akzeptoratome wie Bor, Aluminium, Gallium, Indium; oder

Donoratome wie Phosphor, Arsen, Antimon, Wismut oder Lithium; oder

Germanium, Silizium, Chrom, Nickel, Zinn, Kobalt, Schwefel, Gold und Platin.

4. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Form der Impulsinjektion des Halbleitervorläufers eine Harmonische oder eine Sägezahnwellenform ist.

5. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Gesamtgasstrom unter 2000 sccm liegt, vorzugsweise zwischen 200 und 2000 sccm.

6. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Dauer der Gasinjektion 1% - 50% des Zeitraums beträgt.

7. Verfahren nach einem der vorhergehenden Ansprüche, der Zeitraum der Gasinjektion liegt ^{LU1002343} unter 30 min, vorzugsweise zwischen 1 und 5 min.

8. Reaktor (1) zur Herstellung eines extrinsischen Halbleiters, wobei der Reaktor (1) umfasst:

eine Vakuumkammer (2);

einen Substrathalter (3) innerhalb der Vakuumkammer (2), der Substrathalter (3) kann eine Probe (4) aufnehmen, worin

die Probe (4) ist konfiguriert, um Plasma (5) von einem chemischen Dampfabscheidungssystem aufzunehmen;

mindestens ein Gasinjektionssystem (7), das Wasserstoffgas, einen Halbleitervorläufer und ein Dotierelement in die Vakuumkammer injizieren kann, wobei das Gasinjektionssystem (7) das Wasserstoffgas mit konstantem Durchfluss injizieren kann; und

das Dotierstoffelement unter konstantem Fluss in den Reaktor (1) und den Halbleitervorläufer unter gepulstem Fluss injizieren;

oder

Injizieren sowohl des Dotierstoffelements als auch des Halbleitervorläufers unter Pulsflussrate, wobei die Pulsinjektion des Dotierstoffelements und des Halbleitervorläufers abwechselnd ist; und wobei der Reaktor ferner umfasst:

ein Pumpsystem (8), das die Gase aus der Reaktionskammer (2) evakuieren kann; und

Gasaktivierungssystem (6) konfiguriert, um die durch das Gasinjektionssystem (7) eingebrachten Gase zu aktivieren, um reaktive Spezies für das dotierte Halbleiterwachstum zu bilden.

9. Reaktor (1) nach Anspruch 8, wobei das Gasaktivierungssystem (6) ein Mikrowellenplasma-verstärkter chemischer Gasphasenabscheidungsreaktor ist.

10. Reaktor (1) nach Anspruch 8, wobei das Gasaktivierungssystem (6) ein chemischer Dampfabscheidungsreaktor mit heißem Filament ist.

11. Schicht aus phosphordotiertem Diamant, erhältlich durch das Verfahren nach einem der Ansprüche 1 bis 6, wobei die Phosphordotiermittelkonzentration höher als 220 Dotierelement / cm³ ist.

12. Verwendung der Schicht nach Anspruch 10 als Source oder Drain in einem Transistor oder einer Zwischenschicht zur Bildung eines ohmschen Kontakts in einer diamantbasierten Diode oder einem Transistor.

