



CHEMICAL VAPOUR DEPOSITION FROM A RADIATION-SENSITIVE PRECURSOR

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Publication date:
2017

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Stoot, A. C., & Camilli, L. (2017). IPC No. C23C 16/ 48 A I. CHEMICAL VAPOUR DEPOSITION FROM A RADIATION-SENSITIVE PRECURSOR (Patent No. WO2017153510.)

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(51) International Patent Classification:

C23C 16/26 (2006.01) C23C 16/455 (2006.01)
C23C 16/34 (2006.01) C23C 16/48 (2006.01)
C23C 16/44 (2006.01)

(21) International Application Number:

PCT/EP2017/055523

(22) International Filing Date:

9 March 2017 (09.03.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

16159305.8 9 March 2016 (09.03.2016) EP

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(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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, 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,

[Continued on next page]

(54) Title: CHEMICAL VAPOUR DEPOSITION FROM A RADIATION-SENSITIVE PRECURSOR

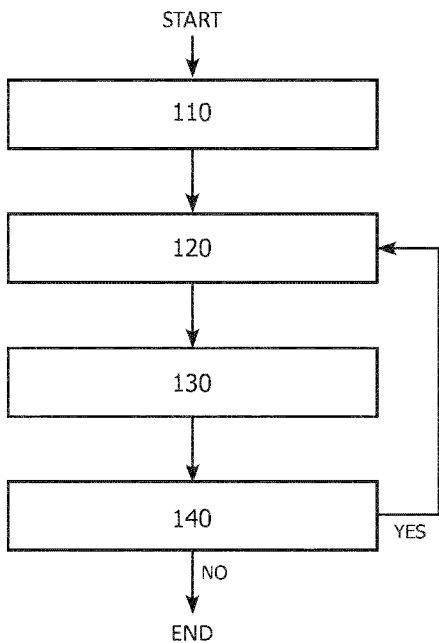


Fig. 1

(57) Abstract: The present invention relates in one aspect to a method of depositing a thin film on a substrate by chemical vapour deposition (CVD) from a radiation-sensitive precursor substance. The method comprises the steps of: (i) placing the substrate in a reaction chamber of a CVD system; (ii) heating the substrate, wherein heating includes the transmission of electromagnetic heating radiation from a controllable radiative heat source through the reaction chamber towards the substrate, wherein the radiative heat source is controlled to provide electromagnetic radiation as one or more heating pulses, each heating pulse followed by an idle period; (iii) during at least one of the idle periods, providing a pressure pulse of precursor substance inside the reaction chamber by feeding at least one precursor substance to the reaction chamber so as to establish a reaction partial pressure for thin film deposition from said pre-cursor substance onto the substrate and subsequently, after a dwell time, removing the precursor substance so as to reduce the partial pressure of the precursor substance in the reaction chamber to below a threshold; and (iv) repeating steps (ii) and (iii) until a desired thin film is formed. According to a further aspect, the invention relates to a chemical vapour deposition (CVD) system for depositing a thin film onto a substrate using precursor substances containing at least one radiation sensitive species.



SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG). **Published:**

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

Chemical Vapour Deposition from a Radiation-Sensitive Precursor

The present invention relates in one aspect to a method and system for depositing a thin film on a substrate by chemical vapour deposition (CVD) from a radiation-sensitive precursor. In a more specific aspect, the invention relates to a method and system for depositing a thin film on a substrate by rapid thermal chemical vapour deposition (RT-CVD) from a radiation-sensitive precursor.

BACKGROUND OF THE INVENTION

Chemical Vapour Deposition (CVD) is a thin film deposition technique that is widely used in all kinds of industrial applications including semiconductor industry, for example for the fabrication of electronic devices, photovoltaic elements, or functional coatings. CVD is particularly useful for the deposition of extremely thin layers of material, with atomic layer precision. Furthermore, CVD is highly scalable, and therefore compatible with high throughput commercial production lines.

During the CVD process, a precursor substance is introduced into a reaction chamber of a CVD system. The precursor substance may be a composition of several species or the precursor substance may be essentially a single species apart from impurities. At least during a CVD deposition process the precursor substance, which is present inside the reaction chamber, is in its vapour phase from which a thin film is then deposited/grown onto a substrate when appropriate catalytic conditions for deposition/growth are provided.

In the recent years, a whole new class of new materials with unique optical and electronic properties has evolved towards their application in industrial application. This new class of materials is two-dimensional, or at least quasi-two-dimensional, in nature, and includes most prominent materials, such as graphene and hexagonal boron nitride (h-BN). Very often, the commercial viability of new materials for e.g. the electronics industry is gauged against the feasibility of their integration with high throughput industrial production processes. For that reason the handling and production by CVD of thin films made from such two-dimensional materials has been the subject of numerous studies. However, an unresolved issue is the incompatibility of certain precursor substances commonly used for depositing these thin films with

the radiative heating techniques often employed in an industrial environment. The reason for this incompatibility is the sensitivity of these precursor substances to the heating radiation, which may cause dissociation of at least some of the molecules species of these precursor substances and may stimulate the collateral deposition of contaminants in the CVD-system. This entails frequent downtime and immense cost for maintenance and repair of the CVD system, which is unacceptable on all scales for both research and industrial production.

In fact, the same issue is not only relevant for the formation of the above-mentioned new class of two-dimensional materials, but is also most relevant for the CVD-deposition of any kind of thin film from a precursor substance comprising radiation sensitive species.

Therefore, there is a need for an improved CVD deposition technique with radiative heating that allows for the use of radiation sensitive precursor substances that overcomes at least some of the disadvantages mentioned above.

SUMMARY OF THE INVENTION

According to one aspect, the object of the invention is achieved by a method for depositing a thin film by chemical vapour deposition (CVD) according to the attached claims and the description below. According to a further aspect, the object of the invention is also achieved by a CVD-system for the deposition of thin films according to the attached claims and the description below.

According to a particular aspect, the method and system is for depositing a thin film onto a substrate by CVD including radiative heating means using at least one radiation sensitive precursor substance susceptible to dissociate when exposed to electromagnetic heating radiation applied in the CVD system for heating purposes. According to a preferred aspect, the CVD is a so-called Rapid Thermal Chemical Vapour Deposition (RT-CVD) system using rapid radiative heating, such as provided by flash lamps primarily emitting in the infrared spectral band.

A first aspect of the invention relates to a method of depositing a thin film on a substrate by chemical vapour deposition (CVD) from a radiation-sensitive precursor

substance, the method comprising the steps of: (i) placing the substrate in a reaction chamber of a CVD system; (ii) heating the substrate, wherein heating includes the transmission of electromagnetic heating radiation from a radiative heat source through the reaction chamber towards the substrate, wherein the radiative heat source is controlled to provide electromagnetic radiation as one or more heating pulses where the radiative heat source is in an ON-state, each heating pulse being followed by an idle period where the radiative heat source is in an OFF-state; (iii) during at least one of the idle periods where the radiative heat source is in the OFF-state, providing a pressure pulse of precursor substance inside the reaction chamber by feeding at least one precursor substance to the reaction chamber so as to establish a reaction partial pressure for thin film deposition from said precursor substance onto the substrate and subsequently, after a dwell time, removing the precursor substance so as to reduce the partial pressure of the precursor substance in the reaction chamber to below a threshold; and (iv) repeating steps (ii) and (iii) until a desired thin film is formed.

Advantageously, the method is for depositing a thin film on a substrate by rapid thermal chemical vapour deposition (RT-CVD), the substrate being placed in a reaction chamber of an RT-CVD system.

More particularly, the method of depositing a thin film on a substrate by means of CVD employs one or more precursor substances containing at least one radiation sensitive species.

Accordingly, the precursor substance comprises molecules that are radiation sensitive by having absorption resonances/bands within the spectral range of the electromagnetic radiation employed for substrate heating. For example, the radiation sensitive molecules may exhibit prominent absorption in the infrared part of the electromagnetic spectrum, i.e. said molecules are infrared-active. When exposed to the heating radiation, the radiation sensitive molecules absorb at least at some wavelengths of the electromagnetic radiation provided by the radiative heat source. When exposed to strong intensities, the radiation sensitive molecules are susceptible of dissociation by absorption of electromagnetic radiation energy, and are further susceptible of being activated for deposition by the electromagnetic radiation.

As used herein, the term 'radiation sensitive' denotes a property of precursor substances or species having molecules with vibrational modes to which electromagnetic radiation can couple in an effective manner. That is, a radiation sensitive precursor substance or species comprises molecules with vibrational modes associated with a change in dipole moment when these vibrational modes are activated. A particularly relevant form of radiation sensitivity is in the following referred to as "infrared active", wherein electromagnetic radiation in the infrared spectral band can effectively couple, in particular resonantly couple, to one or more vibrational modes of the species concerned. Most critically, the radiation sensitivity may result in dissociation of the molecules, possibly further reactions forming larger molecules, and/or the radiation sensitivity may induce deposition of contaminants derived from the radiation sensitive precursor or species depending on the stability of the particular molecules and the radiative intensity employed. Infrared active molecules can be observed using IR-spectroscopy. These typically comprise, but are not limited to, aromatic molecules. As mentioned, most critical are molecules that are susceptible/prone to dissociate easily in the electromagnetic radiation field applied in the reaction chamber for heating purposes, such as infrared radiation. Examples for critically infrared active species include, but are not limited to Borazine, Benzene, Coronene, Ethanol, and Benzoic acid.

