(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 September 2013 (26.09.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/142344 A1

(51) International Patent Classification:
C23C 16/448 (2006.01) *C23C 16/44* (2006.01)

(21) International Application Number:
PCT/US2013/032203

(22) International Filing Date:
15 March 2013 (15.03.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/613,326 20 March 2012 (20.03.2012) US

(71) Applicant: **NORTH CAROLINA STATE UNIVERSITY** [US/US]; 2401 Research Drive, Suite 1122, Box 8210, Raleigh, NC 27695-7003 (US).

(72) Inventors: **PARSONS, Gregory, N.**; 2330 Hathaway Road, Raleigh, NC 27608 (US). **OLDHAM, Christopher, John**; 1305 Lions Way, Raleigh, NC 27604-2319 (US). **JUR, Jesse, S.**; 804 North Bloodworth Street, Raleigh, NC 27604 (US). **MOUSA, Moataz, Bellah**; 3204 Avent Ferry Road, Raleigh, NC (US).

(74) Agent: **TAYLOR, Jr. Arles A.**; Jenkins, Wilson, Taylor & Hunt, P.A., Suite 1200, University Tower, 3100 Tower Boulevard, Durham, NC 27707 (US).

(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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

Published:
— *with international search report (Art. 21(3))*

(54) Title: METHODS AND APPARATUS FOR ATMOSPHERIC PRESSURE ATOMIC LAYER DEPOSITION

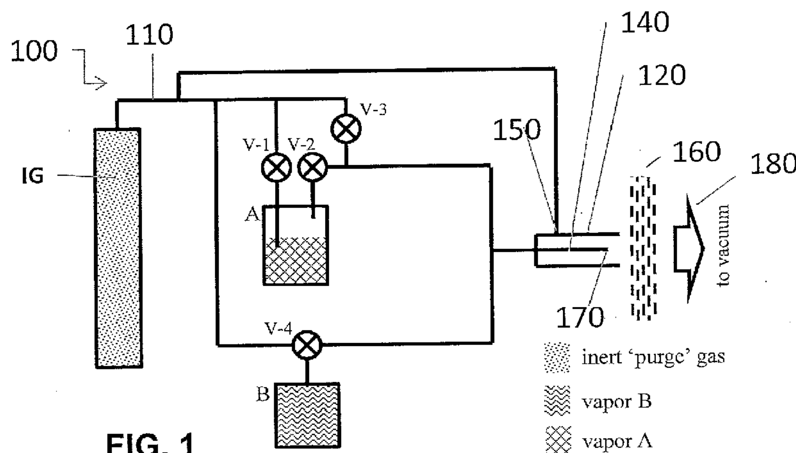


FIG. 1

(57) Abstract: The present subject matter relates to the modification of substrates with low temperature Atomic Layer Deposition (ALD) or related processes that is performed at atmospheric pressure and in the presence or absence of a closed reaction chamber. The substrate can be porous and/or have a non-planar surface. The method can be performed in the absence of substrate movement. The present subject matter also provides an apparatus for performing substrate modification in the absence of a closed reaction chamber and without the need for substrate or apparatus movement.

WO 2013/142344 A1

DESCRIPTION

METHODS AND APPARATUS FOR ATMOSPHERIC PRESSURE ATOMIC LAYER DEPOSITION

5

RELATED APPLICATIONS

The presently disclosed subject matter is based on and claims the benefit of U.S. Provisional Patent Application Serial No. 61/613,326, filed March 20, 2012; the disclosure of which is incorporated herein by reference in its entirety.

10

GOVERNMENT INTEREST

This invention was made with government support under Grant No. 1000382 awarded by the National Science Foundation. The government has certain rights in the invention.

15

TECHNICAL FIELD

The presently disclosed subject matter relates to the modification of substrates, such as porous substrates, by the Atomic Layer Epitaxy (ALE) process, which is also commonly referred to as Atomic Layer Deposition (ALD),
20 and related gas-phase deposition processes. The presently disclosed subject matter relates in particular to processes and apparatuses for the modification of substrates by low-temperature, atmospheric pressure ALD that can be performed in the presence or absence of a closed reaction chamber and without the need for substrate movement.

25

BACKGROUND

Atomic Layer Deposition (ALD), which can sometimes be referred to as Atomic Layer Epitaxy (ALE), Atomic Layer Chemical Vapor Deposition (ALCVD), or Molecular Layer Deposition (MLD), is a process, described, for
30 example, in U.S. Patent No. 4,058,430, for the fabrication of thin films. One representative material deposited by ALD is aluminum oxide (Al_2O_3). Aluminum oxide has many desirable traits such as strong adhesion to various materials, good dielectric properties, and chemical and thermal stability.

Conventional ALD processes are often designed to rapidly pulse different gaseous substances onto a substrate in a closed reaction chamber in a sequence. However, it can be difficult to introduce the gases into the chamber at useful speeds and without unwanted mixing. In order to maximize the flux of gases in to the chamber, they are often pulsed at high pressure and then removed by vacuum. Thus, current nanoscale coating technology often requires expensive vacuum equipment and a complex apparatus.

Accordingly, there is an ongoing need for methods of modifying substrates (e.g., with thin films) such as at atmospheric pressure, that do not require a closed reaction chamber and/or a flat substrate. There is also an ongoing need for low cost methods that do not require complex and/or expensive vacuum systems, or other systems.

SUMMARY

In some embodiments, the presently disclosed subject matter provides a method for modifying a substrate, the method comprising: providing a substrate; contacting the substrate with a vapor-phase precursor comprising an organic or an inorganic component for a first period of time to create a partial atomic layer of the organic or inorganic component on the substrate, wherein the contacting comprises placing the substrate in proximity to an outlet directing a flow of the vapor-phase precursor to the substrate; and contacting the substrate with a vapor-phase reactant for a second period of time to complete the formation of an atomic layer on the substrate, wherein the contacting comprises placing the substrate in proximity to an outlet directing a flow of the vapor-phase reactant to the substrate; wherein said method further comprises providing a flow of a non-reactive gas to the substrate during and/or after one or both of the contacting steps; and wherein said method is performed at atmospheric pressure, wherein the contacting is performed in the presence or absence of a closed reaction chamber, and wherein the method can be performed in the absence of substrate or outlet movement.

In some embodiments, the contacting steps are repeated one or more times to provide a thin film of a desired thickness on the substrate. In some

embodiments, the contacting steps are repeated to provide a thin film having a thickness of between about 1 nanometer and about 10 microns.