13. Elektrode, umfassend die Schicht nach Anspruch 11.

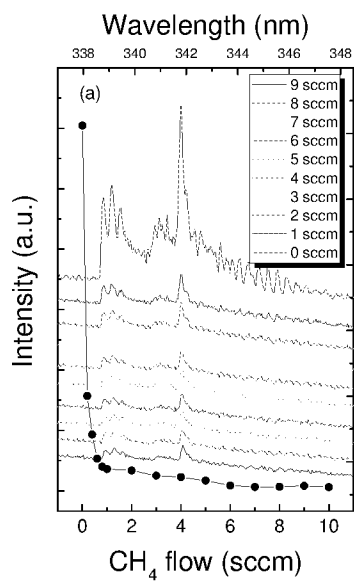


Fig. 1a

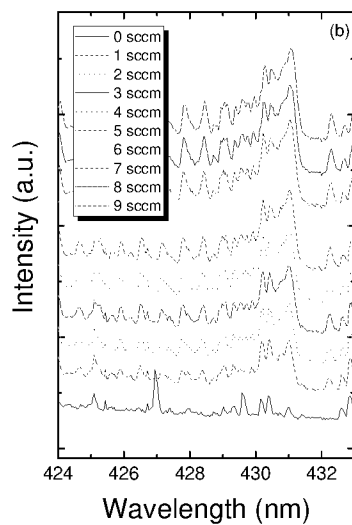


Fig. 1b

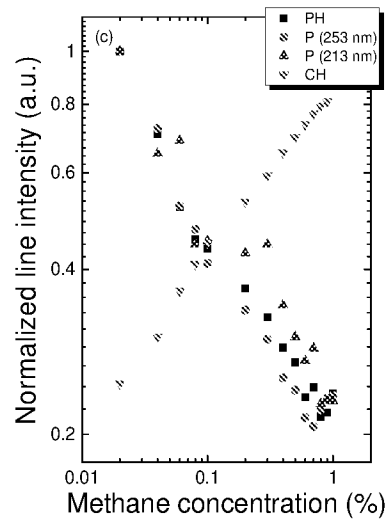


Fig. 1c

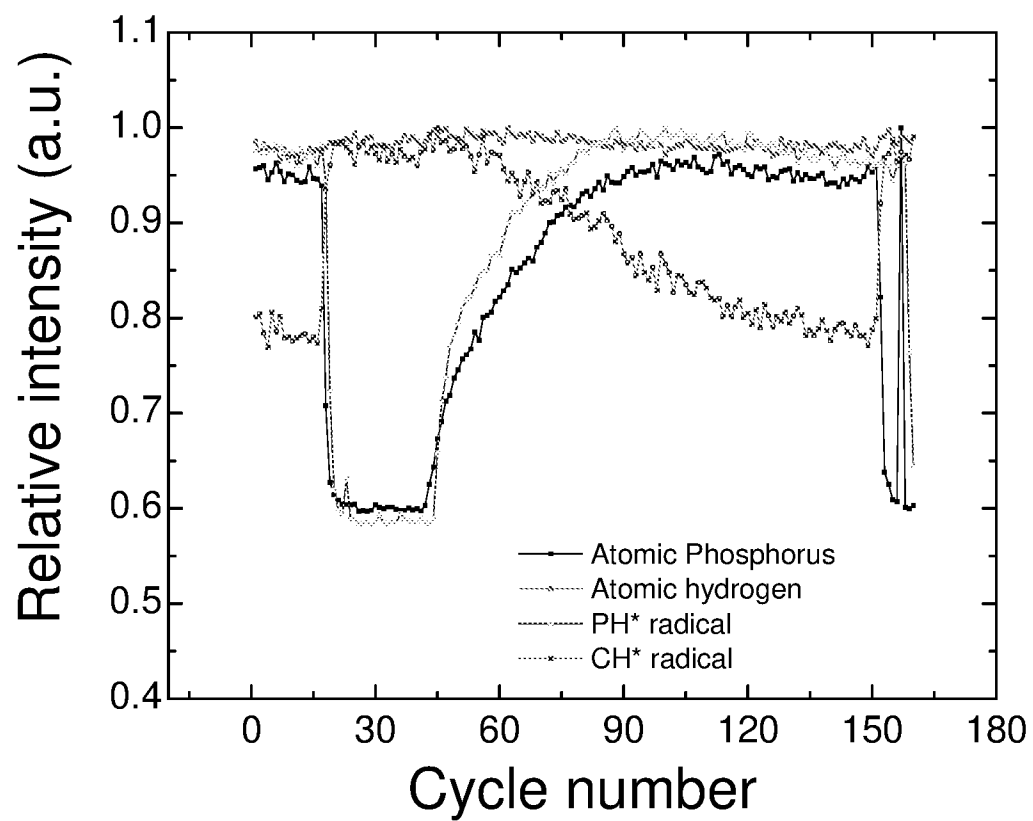
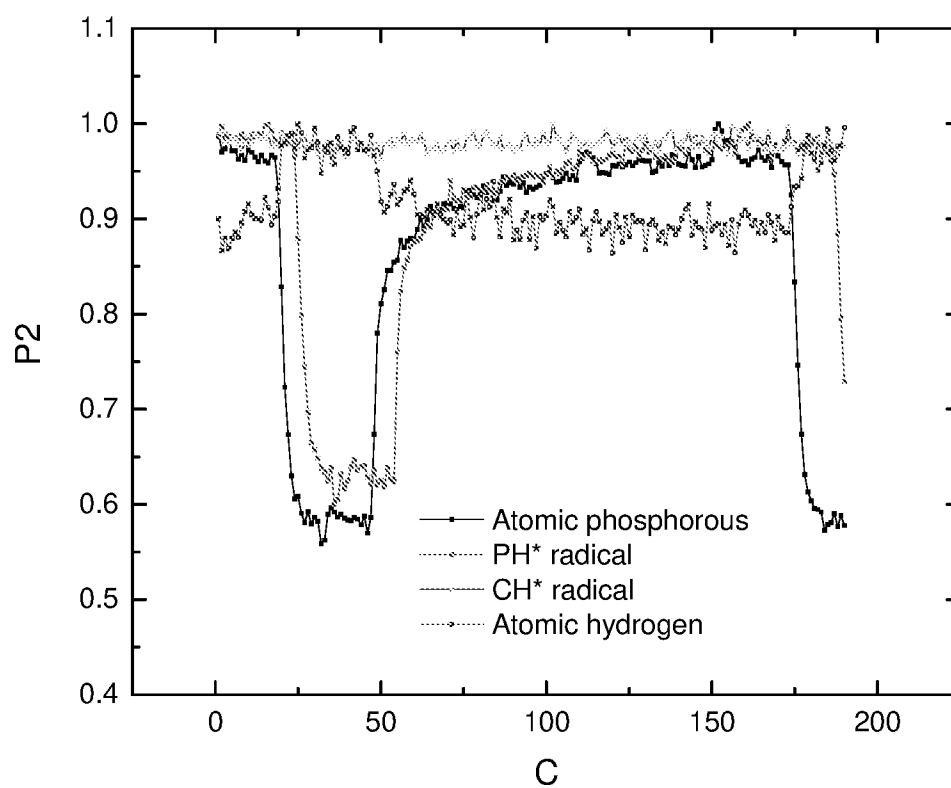