A substrate is placed on a substrate holder inside the reaction chamber of a CVD system, wherein the substrate in one way or another is in thermal contact with the substrate holder, typically by thermal conduction. The substrate is typically heated in order to create adequate conditions for obtaining a desired thin film, such as appropriate catalytic conditions for atomic layer deposition or for a two-dimensional or quasi-two-dimensional crystal growth on the substrate surface. Here, heating involves the radiative transfer of heating energy from a radiative heat source through the reaction chamber towards the substrate. The radiative heating may occur directly by absorption in the substrate, and/or indirectly, e.g. by absorption in the substrate holder and subsequent conductive heat transfer from the substrate holder to the substrate.

Advantageously according to some embodiments, the substrate is in thermally conductive contact with a dedicated heat reservoir designed for temporarily storing heat energy so as to add thermal inertia to the substrate, thereby reducing temperature fluctuations of the substrate. The heat reservoir may be charged by absorption of heat either from the substrate or directly from the applied heating radiation. Accordingly, the heat reservoir may also supply/return heat to the substrate. The heat-reservoir may be an integrated element of the substrate holder, and/or may be a separate component, which may further be in thermally conductive contact with the substrate holder.

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As mentioned above, heating of the substrate includes the transmission of electromagnetic heating radiation from a controllable radiative heat source through the reaction chamber towards the substrate. Advantageously, the heating radiation or at least a major part thereof is radiation within the infrared spectral band. The INFRARED spectral band includes electromagnetic radiation in the wavelength ranges just above the visible region from at about 700nm (430 THz), up to about 1mm (300 GHz), and may be sub-divided in the near infrared region of up to 3-5 μ m, the mid infrared region from 3-5 μ m up to about 20-50 μ m, and the far infrared region for wavelengths above 20-50 μ m. Typically, for infrared active molecules, the most relevant vibrational modes have frequencies coupling to electromagnetic radiation in the mid infrared region, e.g. at wave numbers between 4000–400 cm^{-1} .

20

The substrate is heated using a controllable radiative heat source that is configured for controlled heating of the substrate. The radiative heat source is controlled to provide the heating radiation in the form of pulses. Each heating pulse is followed by an idle period separating the heating pulse from the next heating pulse. In a typical set-up, a rapid thermal chemical vapour deposition (RT-CVD) system is used, wherein said RT-CVD system comprises infrared lamps as radiative heat source, wherein the infrared lamps can be switched like flash lamps. Further, the lamps are preferably powerful to ensure a rapid substrate heating. The radiative heat source may be controllable to be switched between an ON-state and an OFF-state. In the ON-state, the heat source emits electromagnetic radiation above a given threshold intensity and within a given spectral band. In the OFF-state, the heat source does not emit electromagnetic heating radiation, or is at least below a given threshold intensity

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where the radiation may be considered to be switched off. A heating pulse lasts from an instance of switching the radiative heat source to the ON-state to a subsequent (the next) instance of switching the radiative heat source to the OFF-state. The transfer of heat to the substrate, which is arranged on a substrate support inside the reaction chamber, includes the radiative transmission of heating energy in or through the reaction chamber of the CVD system. As mentioned above, the application of heating radiation either directly heats the substrate, e.g. on the surface on which growth is to be performed, or indirectly heats the substrate via the intermediate of a radiation absorber that passes the absorbed heat on to the substrate through further heat transfer mechanisms, typically including heat conduction, from the radiation absorber to the substrate. The radiation absorber may include the substrate support and/or a heat reservoir element.

In addition to the substrate heating being effected by radiative pulses, the precursor substances are also supplied to the CVD-reactor in pulses here referred to as pressure pulses. The pressure pulses may be provided in any suitable manner for controlling the partial pressure of process gases/vapours inside the reaction chamber of a CVD system. Typically, this involves a gas handling system for feeding and exhausting process gases/vapours to and from the reaction chamber. Feed and exhaust of the gas handling system are connected to the reaction chamber and are controlled in combination to provide a partial pressure of precursor substance in the reaction chamber that is sufficiently high to achieve a desired thin film deposition or growth during a given dwell time. The given dwell time may be used to characterize the length of the pulse, and may be fulfilled e.g. by requiring a partial pressure of the process substance exceeding a certain threshold / minimum value/level. The pressure pulse starts when the partial pressure is increased above a pre-determined first threshold, and the pressure pulse ends when the partial pressure drops below a pre-determined second threshold. Advantageously according to some embodiments, the first and second thresholds are chosen the same.

A given pressure pulse is followed by a period of time with a low partial pressure of the corresponding precursor substance as compared to the partial pressure during the pressure pulse, before the partial pressure is increased for a subsequent pressure pulse to be formed. More particularly, a low partial pressure of the precursor

substance is characterized by a partial pressure below a predetermined threshold. Subsequent pressure pulses may be formed by the same or different precursor substances, depending on the thin film layers to be grown.

5 The pressure pulses are each time applied after a heating pulse and during an idle period separating subsequent heating pulses. Accordingly, the pulses of heating radiation are applied during periods of low partial pressure of at least any of the precursor substances sensitive to the heating radiation applied. The pressure pulses and the radiative pulses are therefore separated in time. Thereby, it is achieved that
10 the precursor substances are not, at least at the peak of their partial pressure in the reaction chamber, exposed to electromagnetic radiation that otherwise would lead to a prohibitive level of collateral formation of contaminant deposits throughout the CVD system, and in particular inside the reaction chamber. It thus becomes possible to design a process for the deposition of a thin film by CVD using radiative heating,
15 where it is safe to use radiation sensitive precursors, in particular precursor substances including so-called infrared active species.

The two steps of (a) applying a radiative heating pulse to heat the substrate, followed by an idle period, and (b) during the idle period providing a pressure pulse of
20 pre-cursor substance inside the reaction chamber are performed at least once in this sequence. Most preferably, the sequence of these two steps is repeated at least once, wherein a typical process for forming a desired thin film includes a plurality of two, three or more repetitions.

25 The method thus implements a combination of pulsed heating radiation and pulsed precursor substance supply, wherein the heating pulses and the pressure pulses are separated in time. The method has the advantage that it effectively separates the application of heating radiation from the presence of radiation sensitive precursor substances, such as infrared active precursor substances, inside the reaction
30 chamber at a critical level. Thereby a process for the deposition of an arbitrary thin film may be designed without concern of contamination caused by the use of radiation sensitive precursor substances. How critical an actual level is, may depend on the particularities of a given system, the sensitivity of the precursor substance to the heating radiation, and the actual intensities employed. However, a suitable sub-

critical level / regime of a partial pressure of the radiation sensitive precursor substance may for a given process design be determined by routine experimentation, e.g. varying the partial pressure up to which radiative heating pulses are applied and inspecting the CVD chamber for collateral deposition of contaminants derived from the corresponding precursor substances. A safe process may then be achieved by setting a maximum level below which the partial pressure for a given radiation sensitive precursor substance has to be before a radiative heating pulse may be applied.

Further according to one embodiment of the method the radiation sensitive precursor substance comprises one or more infrared-active species. The radiation sensitive precursor substance may be a mixture, where at least one species is infrared active. Alternatively, the radiation sensitive precursor substance may be of a single species, which is infrared active. As mentioned above, due to the timed separation of heating radiation pulses and precursor substance partial pressure pulses, a process for the deposition of an arbitrary thin film may be designed without concern of contamination caused by the use of radiation sensitive species in a precursor substance.

Further according to one embodiment of the method the precursor substance comprises one or more species selected from the group of Borazine, Benzene, Coronene, Ethanol, and Benzoic acid. Further advantageously, the precursor substance is one of Borazine, Benzene, Coronene, Ethanol, and Benzoic acid. These are examples of species that are infrared active, but that are particularly useful as precursor substances for forming e.g. graphene or h-BN thin films.

Further according to one embodiment of the method a first pressure pulse comprises a first precursor substance composition and a second pressure pulse comprises a second precursor substance composition, wherein the first and second precursor substance compositions are different from each other. Preferably the second precursor substance composition comprises at least one species that is different from the species contained in the first precursor substance composition. Thereby, it is possible to design a process for the production of heterostructures by CVD using radiative heating in combination with at least one radiation sensitive precursor substance.

Advantageously according to one embodiment of the method the precursor substance composition of different pressure pulses is different from each other.