In some embodiments, the substrate is a porous substrate. In some embodiments, the substrate is a fiber-based substrate, a metal organic framework, a zeolite, or anodic aluminum oxide.

In some embodiments, the substrate is a fiber-based substrate comprising natural fibers, synthetic fibers, or both natural and synthetic fibers. In some embodiments, the fiber-based substrate is selected from the group comprising cotton fiber, cotton fabric, woven cotton fabric, non-woven cotton fabric, protein-based fiber, polyvinyl alcohol fiber, polyvinyl alcohol fabric, woven polyvinyl alcohol fabric, non-woven polyvinyl alcohol fabric, polyolefin polymer fiber, polyolefin fabric, woven polyolefin fabric, non-woven polyolefin fabric, polyethylene terephthalate fiber, polyethylene terephthalate fabric, woven polyethylene terephthalate fabric, non-woven polyethylene terephthalate fabric, polyamide fiber, polyamide fabric, woven polyamide fabric, non-woven polyamide fabric, acrylic fiber, acrylic fabric, woven acrylic fabric, non-woven acrylic fabric, polycarbonate fiber, polycarbonate fabric, woven polycarbonate fabric, non-woven polycarbonate fabric, fluorocarbon fiber, fluorocarbon fabric, woven fluorocarbon fabric, non-woven fluorocarbon fabric, glass fiber, glass fabric, woven glass fiber, and non-woven glass fabric. In some embodiments, the substrate comprises nanofibers.

In some embodiments, the substrate comprises a natural or synthetic polymer-based surface. In some embodiments, said polymer-based surface comprises a material selected from polyimide, polyethersulfone, cellophane, polydimethylsiloxane, polytetrafluoroethylene, wood, cellulose, cotton, polyvinyl alcohol, polyvinyl chloride, polystyrene, polyacrylonitrile, polyethylene, polybutylene, and polyethylene terephthalate.

In some embodiments, the substrate is substantially stationary. In some embodiments, the substrate is non-planar.

In some embodiments, the flow of vapor-phase precursor, vapor-phase reactant, and non-reactive gas are provided by an apparatus comprising one or more gas delivery units, each gas delivery unit comprising: a first input for the non-reactive gas; one or more gas delivery channels, wherein a first end of

each gas delivery channel is in flow communication with at least an input for receiving the vapor-phase precursor or the vapor-phase reactant, and wherein a second end of each gas delivery channel comprises an outlet for directing a flow of gas to the substrate; and an output face in flow communication with the outlet of each of the one or more gas delivery channels, with the first input for the non-reactive gas, and with a deposition zone exterior to the gas delivery unit.

In some embodiments, the outlet or outlets of the one or more gas delivery channels are coplanar with the output face. In some embodiments, the outlet or outlets of the one or more gas delivery channels are in an interior space of the gas delivery unit.

In some embodiments, at least one gas delivery unit comprises a gas delivery channel wherein the first end of the gas delivery channel is in flow communication with one or more input for sequentially receiving the vapor-phase precursor, the non-reactive gas, and the vapor-phase reactant, such that the outlet of the gas delivery channel can sequentially direct a flow of vapor-phase precursor, the non-reactive gas, and the vapor-phase reactant to the substrate.

In some embodiments, at least one gas delivery unit comprises at least two gas delivery channels, wherein said at least two gas delivery channels comprise: a first gas delivery channel, wherein said first gas delivery channel has a first end in flow communication with one or more inputs for the vapor-phase precursor or for the vapor-phase precursor and the non-reactive gas, and a second end comprising an outlet for delivering the vapor-phase precursor or for sequentially delivering the vapor-phase precursor and the non-reactive gas; and a second gas delivery channel, wherein said second gas delivery channel has a first end in flow communication with one or more inputs for the vapor-phase reactant or for the vapor-phase reactant and the non-reactive gas, and a second end comprising an outlet for delivering the vapor-phase reactant or for sequentially delivering the vapor-phase reactant and the non-reactive gas.

In some embodiments, the first and second gas delivery channels are substantially parallel to one another. In some embodiments, the gas delivery

unit comprises a partition between the first and second gas delivery channels extending in a direction parallel to said first and second gas delivery channels and at or beyond the outlets of the first and second gas delivery channels toward the output face, and further wherein the gas delivery unit comprises a second input for the non-reactive gas such that the first input for the non-reactive gas is located on one side of the partition and the second input for the non-reactive gas is located on the other side of the partition. In some embodiments, the first and second gas delivery channels join one another near their second ends to form a single outlet.

In some embodiments, providing the substrate comprises positioning an outer or external surface of the substrate between about 0.01 millimeters and about 20 millimeters from an output face of a gas delivery unit. In some embodiments, providing the substrate comprises positioning an outer or external surface of the substrate between about 0.02 millimeters and about 1.0 millimeters from an output face of a gas delivery unit. In some embodiments, providing the substrate comprises positioning an outer or external surface of the substrate between about 0.02 millimeters and about 0.5 millimeters from an output face of a gas delivery unit.

In some embodiments, an outlet for delivering the vapor-phase precursor is located substantially in the center of the output face. In some embodiments, providing the substrate comprises positioning the substrate such that a plurality of portions of an outer or external surface of the substrate are in proximity to the output faces of a plurality of gas delivery units.

In some embodiments, the vapor-phase precursor comprises a metal-containing compound. In some embodiments, the vapor-phase precursor comprises trimethylaluminum (TMA), diethyl zinc (DEZ), titanium tetrachloride ($TiCl_4$), tungsten hexafluoride, titanium isopropoxide, or zirconium tertbutoxide (ZTB).

In some embodiments, the flow of the vapor-phase precursor is provided at a flow rate between about 0.001 and about 5.0 standard liters per minute (slm). In some embodiments, the flow of the vapor-phase precursor is provided at a flow rate between about 0.05 slm and about 0.2 slm. In some embodiments, the first period of time is between about 0.01 seconds and about

60.0 seconds. In some embodiments, the first period of time is between about 0.1 seconds and about 2 seconds.

In some embodiments, the vapor-phase reactant is selected from the group comprising H_2O, NH_3, ozone, O_2, CO_2, CO, NO, N_2O, NO_2, SiH_4, and Si_2H_6. In some embodiments, the vapor-phase reactant is provided at a flow rate between about 0.001 and about 5.0 slm. In some embodiments, the vapor-phase reactant is provided at a flow rate between about 0.05 slm and about 0.2 slm. In some embodiments, the second period of time is between about 0.01 seconds and about 60.0 seconds. In some embodiments, the second period of time is between about 0.1 seconds and about 2 seconds.