Fig. 2a

**Fig. 2b**

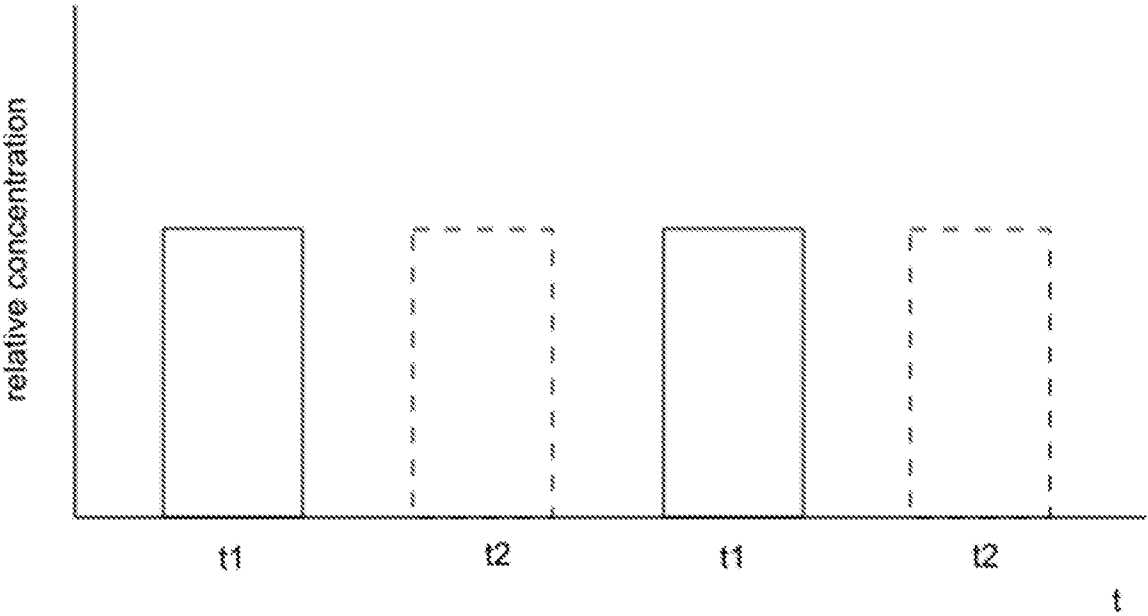


Fig. 2c