- 5 Further according to one embodiment of the method the precursor substance composition of different pressure pulses is alternated between two distinct compositions. Thereby, a process of producing heterostructures with periodically alternating materials may be designed.
- 10 Further according to one embodiment of the method the dwell time of the precursor substance in the pressure pulses is less than 500s, alternatively less than 200s, alternatively less than 150s, alternatively less than 100s, alternatively less than 50s, or even less than 10s. Preferably, a minimum dwell time of at least 1s is applied. A longer pressure pulse applied during a heating idle time results in a larger thermal drift of the substrate during thin film formation as compared to a shorter pressure pulse. The effect of the thermal drift on the actual substrate temperature may be reduced by adding a thermal reservoir thermally coupled to the substrate, which will counteract the decrease in substrate temperature occurring in the absence of heating radiation.
- 15
- 20 Advantageously according to some embodiments, the dwell time has a predetermined fixed value, preferably within the above-mentioned ranges.
- Further advantageously, a dwell time for a precursor substance may be determined by the substrate temperature, wherein the pressure pulse is terminated when a substrate temperature falls below a predetermined substrate temperature threshold, such as a minimum temperature for catalytic growth of a given thin film.
- 25
- 30 Further according to one embodiment of the method the reaction partial pressure for thin film deposition is at least 1 mbar, at least 10 mbar, preferably at least 100 mbar, or even 1000 mbar. A higher partial pressure of precursor substance during the pressure pulse may e.g. be useful for high throughput production applications. A relatively high partial pressure of radiation sensitive precursor substance becomes

possible with the present invention, due to the separation of radiation and pressure pulses as detailed above.

5 Further according to one embodiment of the method the threshold for terminating a pressure pulse by removing the precursor substance is reached when the partial pressure of the precursor substance is below 1mbar, or below 0.1mbar, or even below 0.01mbar. While details may depend on the particular details of the CVD system as well as of the particular growth conditions employed for a particular thin film deposition process it may generally be stated that a reduction of the partial pressure
10 of a radiation sensitive precursor substance with respect to the reaction partial pressure for thin film deposition before a new radiative heating pulse is applied reduces the contamination of the reaction chamber and other exposed parts of the CVD system employed. A reduction below the above-mentioned threshold values will typically reduce the contamination to a practical level allowing for repetitive operation of
15 the CVD system without a significant contamination taking place. A process design goal of lowering the partial pressure as much as possible to lower service, maintenance and repair cost will in practice typically be balanced against the effort, time, and/or equipment cost for achieving that lower pressure.

20 Further according to one embodiment of the method the thin film comprises hexagonal boron nitride (h-BN), graphene, and/or heterostructures thereof. Using the method of the invention a thin film structure including these materials may be produced from infrared active precursor substances, such as those mentioned above. Thereby an economically viable and effective process for the formation of such thin
25 films may be designed.

Further according to one embodiment of the method the substrate is a metal substrate.

30 Further according to one embodiment of the method the substrate is made of nickel, a nickel alloy, copper, a copper alloy, platinum, a platinum alloy, iridium, an iridium alloy, ruthenium, a ruthenium alloy, silicon carbide, or stainless steel.

Further according to one embodiment of the method a spectral distribution of the electromagnetic radiation generated by the radiative heat source has its maximum in the infrared (IR) spectral band.

- 5 Further according to one embodiment of the method the radiative heat source comprises flash-lamps emitting heating radiation in the infrared (IR) spectral band.

While the detailed values will depend on the thermal design of the particular set-up, useful ranges for heating pulse duration may include pulse durations of less than
10 500s, alternatively less than 200s, alternatively less than 150s, alternatively less than 100s, alternatively less than 50s, or even less than 10s. Preferably, a minimum radiation pulse time of at least 1s is applied, wherein idle times between pulses exceed the length of the corresponding pressure pulses.

15 Advantageously according to a particularly preferred embodiment of the method, the CVD process is a rapid thermal CVD (RT-CVD) process, which includes direct or indirect heating of the substrate by means of infrared radiation. Further advantageously according to some embodiments, the spectral distribution of the electromagnetic radiation generated by the radiative heat source has a maximum in the
20 infrared spectral band. Further advantageously according to some embodiments, the radiative heat source has a major part of its spectrally integrated emission power in the infrared spectral band. Further advantageously, embodiments are directed to include the use of heat sources configured for use with an operational waveband over any subset of the infrared spectral band.

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Preferably, according to some embodiments, the infrared radiation for heating the substrate is generated by means of high-power radiative heat sources, such as high power lamps emitting in the infrared (IR) spectral band. Preferably, these high power lamps are flash-lamps adapted for rapid switching between an ON-state and an
30 OFF-state. One of the major advantages of using such radiative heat sources, and in particular of the fast switching type, is the efficient and fast, yet well-controlled heating that can be achieved by this heating technique.

Further according to some embodiments of the method, placing the substrate in the reaction chamber of the CVD system in step (i) includes bringing the substrate in thermally conductive contact with a heat reservoir for temporarily storing heat energy so as to add thermal inertia to the substrate. The advantages of different embodiments including a dedicated heat reservoir have already been discussed above.

Further according to some embodiments, the method further comprises controlling a rate of change in substrate temperature during the pressure pulse of step (iii) to below a predetermined value selected from 50 K/s, 20 K/s, 10 K/s, or 5 K/s. Advantageously, the rate of change may be controlled by providing a dedicated heat reservoir in thermally conductive contact with the substrate as described above. Further, the thermal conductivity of the thermally conductive contact between the substrate and the heat reservoir may be varied. Furthermore a background heating may be applied to the substrate to reduce the difference between substrate and the thermal environment seen by the substrate. However, the means for controlling a rate of change of the substrate temperature should not include use of electromagnetic heating radiation that may cause dissociation and/or otherwise activation for deposition of the radiation sensitive precursor substance. By switching off the heating radiation during the partial pressure pulse of the radiation sensitive precursor substance the substrate temperature during the pressure pulse, and thus the growth conditions for depositing the thin film change as a function of time. By limiting the rate of change of the substrate temperature during the pressure pulse an excessive change of these growth conditions is avoided. Furthermore the overshoot of substrate temperature that may be required to achieve suitable growth conditions is reduced.

More generally, the method and system according to the present invention allows for controlling a change in substrate temperature during the pressure pulse and thus during the time periods where thin film formation may take place, thereby providing an additional handle to the designer of a thin film deposition process.

Further according to some embodiments of the method, the precursor substance comprises at least one component of molecules susceptible to dissociate when exposed to the electromagnetic heating radiation.

According to a second aspect of the invention a chemical vapour deposition (CVD) system is provided, the system being configured for performing the method for depositing a thin film onto a substrate from electromagnetic radiation sensitive precursor substances according to any of the embodiments described herein.

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According to some embodiments of the invention, a rapid thermal chemical vapour deposition (RT-CVD) system for depositing a thin film onto a substrate is provided, the system comprising

- 10 - a reaction chamber comprising a substrate holder adapted for holding the substrate;
- a radiative heat source adapted for transmitting electromagnetic heating radiation through the reaction chamber towards the substrate holder or directly to the sample;
- 15 - a gas handling system comprising a precursor substance supply, feed and exhaust lines connected to the reaction chamber, respective feed and exhaust valves, and a pumping device, the gas handling system being configured for establishing inside the reaction chamber a reaction partial pressure for thin film deposition from said precursor substance onto the substrate, the gas handling system being further configured for exhausting precursor substance so as to reduce the partial pressure of the precursor substance inside the reaction chamber (below a pre-determined threshold); and
- 20 - a control unit configured for controlling the radiative heat source to provide the electromagnetic heating radiation as heating pulses where the radiative heat source is in an ON-state, separated by idle periods where the radiative heat source is in an OFF-state,
- 25 the control unit further being configured for controlling the gas handling system to feed and exhaust the precursor substance in a timed manner to establish the reaction partial pressure above a pre-determined threshold for a dwell time only during idle periods where the radiative heat source is in the OFF-state, i.e. between heating pulses where the radiative heat source is in the ON-state.
- 30

Advantageously according to some embodiments, the rapid thermal chemical vapour deposition (RT-CVD) system is adapted for depositing a thin film onto a sub-

strate using precursor substances containing at least one radiation sensitive species.

5 Further according to one embodiment of the rapid thermal chemical vapour deposition (RT-CVD) system, the radiative heat source is an infrared radiation source, such as comprising infrared heating lamps, said heating lamps preferably configured as flash lamps adapted for rapid thermal operation.

10 Further according to some embodiments, the RT-CVD system further comprises a heat reservoir adapted to be in thermally conductive contact with the substrate when the substrate is held by the substrate holder, wherein the heat reservoir is adapted the substrate is in thermally conductive contact with a dedicated heat reservoir designed for temporarily storing heat energy so as to add thermal inertia to the substrate.

15 Further according to some embodiments of the RT-CVD system, the precursor gas supply comprises a radiation sensitive precursor substance with at least one component having molecules susceptible to dissociate when exposed to the electromagnetic heating radiation from the radiative heat source.

20 Further according to some embodiments of the RT-CVD system, the precursor gas supply comprises one or more radiation sensitive precursor substances selected from Borazine, Benzene, Coronene, Ethanol, and Benzoic acid.

25 By these thin film deposition systems at least the same or at least analogue advantages are achieved as those discussed above with respect to embodiments of the method.

30 Advantageously according to some embodiments, the CVD system, or more particularly the RT-CVD system, is of the so-called cold wall type, where chamber walls defining the reaction chamber are at a temperature well below the reaction temperature during the growth process or even actively cooled to a temperature well below a reaction temperature for thin film deposition directly from the precursor substance.

Thereby, thermally activated collateral deposition of thin films from the precursor on the chamber walls is avoided.