In some embodiments, the vapor-phase precursor is TMA and the method comprises modifying the substrate with aluminum oxide.

In some embodiments, the non-reactive gas is selected from nitrogen and argon. In some embodiments, non-reactive gas is provided at a flow rate between about 1 and about 100 slm. In some embodiments, the non-reactive gas is provided at a flow rate between about 5 and about 20 slm.

In some embodiments, the method comprises providing a flow of a non-reactive gas for between about 1 second and about 300 seconds after the first period of time and before the second period of time and/or after the second period of time. In some embodiments, the method comprises providing a flow of a non-reactive gas for about 40 seconds after the first period of time and before the second period of time and/or after the second period of time. In some embodiments, the method comprises providing a flow of a non-reactive gas for about 10 seconds after the first period of time and before the second period of time and/or after the second period of time. In some embodiments, the method comprises providing a flow of a non-reactive gas for more than about 300 seconds after the first period of time and before the second period of time and/or after the second period of time. In some embodiments, the method comprises providing a flow of a non-reactive gas during the first and/or second periods of time.

In some embodiments, one or both contacting steps are conducted at a temperature between about 20°C and about 200°C. In some embodiments, one or both contacting steps are conducted at a temperature of about 120°C.

In some embodiments, one or both contacting steps are conducted at a temperature of about 50°C.

In some embodiments, the presently disclosed subject matter provides an apparatus for modifying a substrate, wherein the apparatus comprises one or more gas delivery units, each gas delivery unit comprising: a first input for the non-reactive gas; one or more gas delivery channels, wherein a first end of each gas delivery channel is in flow communication with at least an input for receiving the vapor-phase precursor or the vapor-phase reactant, and wherein a second end of each gas delivery channel comprises an outlet for directing a flow of gas to a substrate; and an output face in flow communication with the outlet of each of the one or more gas delivery channels and with the first input for the non-reactive gas, and is adapted for gaseous and/or flow communication with an exterior of the gas delivery unit.

In some embodiments, the outlet or outlets of the one or more gas delivery channels are coplanar with the output face. In some embodiments, the outlet or outlets of the one or more gas delivery channels are in an interior space of the gas delivery unit. In some embodiments, an outlet for delivering a flow of the vapor-phase precursor is at or near the center of the output face. In some embodiments, the outlet or outlets of the one or more gas delivery channels each have a diameter that is between about 0.1 mm and about 0.5 mm.

In some embodiments, the output face is square or rectangular. In some embodiments, the output face is substantially circular. In some embodiments, the output face has a diameter that is about 0.5 cm or smaller. In some embodiments, the output face has a diameter that is between about 0.5 cm and about 4.0 cm. In some embodiments, the output face has one or more openings, wherein the one or more openings each have a diameter that is between about 0.1 mm and about 0.5 mm.

In some embodiments, the gas delivery unit comprises a tubular body comprising an input face at a first end of the tubular body adapted to receive one or more input ports and/or one or more gas delivery channels, and wherein the output face is at a second end of the tubular body. In some embodiments, the tubular body is tapered such that the output face has a smaller diameter

than the input face. In some embodiments, the input face has a diameter that is between about 0.5 and about 4.0 centimeters. In some embodiments, the input face has a diameter that is between about 0.5 and about 1.0 centimeters.

In some embodiments, at least one gas delivery unit comprises a gas delivery channel wherein the first end of the gas delivery channel is in flow communication with one or more input for sequentially receiving the vapor-phase precursor, the non-reactive gas, and the vapor-phase reactant.

In some embodiments, at least one gas delivery unit comprises at least two gas delivery channels, wherein said at least two gas delivery channels comprise: a first gas delivery channel, wherein said first gas delivery channel has a first end in flow communication with one or more inputs for the vapor-phase precursor or for the vapor-phase precursor and the non-reactive gas, and a second end comprising an outlet for delivering the vapor-phase precursor or for sequentially delivering the vapor-phase precursor and the non-reactive gas; and a second gas delivery channel, wherein said second gas delivery channel has a first end in flow communication with one or more inputs for the vapor-phase reactant or for the vapor-phase reactant and the non-reactive gas, and a second end comprising an outlet for delivering the vapor-phase reactant or for sequentially delivering the vapor-phase reactant and the non-reactive gas.

In some embodiments, the first and second gas delivery channels are substantially parallel to one another. In some embodiments, the gas delivery unit comprises a partition between the first and second gas delivery channels extending in a direction parallel to said first and second gas delivery channels and extending beyond the outlets of first and second gas delivery channels toward the output face, and further wherein the gas delivery unit comprises a second input for the non-reactive gas such that the first input for the non-reactive gas is located on one side of the partition and the second input for the non-reactive gas is located on the other side of the partition. In some embodiments, the first and second gas delivery channels join one another near their second ends to form a single outlet.

In some embodiments, the apparatus further comprises a support for supporting a substrate when the substrate is positioned about 20 mm or less

from, but not in direct contact with, the output face. In some embodiments, the support is adapted to hold the substrate stationary. In some embodiments, the support is adapted to translate the substrate with respect to an output face.

In some embodiments, one or more gas delivery units can be translated with respect to a length, width, and/or height of a substrate. In some embodiments, the apparatus further comprises a roller system for positioning a substrate sheet relative to the apparatus.

In some embodiments, the apparatus comprises a plurality of gas delivery units. In some embodiments, the plurality of gas delivery units are arranged in a single row to form a linear array of gas delivery units. In some embodiments, the plurality of gas delivery units are arranged in a plurality of rows to form a square or rectangular array of gas delivery units.

In some embodiments, the apparatus further comprises an exhaust system. In some embodiments, the apparatus further comprises one or more spacers extending from the exterior of the output face to assist in positioning the substrate. In some embodiments, the apparatus further comprises one or more satellite gas delivery units, wherein each satellite gas delivery unit comprises a gas delivery channel for delivery of a flow of non-reactive gas to the substrate.