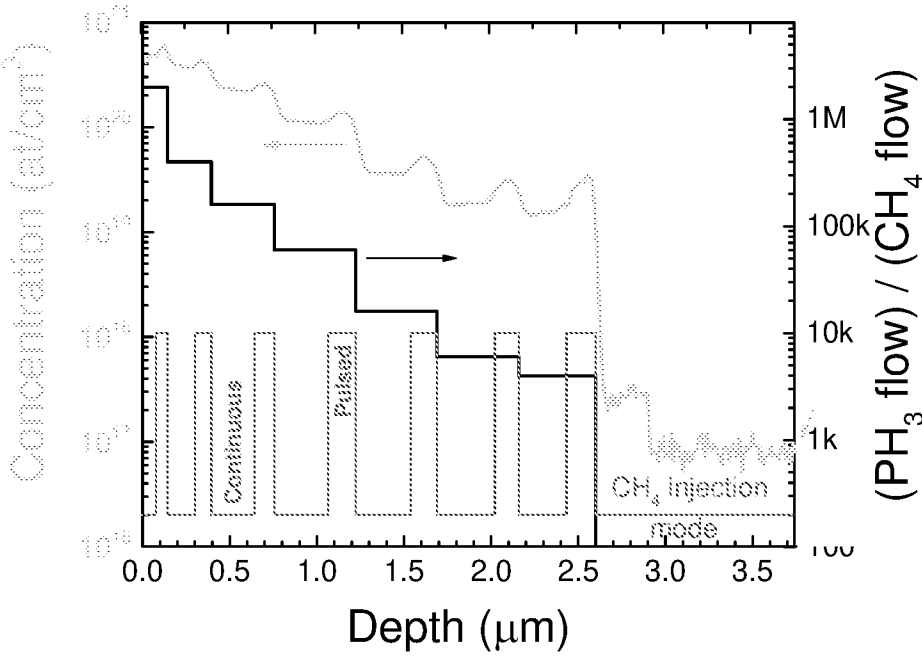


Fig. 3a

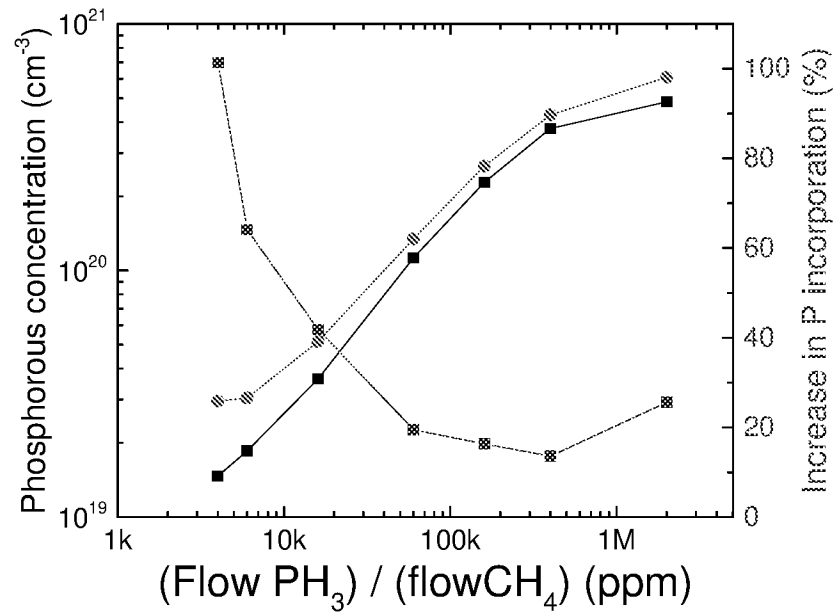