Advantageously according to a further aspect, a control unit for a CVD system is provided, wherein the control unit is configured for controlling at least a radiative heating source and a gas handling system of the CVD system during thin film deposition in a programmed manner, including the following steps:

- (i) receiving a signal indicating that a substrate is provided ready for thin film deposition;
- 10 (ii) communicating a control signal to the radiative heating source to provide electromagnetic radiation as one or more heating pulses, each heating pulse being followed by an idle period;
- (iii) communicating a control signal to the gas handling system to feed and exhaust the precursor substance in a timed manner so as to establish inside a reaction chamber a reaction partial pressure above a pre-determined threshold for a dwell time during idle periods between heating pulses; and
- 15 (iv) initiating a repetition of steps (ii) and (iii) depending on a termination criterion.

20 Advantageously, the termination criterion in step (iv) can be implemented in any conceivable manner. Advantageously according to some embodiments, the termination criterion in step (iv) above is for checking if a pre-determined maximum number of repetition cycles has been performed, wherein repetition of steps (ii) and (iii) is initiated until the pre-determined maximum number repetition cycle has been

25 reached, and wherein thin film deposition is terminated when the pre-determined maximum number repetition cycle has been reached.

Advantageously according to some embodiments, the control unit is further configured for receiving an in-situ monitoring signal input, wherein the in-situ monitoring

30 signal corresponds to at least one measurable parameter characterising the thin film in-situ; and wherein a termination criterion for deciding in step (iv) on repeating steps (ii) and (iii) or terminating the thin film deposition process depends on that measurable parameter obtained in-situ, i.e. obtained directly during formation of the thin film in the reaction chamber of the CVD system. The measurable parameter

may be obtained using measurement devices adapted for determining a measurable parameter characterising the thin film in-situ.

Further advantageously, a control program for implementation in a control unit of a CVD system is provided, the control program being configured to perform the steps
5 for controlling the formation of a thin film on a substrate by CVD as described above.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention will be described in more detail in connection with the appended drawings, which show in
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Fig. 1 a diagram over a process flow for a method according to one embodiment of the invention,

15 Fig. 2 a schematic cross-sectional view of a reaction chamber of a CVD-system according to one embodiment,

Fig. 3 a schematic of a gas handling system for use in a CVD system according to one embodiment,

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Fig. 4 a composite plot with four different process parameters monitoring a thin film formation according to one example with a sequence of ten heating/pressure pulse cycles,

25 Figs. 5 a scanning electron micrograph of h-BN deposited on a Cu-substrate in a sequence of three heating/pressure pulse cycles using Borazine as a precursor substance; isolated hBN islands can be observed, as highlighted by the arrow

30 Fig. 6 a scanning electron micrograph of h-BN deposited on a Cu-substrate in a sequence of six heating/pressure pulse cycles using Borazine as a precursor substance, few holes in the h-BN film can be observed, as highlighted by the arrow

- Fig. 7 a scanning electron micrograph of full coverage h-BN film deposited on a Cu-substrate in a sequence of ten heating/pressure pulse cycles using Borazine as a precursor substance,
- 5 Fig. 8 a graph with Raman spectroscopy data obtained on an example of a thin film heterostructure prepared using a method according to one embodiment.

DETAILED DESCRIPTION

- 10 Fig. 1 shows a diagram over a process flow for a method according to one embodiment of the invention. When the process is started, in step 110 a suitable substrate is provided inside the reaction chamber of a CVD system in a condition ready for depositing a thin film thereon. The preparation of the substrate prior to step 110 may include e.g. polishing, cleaning, mounting onto a substrate holder, introducing the
- 15 substrate into a reaction chamber of the CVD system, further cleaning, pre-heating, and/or performing characterization, such as surface characterization, of the substrate as well as flushing and pumping on it. When the substrate is ready for thin film deposition, the process proceeds to step 120 of heating the substrate to a temperature as required to achieve catalytic conditions for the deposition/growth of the de-
- 20 sired thin film material on the substrate surface. Heating includes the transmission of electromagnetic heating radiation from a controllable radiative heat source through the reaction chamber towards the substrate, which is then either directly absorbed by the substrate or by an absorber surface in thermal contact with the substrate. In the former case, the substrate is directly heated by the electromagnetic radiation,
- 25 and in the latter case the electromagnetic radiation is just one link in a chain for transferring heat from the radiative heat source to the substrate. The chain may include further links, such as the absorption by an absorber, the heat conduction through the absorber and a further transfer across an interface from the absorber to the substrate, etc. In step 120, the radiative heat source is controlled to provide
- 30 electromagnetic radiation as one or more heating pulses, each heating pulse being followed by an idle period. During at least one of the idle periods of step 120, at least one pressure pulse with precursor substance is established inside the reaction chamber at a level corresponding to a desired reaction partial pressure. Typically, a single heating pulse is issued in step 120, followed by an idle period during which

step 130 is performed by forming a single partial pressure pulse of precursor substance. The pressure pulse of pre-cursor substance inside the reaction chamber is provided by feeding at least one precursor substance to the reaction chamber so as to establish a reaction partial pressure for thin film deposition from said precursor substance onto the substrate and subsequently, after a dwell time, removing the precursor substance so as to reduce the partial pressure of the precursor substance in the reaction chamber to below a threshold.

Since the precursor substance pulse is only introduced into the CVD reaction chamber during an idle time of the radiative heating, i.e. after the radiative heating is switched off, radiation sensitive precursor may be used for the thin film deposition without concern about radiation stimulated dissociation of the precursor substance and the formation of contaminants in the reaction chamber. The pressure pulse is terminated by removing the precursor substance before the radiative heating is switched on again. The term removing refers here to a reduction of the partial pressure of the precursor substance with respect to the reaction partial pressure level. Preferably, a threshold criterion for the removal of the precursor substance is defined, wherein the successful removal is achieved when the partial pressure of precursor substance in the reaction chamber is below a pre-determined threshold value. Preferably, the pre-determined threshold value is a value considered uncritical, in particular uncritical with respect to the radiation induced collateral formation of contaminants from the radiation sensitive precursor in the reaction chamber and further components of the CVD system.

Finally, in step 140, it is decided whether or not to repeat steps 120 and 130 in order to continue thin film deposition or to terminate thin film deposition depending on the fulfilment of a termination criterion. In the "YES" branch, the process returns to performing steps 120 and 130 again, wherein parameters of the procedures performed under steps 120 and 130 may be maintained identical or changed depending on the desired thin film deposition/growth. For example, it may be desired to grow the same material in pulsed sequences under identical conditions in order to achieve an increased or full surface coverage, or an increased thickness of the desired thin film, wherein a substrate temperature during deposition/growth in the idle periods is kept above a minimum temperature. Examples for such growth from identical repetition

cycles are given below with respect to Figs.4-7. Alternatively, it may be desired to vary the process parameters in steps 120 and/or 130 from one cycle to another cycle in order to achieve a different deposition/growth. For example, the precursor substance species supplied to the reaction chamber in step 130 may be changed from one cycle to another cycle in order to grow a heterostructure. An example of a heterostructure grown in such a manner is given below with reference to Fig.8. However, other parameters may be varied as well. Further, the two repetition modes may be combined in a modular way, in order to have one or more sequences of identical repetitions, in combination with repetitions where the one or more of the parameters controlled in steps 120 and/or 130 changes. Such parameters controlled in steps 120 and/or 130 may include, but are not limited to, heating power, heating pulse duration, idle period, reaction partial pressure, precursor substance species and/or composition, delays between heating pulses and pressure pulses, dwell time for precursor substance in the reaction chamber, and substrate temperature as determined by thermocouples and/or pyrometric measurements.

Fig. 1 may also be seen as a general flow-diagram of a control program that may be implemented in a control unit of a CVD system, wherein the control unit is configured for controlling at least the heating and precursor substance handling during thin film deposition in a programmed manner. In this case, step 110 corresponds to receiving a signal indicating that a substrate is provided ready for thin film deposition; step 120 corresponds to communicating a control signal to a radiative heating source to provide electromagnetic radiation as one or more heating pulses, each heating pulse being followed by an idle period; step 130 corresponds to communicating a control signal to a gas handling system to feed and exhaust the precursor substance in a timed manner to establish inside a reaction chamber a reaction partial pressure above a pre-determined threshold for a dwell time during idle periods between heating pulses; and step 140 corresponds to initiate a repetition of steps 120 and 130 depending on a termination criterion. The termination criterion in step 140 can be implemented in any conceivable manner. In a particular simple embodiment, the termination criterion in step 140 may be checking if a pre-determined number of repetition cycles have been performed. A more advanced embodiment may include determining a measurable parameter characterising the thin film in-situ, and formulating a termination criterion in step 140 depending on that measurable

parameter, i.e. deciding in step 140 on repeating steps 120 and 130 or terminating the thin film deposition process depending on the value determined for that measurable parameter.