In some embodiments, the presently disclosed subject matter provides a modified substrate created by a method comprising: providing a substrate; contacting the substrate with a vapor-phase precursor comprising an organic or an inorganic component for a first period of time to create a partial atomic layer of the organic or inorganic component on the substrate, wherein the contacting comprises placing the substrate in proximity to an outlet directing a flow of the vapor-phase precursor to the substrate; and contacting the substrate with a vapor-phase reactant for a second period of time to complete the formation of an atomic layer on the substrate, wherein the contacting comprises placing the substrate in proximity to an outlet directing a flow of the vapor-phase reactant to the substrate; wherein said method further comprises providing a flow of a non-reactive gas to the substrate during and/or after one or both of the contacting steps; and wherein said method is performed at atmospheric pressure, wherein the contacting is performed in the presence or absence of a closed reaction

chamber, and wherein the method can be performed in the absence of substrate or outlet movement. In some embodiments, the modified substrate is patterned with a thin film.

In some embodiments, the presently disclosed subject matter provides a modified substrate produced using an apparatus that comprises one or more gas delivery units, each gas delivery unit comprising: a first input for the non-reactive gas; one or more gas delivery channels, wherein a first end of each gas delivery channel is in flow communication with at least an input for receiving the vapor-phase precursor or the vapor-phase reactant, and wherein a second end of each gas delivery channel comprises an outlet for directing a flow of gas to a substrate; and an output face in flow communication with the outlet of each of the one or more gas delivery channels and with the first input for the non-reactive gas, and is adapted for gaseous and/or flow communication with an exterior of the gas delivery unit. In some embodiments, the modified substrate is patterned with a thin film.

In some embodiments, the presently disclosed subject matter provides an apparatus for modifying a substrate, wherein the apparatus comprises a roller system and an array of vapor-phase precursor delivery units and vapor-phase reactant delivery units, wherein each vapor-phase precursor delivery unit comprises a vapor-phase precursor delivery channel, wherein a first end of the channel is in flow communication with one or more inputs for receiving the vapor-phase precursor or receiving the vapor-phase precursor and a non-reactive gas, and wherein a second end of the channel comprises an outlet for directing a flow of vapor-phase precursor and/or non-reactive gas to a substrate; wherein each vapor-phase reactant delivery unit comprises a vapor-phase reactant delivery channel, wherein a first end of the channel is in flow communication with one or more inputs for receiving the vapor-phase reactant or receiving the vapor-phase reactant and a non-reactive gas, and wherein a second end of the channel comprises an outlet for directing a flow of vapor-phase reactant and/or non-reactive gas to a substrate; and wherein the roller system can translate a substrate relative to the outlets of the array, such that a portion of the substrate is sequentially in contact with a flow from the outlet of a

vapor-phase precursor delivery unit and a flow from the outlet of a vapor-phase reactant delivery unit.

In some embodiments, the apparatus further comprises an exhaust system for creating a pressure differential between the outlets of the delivery channels and the substrate and/or to remove excess vapor-phase precursor, excess vapor-phase reactant, non-reactive gas, and/or any gaseous side products formed during use of the apparatus.

In some embodiments, the presently disclosed subject matter provides a modified substrate produced using said apparatus. In some embodiments, an inner surface or both an outer surface and an inner surface of the substrate are modified. In some embodiments, directing a flow of gas to the substrate comprises directing the flow of gas to an outer and/or an inner surface of the substrate.

It is an object of the presently disclosed subject matter to provide methods and apparatuses for the modification of substrates, including porous substrates, such as textiles, at atmospheric pressure and, if desired, in the absence of a closed reaction chamber.

An object of the presently disclosed subject matter having been stated hereinabove, and which is achieved in whole or in part by the presently disclosed subject matter, other objects will become evident as the description proceeds when taken in connection with the accompanying drawings as best described hereinbelow.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic drawing illustrating a single channel apparatus **100** of the presently disclosed subject matter. Apparatus **100** has a valve design and gas lines **110** suitable for vapor delivery from a liquid source for vapor-phase precursor **A** (shown by cross-hatching) and a high pressure gas source for vapor-phase reactant **B** (shown by zigzag lines). The flow of inert gas (shown by stippling) from inert gas source **IG** to a liquid source for vapor-phase precursor **A** can be controlled via valve **V-1**. Valve **V-2** can control the flow from the liquid source to the single gas delivery channel in the delivery head. Valve **V-3** can control the flow of inert gas into gas delivery channel **140**,

e.g., allowing gas delivery channel **140** to be purged of **A** or **B** as necessary. Valve **V-4** controls flow between inert gas source **IG**, the liquid source for vapor-phase reactant **B**, and gas delivery channel **140** in delivery head **120**. Delivery head **120** also contains separate input **150** for the inert gas. Delivery
5 head **120** can direct the flow of **A**, **B** and the inert gas to a surface of substrate **160** from outlet **170**. Optional exhaust system **180** can draw excess gases from the opposite side of the porous substrate to a vacuum.

Figure 2 is a schematic drawing illustrating single channel apparatus **200** of the presently disclosed subject matter. Apparatus **200** includes single gas
10 delivery channel **210** with inlet **212** that can sequentially direct a flow of vapor **A** (i.e., a vapor-phase precursor; shown by cross-hatching), inert "purge" gas (**IG**, shown by stippling), vapor **B** (i.e., a vapor-phase reactant; shown by zigzag lines) and inert "purge" gas to a surface of substrate **260** (e.g., a porous substrate) via outlet **270**. Gas delivery unit **220** includes separate input **215** for
15 inert "purge" gas that allows further inert gas to be directed to the surface of substrate **260** from output face **240** of delivery unit **220**. On an opposite side of substrate **260** from delivery unit **220**, an optional exhaust system **280** can carry excess gas away from substrate **260**. Substrate **260** can optionally be translated relative to output face **240** as indicated by the heavy solid arrows.

20 Figure 3 is a schematic drawing illustrating dual channel apparatus **300** of the presently disclosed subject matter. Apparatus **300** includes gas delivery unit **380** that includes two gas delivery channels, **320** and **340**. Gas delivery channel **320** with inlet **318** can sequentially deliver vapor **A** (i.e., a vapor-phase precursor, shown by cross-hatching) and inert "purge" gas (**IG**, shown by
25 stippling). Gas delivery channel **340** with inlet **338** can sequentially deliver vapor **B** (i.e., a vapor-phase reactant, shown by zigzag lines) and inert "purge" gas. Gas delivery channels **320** and **340** are oriented such that they form single output **385** at the vertex of a right or acute angle formed between terminal portions **322** and **342** of the two channels. Delivery unit **380** also
30 includes separate input **360** for an inert "purge" gas. Gases from output face **390** of delivery unit **380** are directed to a surface of substrate **395** (e.g., a porous substrate), which can optionally be translated relative to output face **390** as indicated by the heavy arrows. On a side of the substrate opposite to output

face **390**, optional exhaust system **397** can be used to carry excess gases away from substrate **395**.