Fig. 3b

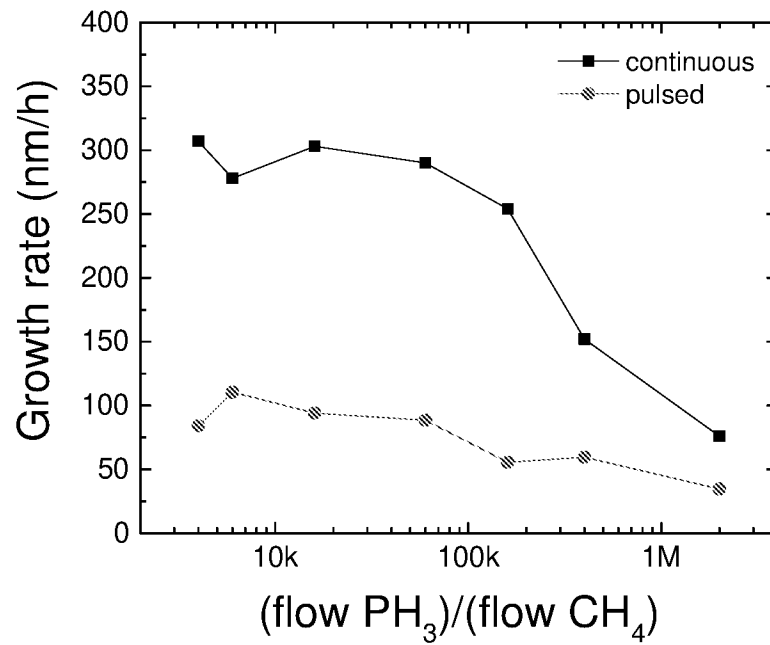


Fig. 4