5 Referring to Figs.2 and 3, an RT-CVD system 1 according to one embodiment is now described. Fig.2 shows schematically a cross-sectional view of a reaction chamber 10 and further parts of the RT-CVD system. A substrate 99 is placed inside the reaction chamber 10 on a substrate holder (not shown). The reaction chamber 10 is defined by side walls 11, top window 12, and bottom window 13, which is supported by the bottom wall 14. The wall portions may e.g. be made of stainless steel. 10 The bottom wall 14 comprises a vacuum port 15 for evacuating the chamber 10. The bottom wall 14 further comprises view ports 16 giving line of sight access to different locations on the sample, here shown for an edge view and a central view. The view ports 16 may be equipped with a pyrometer 17 for determining a substrate temperature at the different locations to which the view ports 16 give access. A temperature 15 of the substrate 99 may further be derived using thermocouples 18 probing different locations of the substrate 99, or at least of adjacent locations on a substrate holder that is in good thermal contact with the substrate 99. Gas or vapour may be fed to the reaction chamber 10 through an inlet 19 and the gas or vapour may be removed 20 e.g. through the vacuum port 15. The RT-CVD system 1 is further equipped with a radiative heat source 2, which is here an arrangement of infrared lamps 20, more particularly flash lamps configured for use with an operational waveband over any subset of the infrared spectral band, and adapted to provide heating radiation for heating the substrate 99. Fig.3 shows schematically a gas handling system connected to the reaction chamber 10. The gas handling system comprises sources 30 with a selection of different precursor substances that can be fed to the reaction chamber via feed lines 33, wherein the precursor substance flow can be precisely controlled by means of mass flow controllers 31, also labelled MFC in Fig.3. Instead 25 of a multitude of feed lines 33 being connected directly to the oven, a manifold with a gas selector valve (not shown) may be interposed between the mass flow controllers (31) and the reaction chamber (10). Thereby, the number of vacuum tight connections to be made to the reaction chamber may be reduced. The gas handling system may further comprise an outlet 34 and a vacuum pumping arrangement 35 for removal of any gas or vapour present in the reaction chamber 10. The gas han-

dling system 3 of the RT-CVD system 1 further comprises a nitrogen supply 36 that may be fed to the reaction chamber 10, e.g. for flushing and/or purging operations.

Fig. 4 shows a composite graph with an example of four different process parameters measured as a function of time during a pulsed deposition carried out by a method according to one embodiment of the invention. In the example shown, a sequence of ten essentially identical cycles is applied, each cycle comprising a heating pulse, followed by an idle period during which a pressure pulse of a precursor substance is applied. In this example, the precursor substance is Borazine. The result of this growth sequence is shown in Fig.7 below. Corresponding growth sequences are also used for obtaining the thin film deposition results shown in the micrographs of Fig.5 and Fig.6 – only with 3 and 6 cycles, respectively.

From top to bottom the composite graph shows in subgraph (a) a power readout representative of the radiative heating power supplied by the radiative heating source; in subgraph (b) a pyrometer readout representative of the substrate temperature; in subgraph (c) a mass flow controller readout representative of the precursor substance feed to the reaction chamber; and in subgraph (d) a pressure gauge readout representative of the pressure inside the reaction chamber, which here is the same as the partial pressure of the precursor substance, since only a single precursor species is fed to the reaction chamber. In case a mixture of substances comprising the precursor substance in a given mixing ratio is fed to the reaction chamber a value corresponding to the partial pressure may be derived accordingly from the same pressure readout.

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The subgraphs are synchronized with respect to each other on the same time axis. Up to about 300 s no heating power is applied and the substrate is roughly at room temperature. An initial heating pulse is applied between about 300s and 550s to bring the substrate up to a stabilized process temperature of about 1000 degrees Celsius; The extended period of stabilized temperature in the beginning may further serve as a heat treatment preparing the pristine substrate surface for thin film deposition. The broken lines are guides to the eye marking the same point in time for all subgraphs, each time the radiative heating power is switched off at the end of a radiative heating pulse. As soon as the radiative heating is switched off, precursor

substance is fed to the reaction chamber in a short pulse as seen in the mass flow controller readout of subgraph (c). As best seen in subgraph (d), the injection of the precursor substance results in a spike in the pressure readout and stabilizes at a desired reaction partial pressure for the precursor substance, here about 300 Pa.

5 The reaction partial pressure is maintained for a dwell time, here for about 80s, before the precursor substance is removed from the reaction chamber, e.g. by evacuating the reaction chamber to a low pressure level, here below about 30 Pa. using a pumping system connected to a vacuum port of the reaction chamber. Once the precursor substance is removed from the reaction chamber, the heating radiation
10 may be switched on again for a new heating pulse and a new cycle may begin. Here a sequence of ten cycles with a radiative heating pulse followed by an idle period during which a pressure pulse of precursor substance at a reaction partial pressure is established in the reaction chamber for a pre-determined dwell time.

15 It may be noted that all along during a precursor pressure pulse, due to the absence of radiative heating, the temperature gradually drops to about 600 degrees Celsius, as best seen in subgraph (b). The temperature decay will depend on the particular thermal design of the substrate support and may be controlled on a design level of the CVD system used, e.g. by adding a heat reservoir in thermal contact with the
20 substrate to the sample mount, which will reduce the rate of the temperature drop. Alternatively or in addition thereto, it may be conceived that a non-radiative background heating may be added to the substrate mount to actively counteract the temperature drop. The background heating may be adapted to raise the substrate temperature well above room temperature and may further be adapted to provide a
25 temperature level below catalytic conditions for thin film deposition.

Figs. 5-7 show examples of pulsed deposition of a h-BN thin film on a polycrystalline copper substrate using a process as described above with respect to Fig.4. The grains of the substrate are seen as larger areas separated by straight line
30 grain boundaries in particular in Fig.5 (four grains visible) and Fig.6 (three grains visible). Fig.5 shows an h-BN thin film deposition as obtained from three cycles of heating and pressure pulses. The thin film of h-BN deposits is discontinuous with more or less regularly distributed islands of h-BN seen as small dark spots distributed over the entire surface, separated by brighter, continuous areas of blank sub-

strate where no h-BN has formed. Fig.6 shows an h-BN thin film deposition as obtained from a sequence of six cycles of heating and pressure pulses. The h-BN thin film is now connected with more or less regularly distributed islands of blank substrate seen as small brighter spots distributed over the entire surface, separated by the darker, continuous areas where the h-BN thin film has been formed. Fig.7 shows an h-BN thin film deposition as obtained from a sequence of ten cycles of heating and pressure pulses. An essentially full coverage of the substrate by an h-BN thin film is clearly discernible as dark domains separated by thin, bright borderlines.

10 Fig.8 shows a graph with data from a Raman spectroscopic analysis of a heterostructure thin film disposed on a silicon oxide substrate. The heterostructure thin film was first deposited onto a growth substrate using a sequence of pulsed deposition cycles with separated heating and pressure pulses as described above, wherein two different precursor substances have been used. The precursor substances are Borazine for h-BN growth and Methane for graphene growth. The heterostructure film was then removed from the growth substrate and transferred onto a silicon oxide substrate. The resulting heterostructure film consists of small graphene islands (sub-micrometer size) embedded in an h-BN matrix. The Raman spectroscopic analysis confirms the formation of a heterostructure film of h-BN laterally intercalated with graphene through the following indications in agreement with literature. The Raman spectrum shows from left to right five peaks, namely at about 1400 cm^{-1} , at about 1600 cm^{-1} , at about 2300 cm^{-1} , at about 2750 cm^{-1} , and at about 2900 cm^{-1} . The first peak, at about 1400 cm^{-1} , is very pronounced and is a superposition of the so-called "D-peak" of graphene and the pure h-BN peak. The very pronounced presence of this peak is indicative of the presence in the thin film of h-BN intercalated with graphene. The second peak at about 1600 cm^{-1} is also very pronounced. This is the so-called "G-peak" of graphene, which here has an asymmetric peak-shape with a pronounced shoulder on the flank of the peak towards larger wavenumbers. The presence of the pronounced shoulder is also indicative of the presence of h-BN in the graphene layer. The narrow peak at about 2300 cm^{-1} is for gaseous nitrogen, since the Raman spectrum was taken in air. The broader peak at about 2700 cm^{-1} is the so-called 2D-peak, which is usually an indicator of the crystalline quality of a pure graphene film. The peak is relatively small as compared to a graphene film with a long-range crystalline order. This is also due to the fact that a heterostructure film of

h-BN and graphene has been formed. Finally, the peak present at about 2900 cm^{-1} would, in the case of a pure graphene film, be indicative of scattering defects in the film, but are here also indicative of the presence of h-BN in the deposited film, laterally intercalated with graphene.

CLAIMS

1. Method of depositing a thin film on a substrate by chemical vapour deposition (CVD) from a radiation-sensitive precursor substance, the method comprising the steps of:
- 5
- (i) placing the substrate in a reaction chamber of a CVD system;
- (ii) heating the substrate, wherein heating includes the transmission of electromagnetic heating radiation from a radiative heat source through the reaction chamber towards the substrate, wherein the radiative heat
- 10
- source is controlled to provide electromagnetic radiation as one or more heating pulses where the radiative heat source is in an ON-state, each heating pulse being followed by an idle period where the radiative heat source is in an OFF-state;
- (iii) during at least one of the idle periods where the radiative heat source is
- 15
- in the OFF-state, providing a pressure pulse of a precursor substance inside the reaction chamber by
- feeding at least one precursor substance to the reaction chamber so as to establish a reaction partial pressure for thin film deposition from said precursor substance onto the substrate and subsequently, after a
- 20
- dwelt time,
- removing the precursor substance so as to reduce the partial pressure of the precursor substance in the reaction chamber to below a threshold; and
- (iv) repeating steps (ii) and (iii) until a desired thin film is formed.
- 25
2. Method according to claim 1, wherein the precursor substance comprises one or more infrared-active species that are susceptible to dissociate when exposed to the electromagnetic heating radiation, wherein the electromagnetic heating radiation includes a spectral component in the infrared spectral band.
- 30
3. Method according to any of the preceding claims, wherein the precursor substance comprises one or more species selected from the group of Borazine, Benzene, Coronene, Ethanol, and Benzoic acid.