Figure 4 is a schematic drawing illustrating dual channel apparatus **400** of the presently disclosed subject matter. Apparatus **400** includes gas delivery unit **405** that includes two substantially parallel gas delivery channels **410** and **415**. Parallel gas delivery channel **410** with inlet **408** can direct a flow of vapor **A** (i.e., a vapor-phase precursor, shown by cross-hatching) to a surface of substrate **460** (e.g., a porous substrate) via outlet **412**, while gas delivery channel **415** with inlet **413** can direct a flow of vapor **B** (i.e., a vapor-phase reactant, shown by zigzag lines) to the surface of the substrate through outlet **417**. Outlets **412** and **417** are coplanar with output face **440** of gas delivery unit **405**. Partition **420** is located between and parallel to gas delivery channels **410** and **415**, and extends beyond output face **440** toward substrate **460**. Gas delivery unit **405** includes additional inputs **430** and **435** for inert "purge" gas **IG** (shown by stippling), one on each side of partition **420**, such that the flow from each of gas delivery channels **410** and **415** is surrounded by a flow of inert gas. Substrate **460** can optionally be translated relative to output face **440** as indicated by the heavy arrows. On a side of the substrate opposite to output face **440**, optional exhaust system **480** can be used to carry excess gases away from substrate **460**.

Figure 5 is a schematic drawing illustrating a bottom view of a gas delivery unit having a circular output face. The outlet of a single gas delivery channel (cross-hatching) is located substantially in the center of the output face, having a diameter **d**. An input for non-reactive gas (e.g., an inert gas **IG**, shown by stippling) feeds non-reactive gas into the delivery unit so that a sheath of non-reactive gas can surround the outlet of the gas delivery channel.

Figure 6 is a schematic drawing illustrating a bottom view of a gas delivery unit having a rectangular output face. A rectangular output of a gas delivery channel (cross-hatching) is located substantially in the center of the output face and has dimensions **l** and **w**. An input for non-reactive gas (e.g., an inert gas **IG**, shown by stippling) feeds non-reactive gas into the delivery unit so that a sheath of non-reactive gas can surround the outlet of the gas delivery channel.

Figure 7 is a schematic drawing illustrating the modification of the surface of substrate **720** wherein single channel gas delivery unit **710** is rastered over the surface of the substrate to provide patterned film **725**. Single gas delivery channel **712** of unit **710** can sequentially deliver vapor-phase precursor **A**, inert gas (inert), vapor-phase reactant **B**, and inert gas. Unit **710** also includes separate input **714** for inert gas. Optional exhaust system **730** is located under the substrate to direct excess gases away from the substrate.

Figure 8 is a schematic drawing illustrating an apparatus of the presently disclosed subject matter containing an array of single point reactors (gas delivery units). Apparatus **800** includes array **810** of reactors **812** wherein each reactor can deliver either only the vapor-phase precursor (**A**) and inert gas (**I**) or only the vapor-phase reactant (**B**) and the inert gas (**I**). Apparatus **800** also includes roller system **820** for moving substrate **840** (e.g., a porous substrate) past array **810**. Optional exhaust system **860** can be used to direct excess gases away from the substrate.

Figure 9 is a schematic drawing illustrating an apparatus of the presently disclosed subject matter. Apparatus **900** shows linear array **902** of single point reactors **904** (i.e., gas delivery units), wherein each single point reactor includes separate delivery channels **906** for a vapor-phase reactant **R** (e.g., water) and a vapor-phase precursor **P** (e.g., trimethylaluminum, TMA) and inlet **908** for a non-reactive (e.g., nitrogen, N_2) gas. Outlets **910** and **912** of the delivery channels can be located at (i.e., be co-planar with) or near (e.g., recessed about 1 to 20 millimeters from) output face **914** of the single point reactor. A substrate **S**, which can be movable or fixed, is positioned such that an outer surface of the substrate is in proximity to the output faces (e.g., within about 20 mm or less) of the reactors. Gases can be removed from the underside of the substrate by an optional exhaust system. The flow of gases from each reactor provides a deposition zone **DZ** over a portion of the substrate where an atomic layer is deposited to provide a coated substrate **CS**. In the linear array shown, a series of adjoining portions of the substrate can be modified/coated. At its widest point, single point gas delivery reactor **904** can have an outer diameter of between about 0.5 cm and about 1.0 cm, and tapers toward the output face.

Figure 10 is a schematic drawing illustrating an apparatus of an embodiment of the presently disclosed subject matter. Apparatus **1000** comprises single point reactor **1010** with two delivery channels, **1020** and **1030** (i.e., one for delivery of a vapor phase precursor (**A**) and one for delivery of a
5 vapor phase reactant (**B**)) and side input **1040** for a non-reactive gas (**NRG**). Outlets **1050** of delivery channels **1020** and **1030** are in the interior of single point reactor **1010**, recessed from output face **1060**. Gas flow is directed from opening **1070** in output face **1060** to substrate **1080**. Spacers **1075** are extended from output face **1060** toward substrate **1080**. Satellite non-reactive
10 gas delivery units **1090** are positioned on either side of the single point reactor **1010**. Exhaust gases **1095** can exit from openings between spacers **1075** of single point reactor **1010** and satellite non-reactive gas delivery units **1090**.

Figure 11 is a graph showing the average growth (in nanometers, nm) of an aluminum oxide film on a silicon substrate as a function of the number of
15 atomic layer deposition (ALD) cycles to which the substrate is exposed. Each ALD cycle includes a 1.0 second dose of trimethylaluminum (TMA, 0.05 standard liters per minute (slm)) and a 1.0 second dose of water (0.05 slm). Nitrogen gas was used as a purge at a flow rate of 10 slm. The bulk nitrogen flow was heated to 120°C. The data (diamonds) is given for 0, 50, 150, 225,
20 and 300 ALD cycles as indicated at the x axis. The error bars represent the extra film growth observed at the center of the substrate (i.e., at the center of the ALD deposition zone) or the reduced growth at the substrate border. The single data point shown by a circle represents aluminum oxide film growth after 300 cycles of TMA only dosing (i.e., no water dose).
25 Figure 12 is a micrograph image of a silicon substrate after 300 cycles of atomic layer deposition (ALD) process as described in Figure 11. The labeled regions (i.e., **SP**, i.e., Stagnant point; **Z1**, i.e., Zone 1; **Z2**, i.e., Zone 2; and **Z3**, i.e., Zone 3) represent different deposition regions within the total deposition zone. The relative sizes and/or presence of the different regions can be
30 controlled by ALD reactor dimensions and ALD deposition conditions (e.g., inert gas flow rate, dose times, purge times, etc.). **SP** is at the center of a flat, rigid, fixed substrate region in proximity to a single point reactor, where gas from the reactor impinges the substrate in an approximately vertical flow. **SP** has a