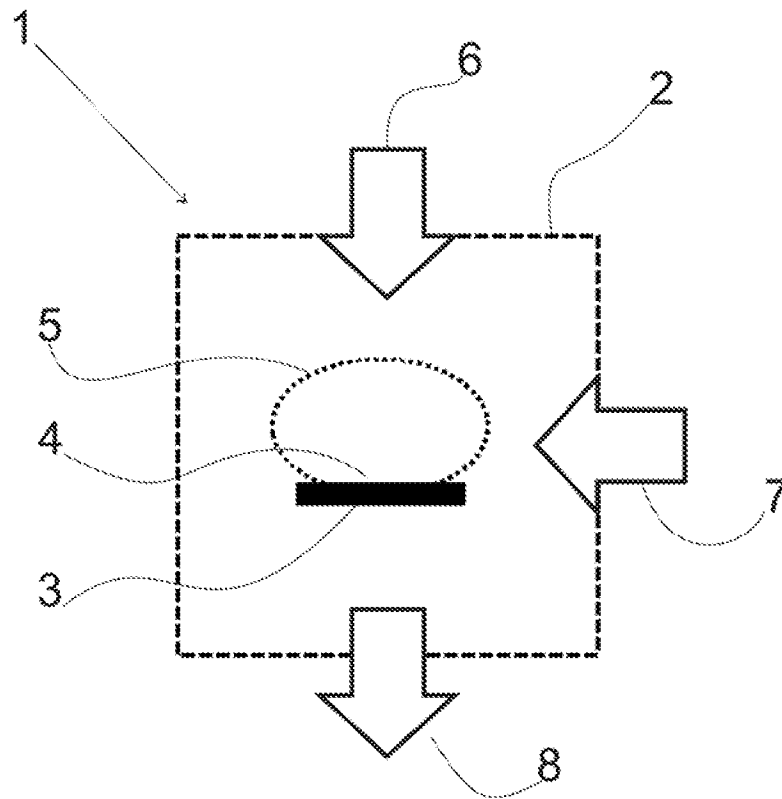


Fig. 5

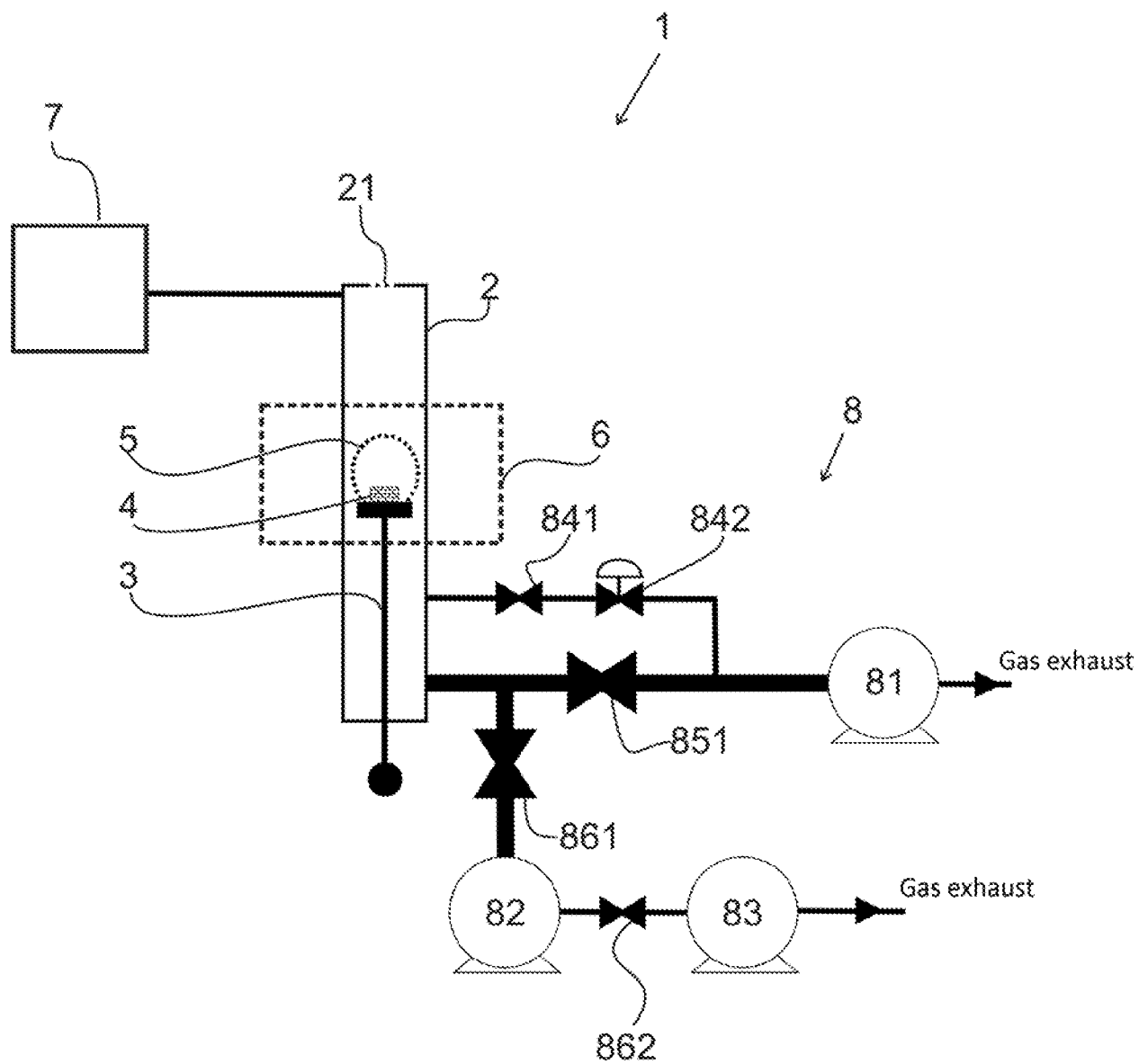