4. Method according to any of the preceding claims, wherein a first pressure pulse comprises a first precursor substance composition and a second pressure pulse comprises a second precursor substance composition, wherein the second precursor substance composition comprises at least one species that is different
5 from the species contained in the first precursor substance composition.
5. Method according to any of the preceding claims, wherein the precursor substance composition of different pressure pulses is alternated between two distinct compositions.
10
6. Method according to any of the preceding claims, wherein the dwell time of the precursor substance in the pressure pulses is less than 500 s, alternatively less than 200 s, alternatively less than 150 s, alternatively less than 100 s, alternatively less than 50 s, or even less than 10 s.
15
7. Method according to any of the preceding claims, wherein the reaction partial pressure for thin film deposition is at least 1 mbar, at least 10 mbar, preferably at least 100 mbar, or even 1000 mbar.
- 20 8. Method according to any of the preceding claims, wherein the threshold for terminating a pressure pulse by removing the precursor substance is reached when the partial pressure of the precursor substance is below 1mbar, or below 0.1mbar, or even below 0.01mbar.
- 25 9. Method according to any of the preceding claims, wherein the thin film comprises hexagonal boron nitride (h-BN), graphene, and/or heterostructures thereof.
10. Method according to any of the preceding claims, wherein the substrate is a metal substrate.
30
11. Method according to any of the preceding claims, wherein the substrate is made of nickel, a nickel alloy, copper, a copper alloy, platinum, a platinum alloy, iridium, an iridium alloy, ruthenium, a ruthenium alloy, silicon carbide, or stainless steel.

12. Method according to any of the preceding claims, wherein a spectral distribution of the electromagnetic radiation generated by the radiative heat source has its maximum in the infrared spectral band.
- 5
13. Method according to any of the preceding claims, wherein the radiative heat source comprises flash-lamps emitting heating radiation in the infrared spectral band.
- 10
14. Method according to any of the preceding claims, wherein placing the substrate in the reaction chamber of the CVD system in step (i) includes bringing the substrate in thermally conductive contact with a heat reservoir for temporarily storing heat energy so as to add thermal inertia to the substrate.
- 15
15. Method according to any of the preceding claims, further comprising controlling a rate of change in substrate temperature during the pressure pulse of step (iii) to below a predetermined value selected from 50 K/s, 20 K/s, 10 K/s, or 5 K/s.
- 20
16. Method according to any of the preceding claims, wherein the precursor substance comprises at least one component of molecules susceptible to dissociate when exposed to the electromagnetic heating radiation.
17. Rapid thermal chemical vapour deposition (RT-CVD) system for depositing a thin film onto a substrate, the system comprising
- 25
- a reaction chamber comprising a substrate holder adapted for holding the substrate;
 - a radiative heat source adapted for transmitting electromagnetic heating radiation through the reaction chamber towards the substrate holder;
 - a gas handling system comprising a precursor substance supply, feed and exhaust lines connected to the reaction chamber, respective feed and exhaust
- 30
- valves, and a pumping device, the gas handling system being configured for establishing inside the reaction chamber a reaction partial pressure for thin film deposition from said precursor substance onto the substrate, the gas handling system being further configured for exhausting precursor substance so as to re-

- duce the partial pressure of the precursor substance inside the reaction chamber below a pre-determined threshold; and
- a control unit configured for controlling the radiative heat source to provide the electromagnetic heating radiation as heating pulses where the radiative heat source is in an ON-state, separated by idle periods where the radiative heat source is in an OFF-state, the control unit further being configured for controlling the gas handling system to feed and exhaust the precursor substance in a timed manner to establish the reaction partial pressure above a pre-determined threshold for a dwell time during idle periods where the radiative heat source is in the OFF-state, i.e. between heating pulses where the radiative heat source is in the ON-state.
- 5
- 10
18. Rapid thermal chemical vapour deposition (RT-CVD) system according to claim 14, wherein the radiative heat source is an infrared radiation source, such as comprising infrared heating lamps, said heating lamps preferably being configured as flash lamps adapted for rapid thermal operation.
- 15
19. Rapid thermal chemical vapour deposition (RT-CVD) system according to claim 16 or 17, further comprising a heat reservoir adapted to be in thermally conductive contact with the substrate when the substrate is held by the substrate holder, wherein the heat reservoir is adapted for temporarily storing heat energy so as to add thermal inertia to the substrate.
- 20
20. Rapid thermal chemical vapour deposition (RT-CVD) system according to any one of claims 16-18, wherein the precursor gas supply comprises a radiation sensitive precursor substance with at least one component having molecules susceptible to dissociate when exposed to the electromagnetic heating radiation from the radiative heat source.
- 25
- 30 21. Rapid thermal chemical vapour deposition (RT-CVD) system according to any one of claims 16-19, wherein the precursor gas supply comprises one or more radiation sensitive precursor substances selected from Borazine, Benzene, Coronene, Ethanol, and Benzoic acid.