diameter approximately equivalent to a reactor outlet/output face opening. **SP** gives rise to deposition of a relatively thicker film at the center of the substrate surface. Beyond **SP**, the gas starts accelerating radially, leading to a laminar flow region (**Z1**), followed by a transition zone (**Z2**), which is turbulent and full of eddies. ALD deposition can be relatively thicker in **Z2** than in **Z1** due to these eddies. Past transition zone **Z2**, the gas starts decelerating as it goes further away from the reactor outlet, which gives rise to a third deposition zone, **Z3**, with less uniform coating.

Figure 13 is a drawing showing a schematic illustration of the image shown in Figure 12. **SP** is shown in light grey, **Z1** in medium grey, **Z2** in black, and **Z3** in dark grey.

Figure 14 shows, in the top view, a side-on schematic illustration of gas (flow indicated by arrows) impinging a flat, non porous substrate **1420** from an opening **1410** in the output face **1415** of a single point reactor **1400** of the presently disclosed subject matter. The middle view of Figure 14 shows a schematic illustration of the laminar and turbulent boundary gas layers that form as gas flows in a radial direction away from a point under opening **1410**. The bottom view of Figure 14 is a schematic illustration of radial gas flow velocity (in arbitrary units) from the impinging gas along the substrate surface.

Figure 15 is a micrograph image of a silicon substrate treated to 300 cycles of atomic layer deposition (ALD) as described above for Figure 11, only wherein the nitrogen gas is provided at a flow rate of 7 standard liters per minute (slm) instead of 10 slm.

DETAILED DESCRIPTION

The presently disclosed subject matter relates generally to methods and apparatuses for the modification of substrates, such as fibers and textile media or other porous substrates. More particularly, the presently disclosed subject matter relates to methods and apparatuses for ALD and related processes that can be performed at atmospheric pressure, low temperature, and wherein the substrate can be present in the ambient environment (i.e., not inside a closed reaction chamber, such as a chamber or vessel than can be placed under vacuum). The substrate can have a variety of different shapes and can be

stationary or moving. In some embodiments, movement of neither the substrate nor the apparatus delivering the reactants is necessary.

The presently disclosed subject matter will now be described more fully hereinafter with reference to the accompanying Examples, in which
5 representative embodiments are shown. The presently disclosed subject matter can, however, be embodied in different forms and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the embodiments to those skilled in
10 the art.

All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety.

I. Definitions

15 While the following terms are believed to be well understood by one of ordinary skill in the art, the following definitions are set forth to facilitate explanation of the presently disclosed subject matter.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the
20 art to which the presently disclosed subject matter belongs. Although any methods, devices, and materials similar or equivalent to those described herein can be used in the practice or testing of the presently disclosed subject matter, representative methods, devices, and materials are now described.

Following long-standing patent law convention, the terms “a”, “an”, and
25 “the” refer to “one or more” when used in this application, including the claims.

The term “and/or” when used in describing two or more items or conditions, refers to situations where all named items or conditions are present or applicable, or to situations wherein only one (or less than all) of the items or conditions is present or applicable.

30 The term “comprising”, which is synonymous with “including,” “containing,” or “characterized by” is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. “Comprising” is a term of art used in claim language which means that the named elements are

essential, but other elements can be added and still form a construct within the scope of the claim.

As used herein, the phrase "consisting of" excludes any element, step, or ingredient not specified in the claim. When the phrase "consists of" appears in 5 a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole.

As used herein, the phrase "consisting essentially of" limits the scope of a claim to the specified materials or steps, plus those that do not materially 10 affect the basic and novel characteristic(s) of the claimed subject matter.

With respect to the terms "comprising", "consisting of", and "consisting essentially of", where one of these three terms is used herein, the presently disclosed and claimed subject matter can include the use of either of the other two terms.

15 Unless otherwise indicated, all numbers expressing quantities of time, temperature, thickness, diameter, distance, flow rate, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about". Accordingly, unless indicated to the contrary, the numerical parameters set forth in this specification and attached claims are 20 approximations that can vary depending upon the desired properties sought to be obtained by the presently disclosed subject matter.

As used herein, the term "about", when referring to a value or to an amount of time, flow rate, temperature, distance, diameter, or thickness is meant to encompass variations of in one example ±20% or ±10%, in another 25 example ±5%, in another example ±1%, and in still another example ±0.1% from the specified amount, as such variations are appropriate to perform the disclosed methods.

Any suitable substrate can be used according to the presently disclosed subject matter. The substrate can be porous or non-porous. The substrate can 30 be flexible or non-flexible. The substrate can have any suitable shape, such as but not limited to, planar, conical, rod-shaped, spherical, irregular or combinations thereof.

The term "porous substrate" refers to a substrate that contains pores or voids. Porous substrates can comprise inorganic, organic, or hybrid inorganic-organic materials. Porous substrates can have outer surfaces and inner surfaces, wherein the term "inner surface" refers to the surface of the substrate
5 located within a pore or void and wherein the term "outer surface" refers to a substrate surface located on an exterior surface of the porous substrate (e.g., as a whole). Thus, in some embodiments, the term "a surface" can refer to an interior surface, an exterior surface or both an interior and an exterior surface.

The term "metal-organic framework" refers to porous substrates
10 comprising crystalline compounds of metal ions or metal clusters coordinated to organic molecules (e.g. rigid organic molecules). In some embodiments, the organic molecules can be mono- or multi-dentate. Suitable organic molecules for metal-organic frameworks include bi- and tri-dentate carboxylates or amides, as well as triazole and other nitrogen-containing aromatics.

15 The terms "fiber" and "fiber-based substrate" as used herein, are meant in their broadest sense to encompass all materials having a fibrous structure. For example, any polymer, fiber or textile material of a continuous shape is encompassed within the meaning of the terms fiber and fiber-based substrate as they are used herein. Accordingly, the fiber and fiber-based substrates of
20 the presently disclosed subject matter include both synthetic and natural fibers as well as fiber-based materials produced by natural or synthetic approaches, such as but not limited to, cotton fibers and fabrics, protein-based fibers such as silk, elastomeric polymers and fabrics (e.g., polyolefins such as polypropylene) and polyvinyl alcohol polymers and fabrics. The fabrics of the
25 presently disclosed subject matter include both woven and non-woven fabrics, and include, for example, a woven cotton fabric comprising yarns made up of many cotton fibers of different sizes and shapes.