Fig. 6

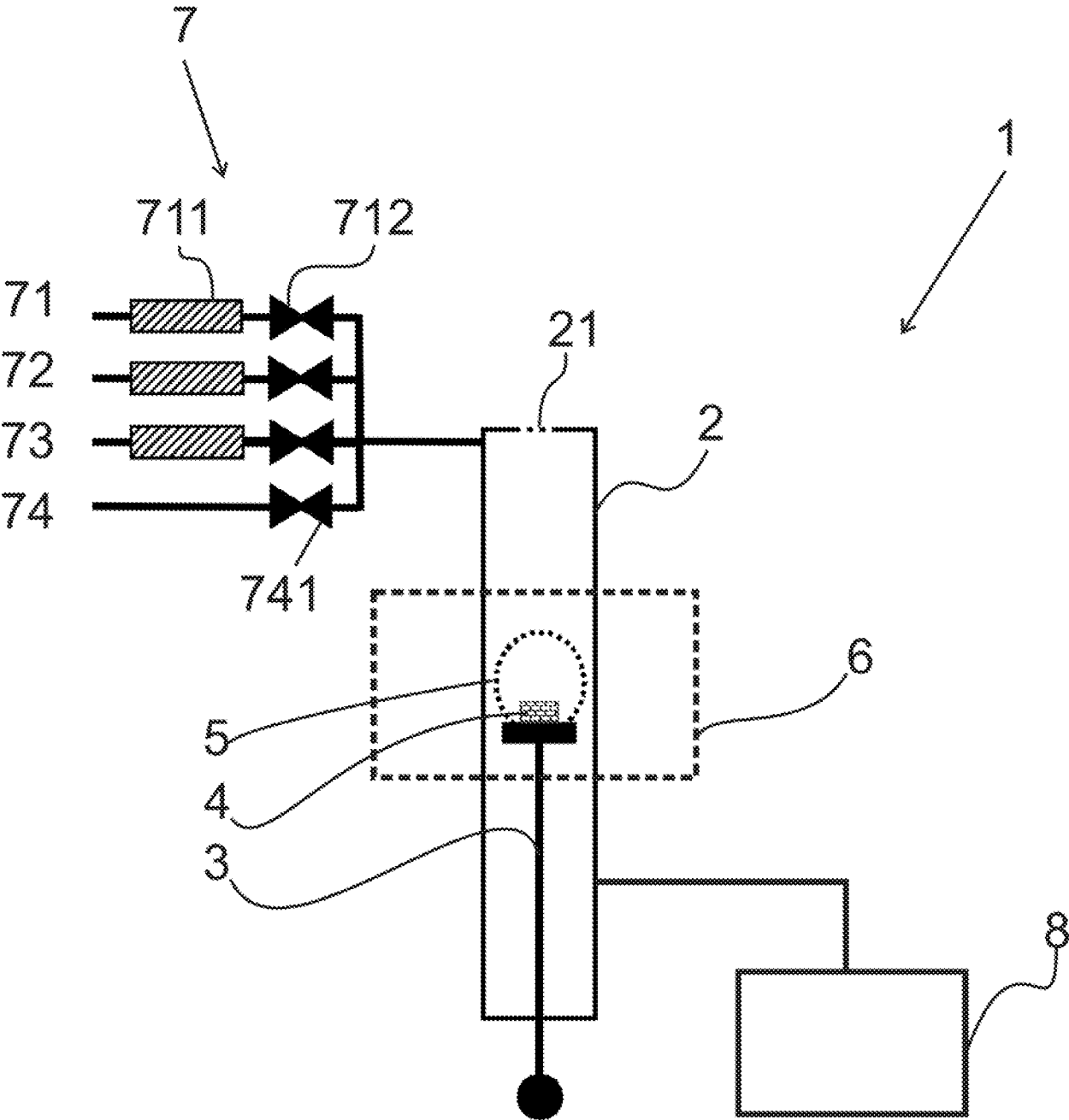


Fig. 7