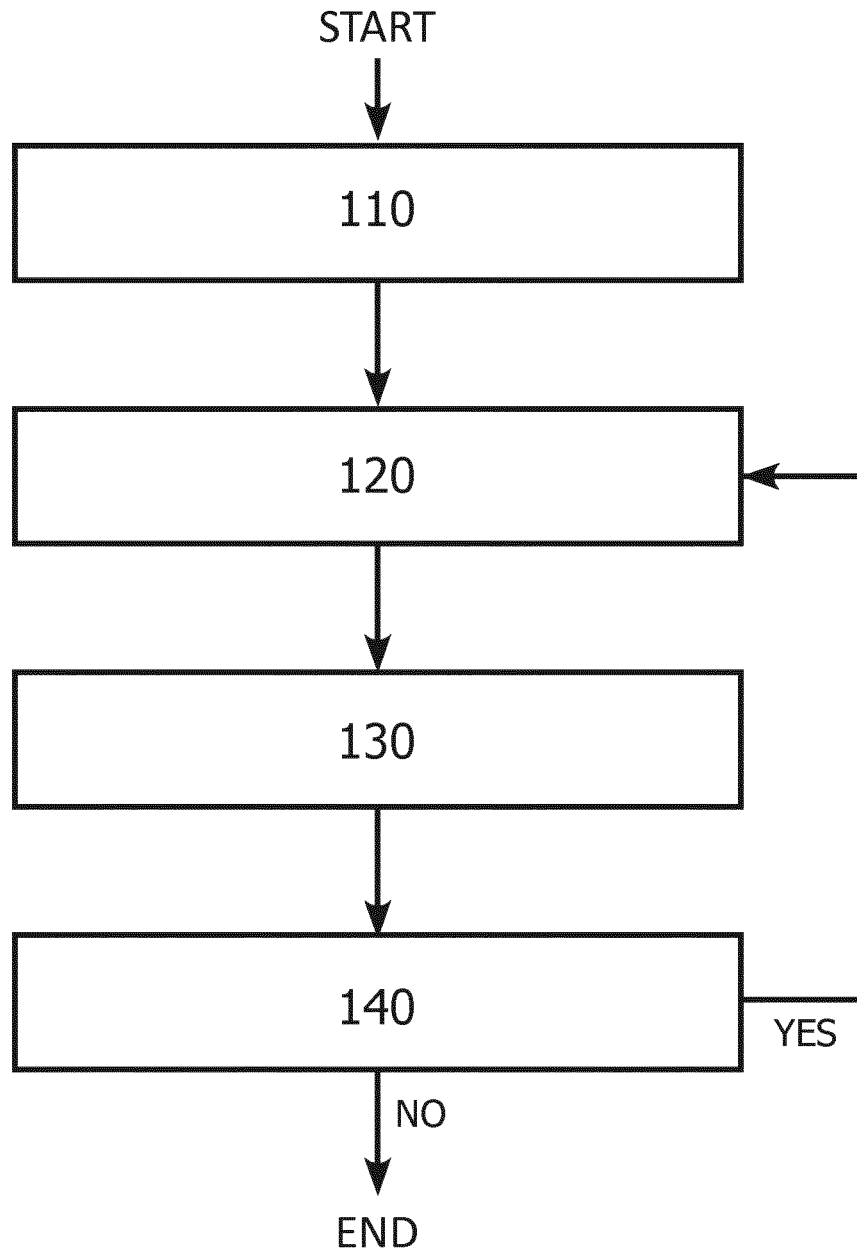


Fig. 1

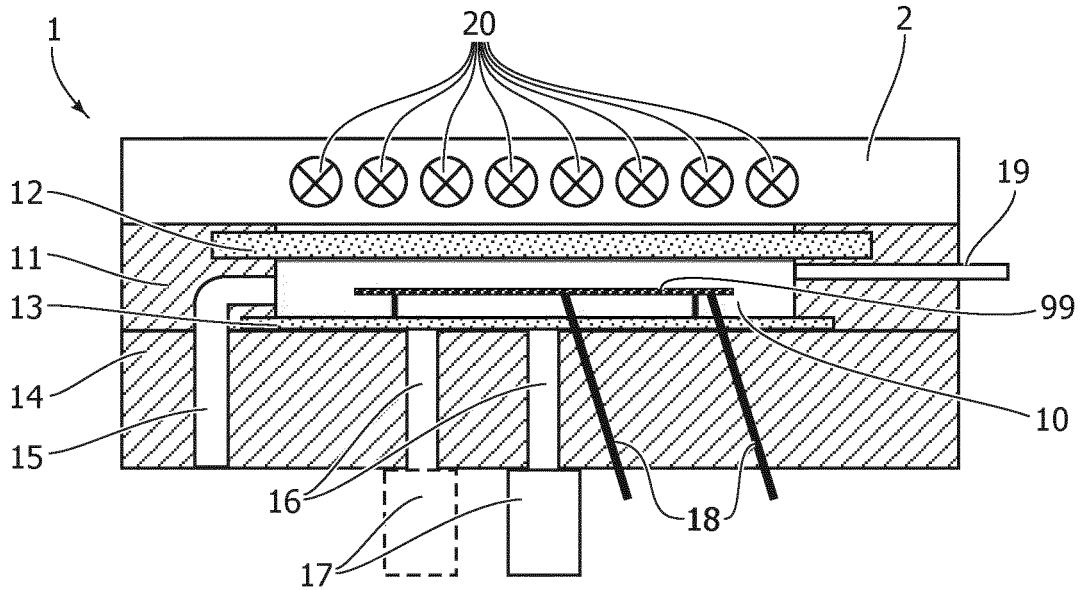


Fig. 2

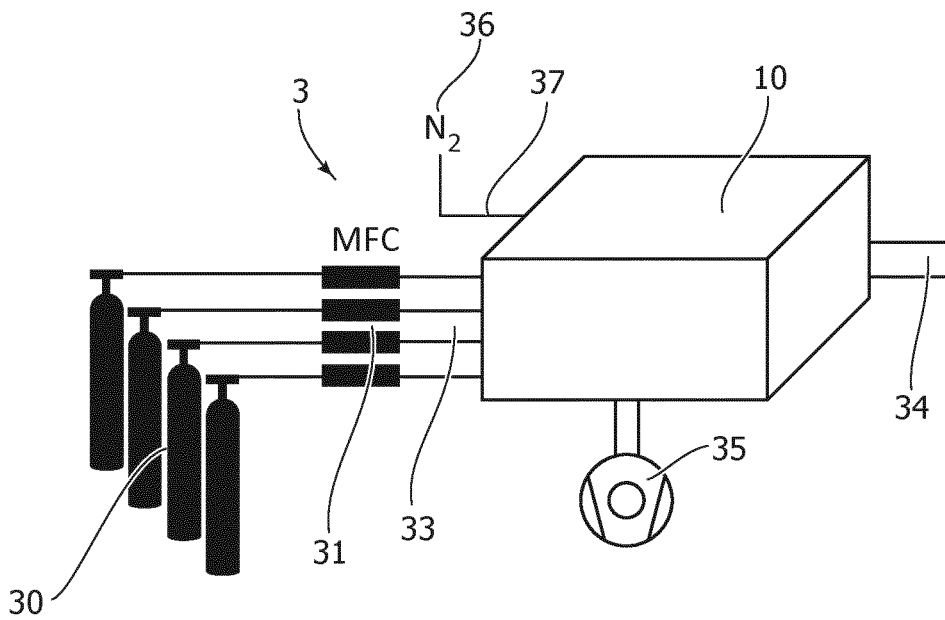


Fig. 3

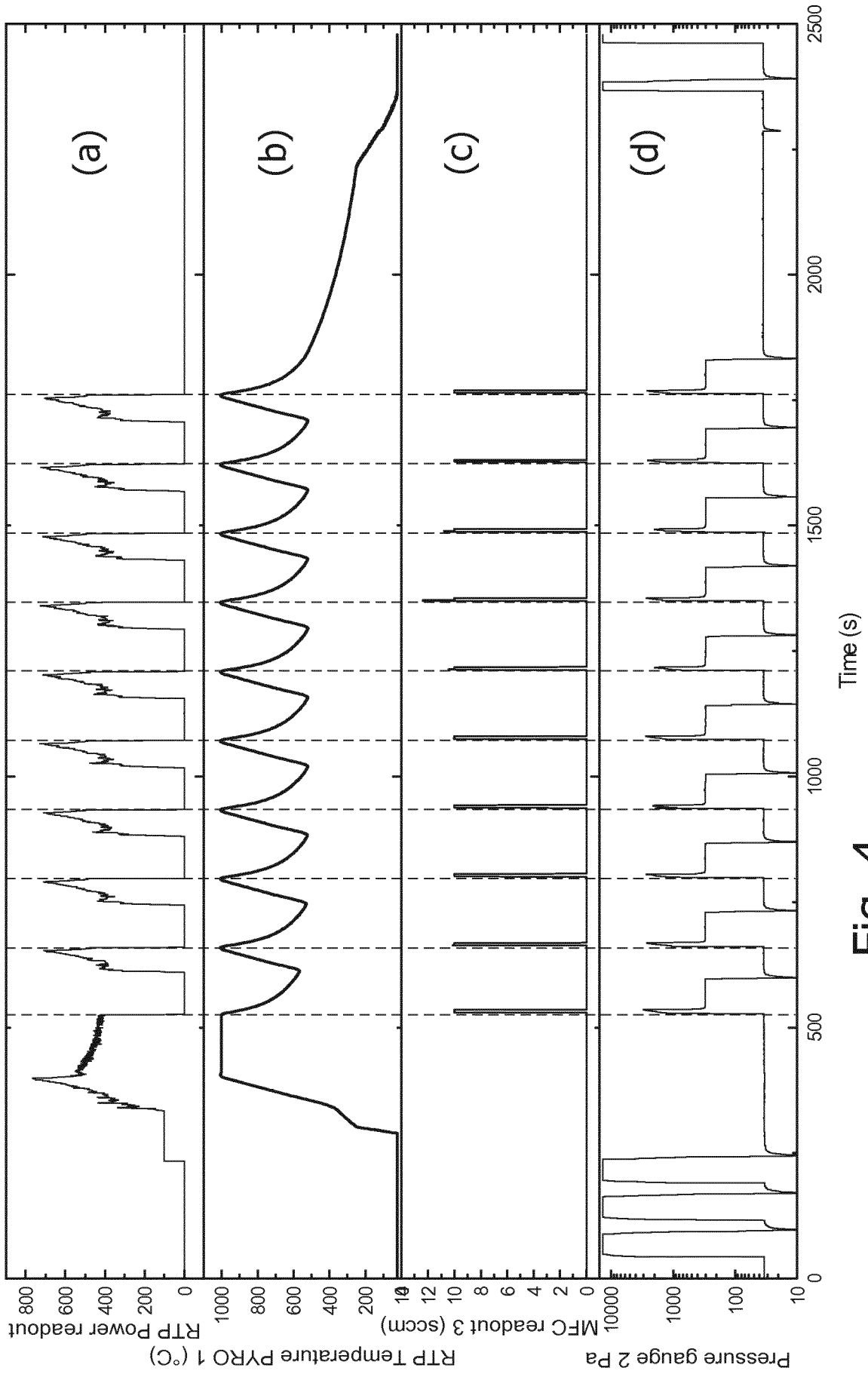


Fig. 4

Fig. 5

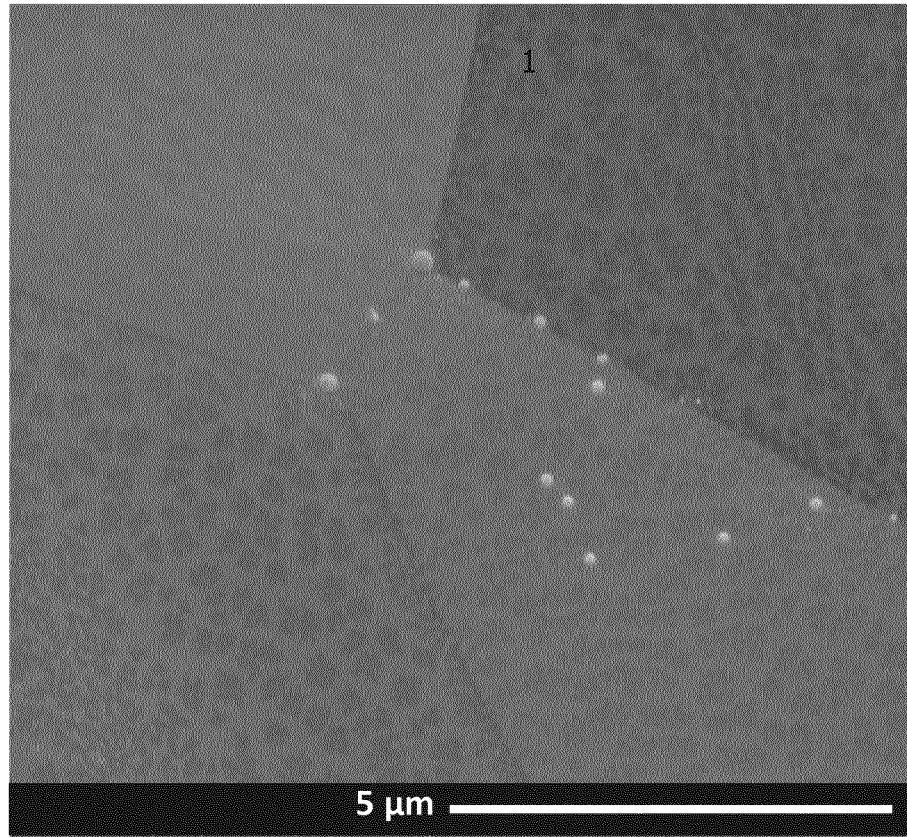
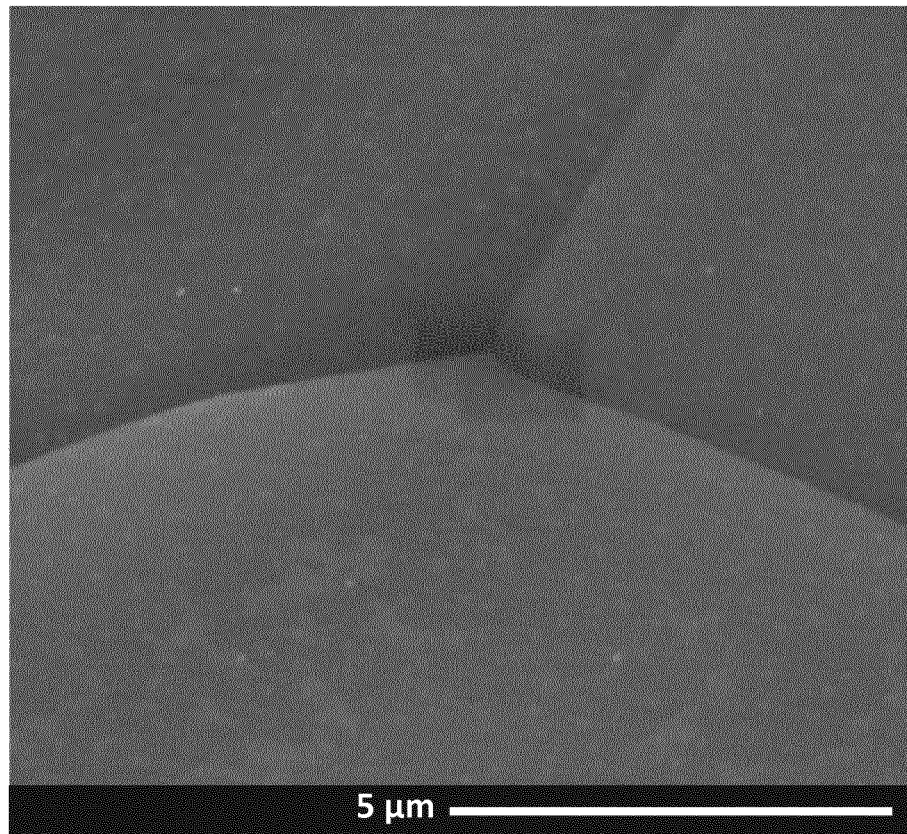


Fig. 6



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Fig. 7

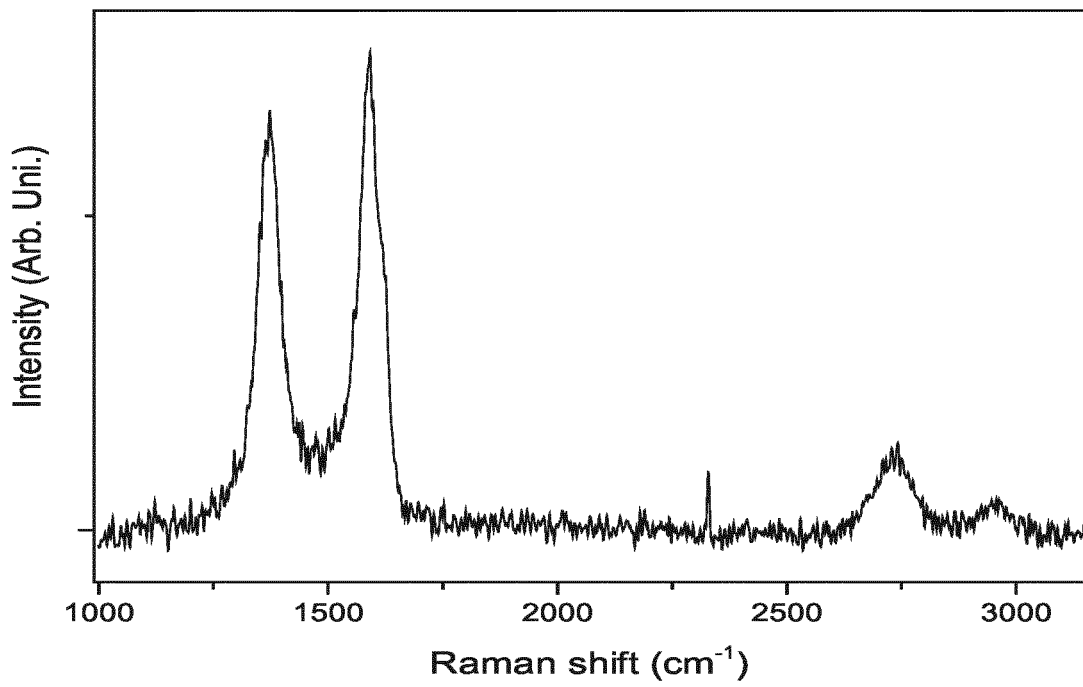
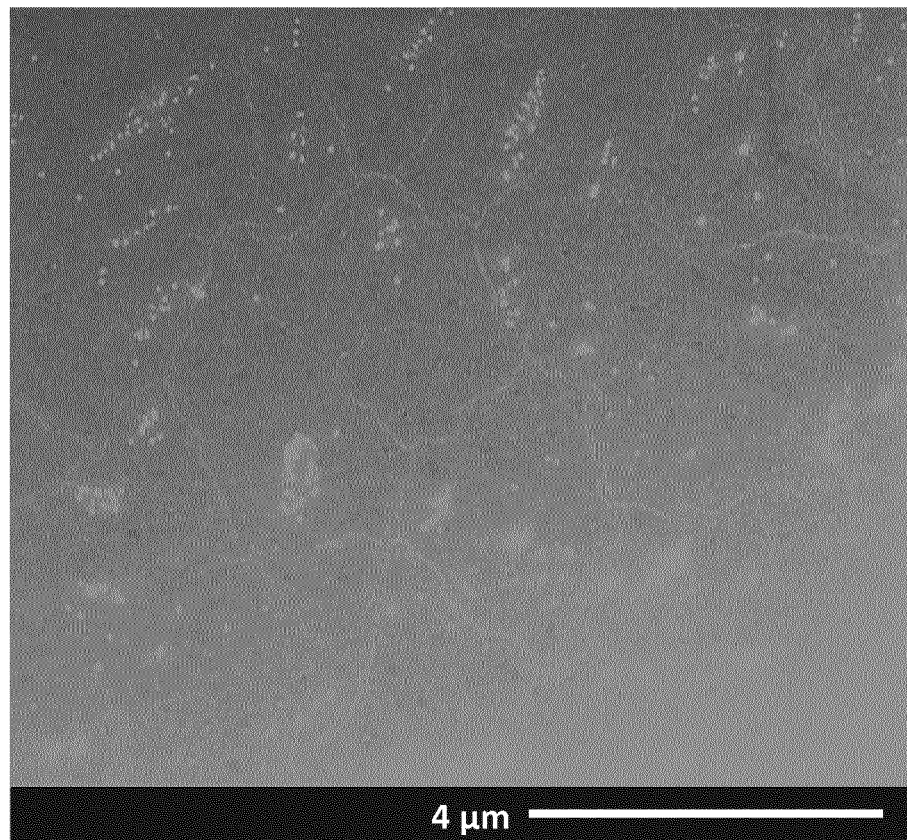


Fig. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/055523

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C23C16/26 C23C16/34 C23C16/44 C23C16/455 C23C16/48
 ADD.

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)
 C23C

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data, IBM-TDB

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/066411 A1 (CHIANG TONY P [US] ET AL) 6 June 2002 (2002-06-06) paragraphs [0023], [0030], [0033] - [0043], [0047], [0049]; figures 1,3 -----	1-21
X	US 2003/175423 A1 (SAENGER ANNETTE [DE] ET AL) 18 September 2003 (2003-09-18) paragraphs [0035] - [0042], [0065]; figure 1; example 1 -----	1-21

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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- "O" document referring to an oral disclosure, use, exhibition or other means
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- "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 16 May 2017	Date of mailing of the international search report 24/05/2017
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Peijzel, Paul
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/055523

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002066411	A1	06-06-2002	NONE

US 2003175423	A1	18-09-2003	DE 10208450 A1 11-09-2003
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			US 2003175423 A1 18-09-2003