As used herein the terms "micro-" and "nano-" have the meaning that would be ascribed to them by one of ordinary skill in the art. In some
30 embodiments, "micro" can refer to a structural feature having a dimension (e.g., a thickness) ranging from about 100 microns to about 1 nanometer in size. In some embodiments, the structural feature has a dimension ranging from about 10 microns to about 1 micron in size. In some embodiments, "nano" refers to a

structural feature having a dimension ranging from about 1 micron to about 1 nm in size. In some embodiments, the structural feature has a dimension ranging from about 1 micron to about 10 nm in size. In some embodiments, the structural feature has a dimension ranging from about 100 nm to about 1 nm in
5 size.

In some embodiments, the term "thin film" refers to a film deposited on a surface of a substrate wherein the film has a thickness ranging between about .1 nm to about 100 microns. In some embodiments, the thin film has a thickness that is between about 1 nm and about 10 microns.

10 The terms "non-reactive" or "inert" refer to a gas that does not react with any component present in the process (e.g., with a vapor-phase reactant or vapor-phase precursor or with the substrate surface). In some embodiments, the non-reactive gas is a noble gas (e.g., argon (Ar), helium (He), or neon (Ne)) or nitrogen (N_2) gas.

15 The term "closed reaction chamber" refers to a chamber that can be maintained under vacuum. In some embodiments, a closed reaction chamber refers to a chamber or a vessel than can be maintained under a vacuum of about 10^{-1} Torr to about 10^{-4} Torr. In some embodiments, a closed reaction chamber refers to a chamber or a vessel that can be maintained at a pressure
20 of about 0.0001 Torr to about 500 Torr.

A process for low temperature ALD is described, for example, in U.S. Patent No. 6,090,442. "Low temperature" ALD can be considered deposition at temperatures less than about 200°C. For instance, the temperature can approach room temperature (i.e., about 20 or 25°C), depending on the reactant
25 chemicals and reaction conditions employed.

The use of the term "or" in the claims is used to mean "and/or" unless explicitly indicated to refer to alternatives only or the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and "and/or." As used herein "another" can mean at least a second
30 or more.

II. General Considerations

The presently disclosed subject matter relates generally to methods and apparatuses for modifying a substrate (e.g., depositing a thin film) by an ALD or similar process (e.g., molecular layer deposition (MLD), sequential vapor infiltration (SVI), and multi-pulse infiltration (MPI)). For example, an ALD process can be defined by sequential exposures of a substrate to vapors that react with a surface of the substrate, separated by an inert gas purge. An SVI process can be defined by increased exposure of a gas to a surface and material growth that is characterized as being sub-surface.

More particularly, ALD can comprise a repeated binary sequence of self-limiting precursor adsorption and reaction steps. During the process, the self-limiting nature of the precursor adsorption results in material being built up as a series of atomic layers. Vapor-phase precursor molecules can be pulsed over a substrate and react with available substrate surface groups, creating a saturated substrate surface. Excess precursor can be removed from the vapor phase by a purge gas (e.g., Ar). Then, the reactant gas can be pulsed onto the substrate, where it reacts with the adsorbed precursor layer to form a layer of the target film-forming material. Since no gas phase reaction occurs, the target film can be grown layer-by-layer on the substrate. Therefore, the film thickness is directly controlled by the number of reactant exposure cycles used.

A single ALD cycle can typically deposit about 0.1 to about 0.5 nm of a film. Thin film thicknesses of from about 3 nm to about 30 nm can be formed by repeated ALD cycles for semiconductor applications. Even thicker films (e.g., up to 100 nm, up to 1 micron, or up to 10 microns or more) can be provided by repeated ALD cycles for other applications. The growth rate can be adjusted by changing one or more of a number of parameters of the ALD process (e.g., the precursor and reactant, pulse time, gas flow, gas velocity, temperature, pressure, and such).

The self-limitation of the ALD process can allow increased conformality of ALD films on various substrates. Due to the fact that surface saturation can occur on all surfaces, conformality can be achieved for very high aspect ratio substrates. The partial reaction of the precursor in each deposition cycle

differentiates ALD from more common chemical vapor deposition (CVD) processes and provides ALD an ability for high precision film formation.

According to the presently disclosed subject matter, the modification process can be performed at atmospheric pressure and in the absence of a closed reaction chamber. Generally, the presently disclosed processes and/or apparatuses do not rely on the movement of the substrate (e.g., to complete the formation of a complete atomic layer by moving the substrate between a zone for depositing one reactant (e.g., a precursor) and a zone for depositing a second reactant). Thus, in some embodiments, the presently disclosed subject matter does not relate to a "spatial" ALD process.

In some embodiments, the substrate of the presently disclosed subject matter can be porous and the reactant and/or non-reactive gases can be directed in a flow or flows to an outer surface of the substrate and/or within the substrate (e.g., to an interior surface of the substrate). In some embodiments, the flow or flows can be directed through a substrate. Thus, in some embodiments, the presently disclosed apparatus or methods can provide infiltration or bulk modification of a porous substrate. In some embodiments, all of the surfaces (both inner and outer) of a substrate are coated to provide a conformally coated porous substrate.

In some embodiments, the presently disclosed subject matter more particularly relates to the production of conformal, uniformly thin films on a surface of a substrate with precise thickness and composition control over large scales. Thus, in some embodiments, the presently disclosed subject matter provides a relatively low cost method to deposit thin conformal coatings of metal oxides and other materials onto surfaces with arbitrary size and shape, wherein the surface can be maintained in the ambient environment during the deposition.

A wide variety of materials can be deposited by the present methods, including metals, metal oxides, metal nitrides, polymers, organic-inorganic hybrid layers, and other materials. Specifically, the deposition of certain materials, such as, but not limited to, Al_2O_3, TiO_2, TiN, and SiO_2 for example, can be conducted by ALD at relatively low temperatures (e.g., less than about 200°C, less than about 150°C, less than about 100°C), thereby limiting thermal

damage to temperature-sensitive materials, such as textiles and polymer fiber media. In addition to creating thin films of one material, ALD can also be used to create microstructures and nanostructures, such as but not limited to nanolaminates of different materials.