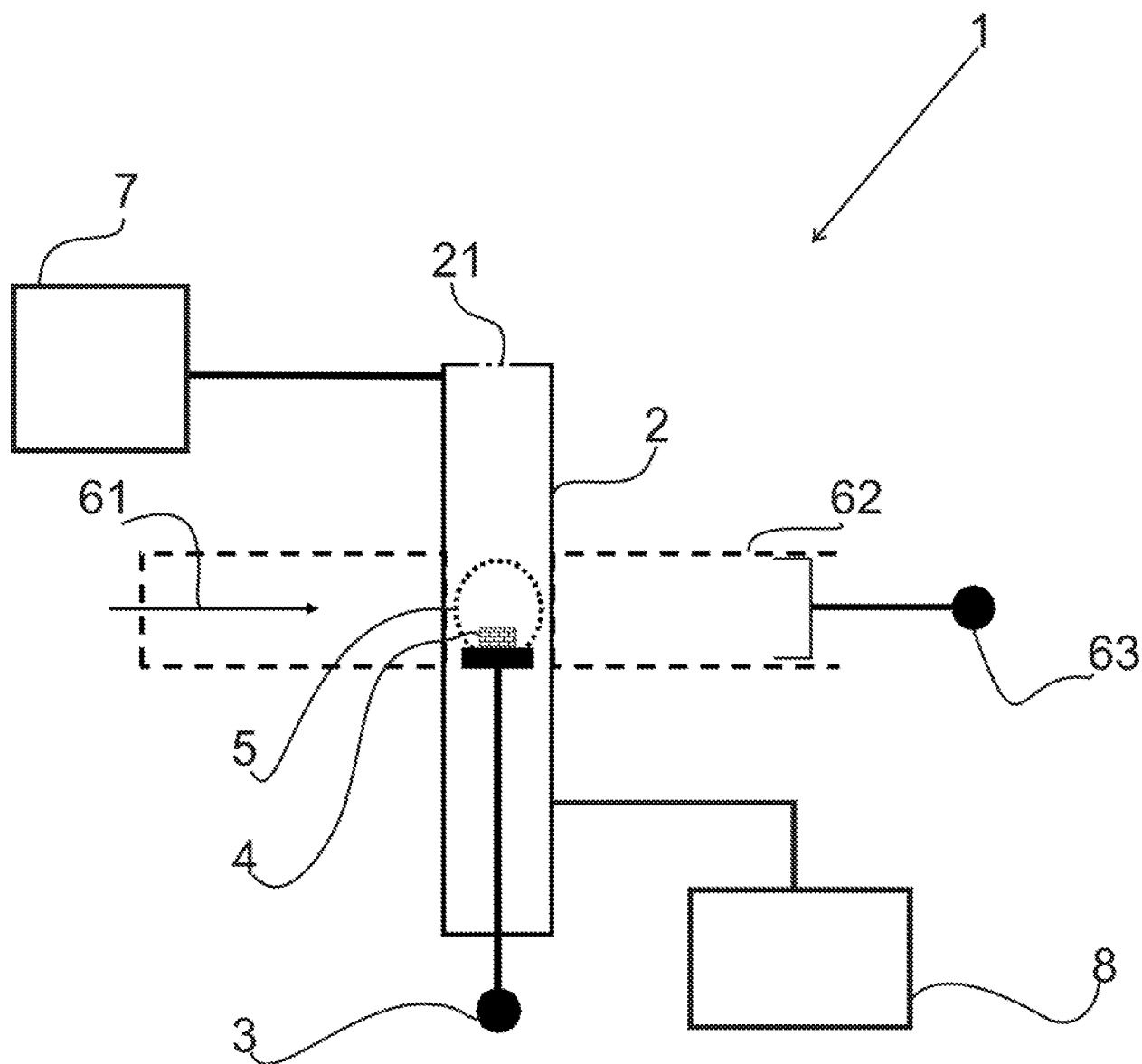


Fig. 8

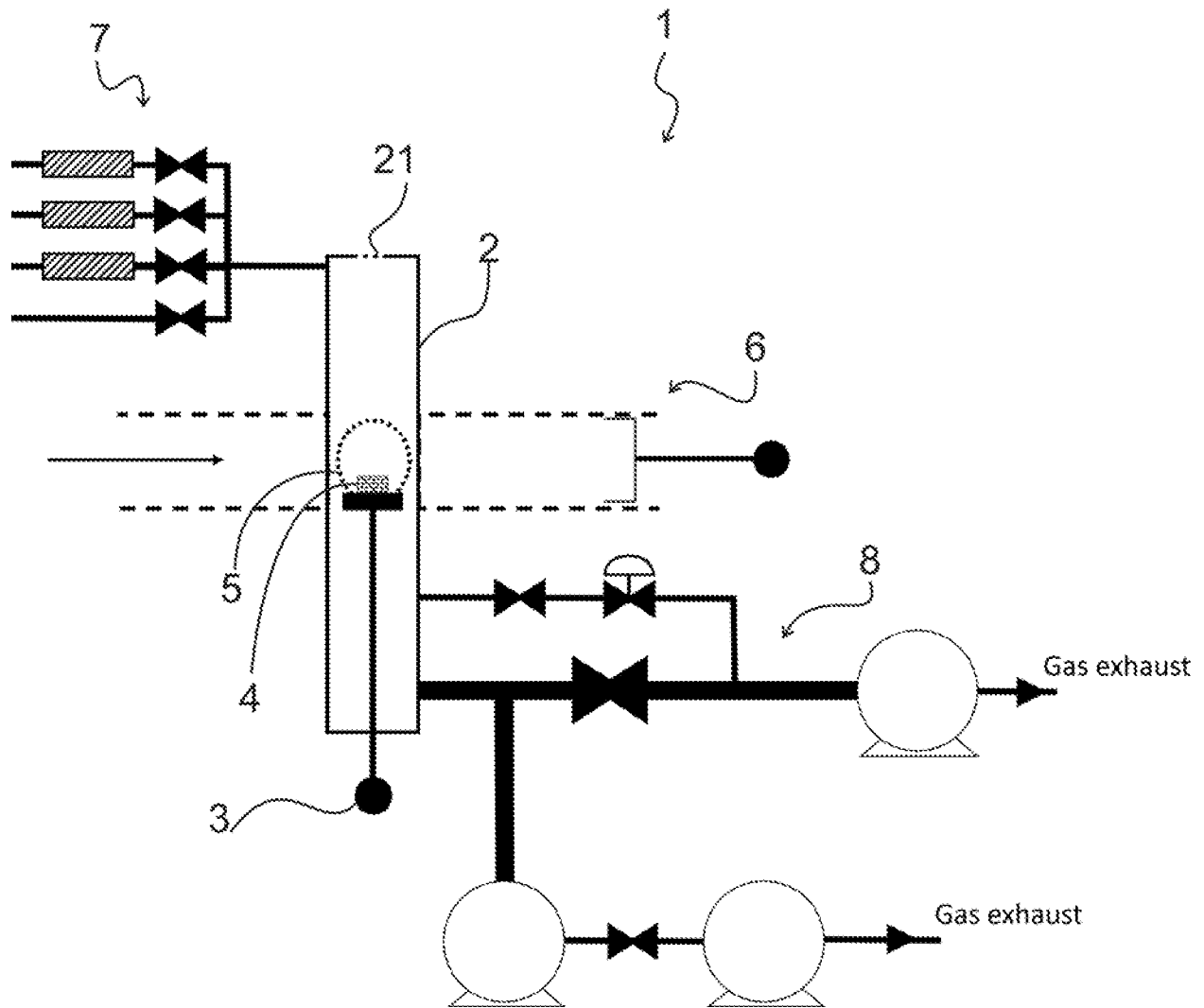


Fig. 9