5 Thus, the presently disclosed subject matter pertains in some embodiments to the use of ALD as a method of coating fiber-based substrates (e.g., textiles or polymer fiber-based materials) or fibers (e.g., nanofibers) with thin films of materials, such as but not limited to metals and metal oxides. Due to the high curvature and heterogeneous nature of fibrous structures, existing 10 surface modification technologies often provide less than complete and uniform coverage of a textile material's surface. However, the use of self-limiting reactant adsorption processes enables achievement of fully conformal functionalization of textile fibers of any continuous shape. This can allow for well-controlled surface energy modification of fibrous substrates.

15 The coating of textile media can provide UV protection (e.g., in clothing applications), pigment protection, chemical protection and/or mechanical or chemical stabilization. The textile materials that can be coated can comprise fibers, yarns, and fabrics either natural, man-made, or combinations of the two, and the textile materials can be in woven, knit, or nonwoven form. For 20 instance, inorganic coatings, including coatings of silver, copper, and various metal oxides, can increase the conductivity of textile material (e.g., carpet) to reduce static electricity build-up. Coatings of inorganic materials also allow the creation of multifunctional textiles. Multifunctional textiles are materials that possess a combination of many different properties such as flame retardancy, 25 water repellency, and antibacterial activity. These multifunctional textiles can be used for a number of different tasks, for example in such industries as medical, geotextiles and construction, upholstery, and filtration, to name a few. Also, modified textile materials can protect against mechanical, thermal, chemical, and biological attacks, and at the same time offer improved durability 30 and performance. Thus, the ALD-grown conformal thin films provided by the presently disclosed methods and apparatuses can be utilized, for example, as coatings for the creation of fabrics, such as cotton fabrics, with improved

moisture barrier properties, as well as for the functionalization of polypropylene and other polymer-based materials.

Inorganic materials are of particular interest as thin film coatings for fiber and textile materials. Coatings that are of particular interest are those which (1) improve stability of a material for mechanical, chemical, photo-chemical, or thermal destruction, (2) improve water, oil, and soil repellency properties of a material, (3) exhibit unique light absorption and emission properties in the UV and IR regions, (4) change the electrical conductivity of a material, (5) control release or immobilization of various active species. In addition, fibers and textile materials that are modified by such films can exhibit increased yield strength, reduced strain at yield stress, increased elastic modulus, increased fiber toughness, as well as increased wettability. It will be recognized by one of ordinary skill in the art upon a review of the instant disclosure that many materials are useful for more than one of these applications and that inorganic thin films will be useful for other applications not described here.

Examples of inorganic materials that can change the physical properties of fiber and textiles materials include, for example, various oxides, nitrides, and non-oxide materials. Titanium dioxide is a particular example of an oxide that can influence many different properties. Titanium dioxide is a wide band-gap semiconductor and is known to be a good oxidizing agent for photo-excited molecules and functional groups, making it useful as a photocatalyst or sensor material. Fibers coated with a thin film of titanium dioxide could provide high surface area catalytic mantles. Aluminum oxide is another good example of a coating material that can be deposited using ALD. Aluminum oxide has many favorable traits including strong adhesion to different substrate surfaces, good dielectric properties, and good chemical and thermal stability. Inorganic materials useful in the controlled release or immobilization of active species include, for example, titanium nitride, silver, and copper.

III. Methods of Modifying a Substrate

The presently disclosed subject matter provides, in some embodiments, methods of performing modification of substrate surfaces via atmospheric atomic layer deposition or related processes. The methods can be performed

without having to place the substrate in a closed reaction chamber. In some embodiments, the method does not comprise "spatial" ALD. Thus, generally, the methods do not rely on movement of the substrate or the apparatus providing chemical reactants to complete a deposition cycle.

5 In some embodiments, the presently disclosed subject matter provides a method for modifying a substrate, the method comprising: providing a substrate; contacting the substrate with a vapor-phase precursor comprising an organic or an inorganic component for a first period of time to create a partial layer (e.g., a partial atomic or molecular layer) of the organic or inorganic 10 component on the substrate, wherein the contacting comprises placing the substrate in proximity to an outlet directing a flow of the vapor-phase precursor to the substrate (e.g., to an outer and/or inner surface of the substrate or through the substrate); and contacting the substrate with a vapor-phase reactant for a second period of time to complete the formation of a layer (e.g., 15 an atomic or molecular layer) on the substrate, wherein the contacting comprises placing the substrate in proximity to an outlet directing a flow of the vapor-phase reactant to the substrate (e.g., to an outer and/or inner surface of the substrate); wherein said method further comprises providing a flow of a non-reactive gas to the substrate (e.g., to an outer and/or inner surface of the 20 substrate) during and/or after one or both of the contacting steps; and wherein said method is performed at atmospheric pressure, wherein the contacting is performed in the presence or absence of a closed reaction chamber, and wherein the method can be performed in absence of substrate or outlet movement. Providing a flow of non-reactive gas to the substrate during and/or 25 after one or both of the contacting steps can purge excess vapor-phase precursor and/or excess vapor-phase reactant. Provision of the flow of non-reactive gas can also prevent undesired non-surface reaction of the precursor and the reactant.

The contacting (or "dosing") steps can be repeated one or more times, 30 e.g., until the film attains the desired thickness. In some embodiments, the contacting steps are repeated to provide a thin film having a thickness of between about 1 nanometer (nm) and about 10 microns (i.e., about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95,

100, 125, 150, 175, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, or 950 nm or about 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5 or 10 microns). In some embodiments, the contacting steps are repeated at least 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 75,
5 100, 200, 300, 400, 500, or 1000 times or more.

In some embodiments, the film can have a thickness of less than about 1 nanometer. In some embodiments, the film can have a thickness that is about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, or about 0.9 nm.

A variety of different types of substrate can be modified according to the
10 presently disclosed methods. The substrate can have any shape (e.g., planar, curved, pointed, spherical, cylindrical, cubic, irregular, etc.) and can comprise any suitable material or combination of materials. In some embodiments, the substrate is non-planar (e.g., curved, pointed, spherical, irregular, etc). In some embodiments, the substrate is flexible. In some embodiments, the substrate is
15 non-flexible. In some embodiments, the substrate is non-porous. In some embodiments, the substrate is a porous substrate. In some embodiments, the substrate (e.g., the porous substrate) can be selected from the group including, but not limited to, a fiber-based substrate, a metal organic framework, a zeolite, or anodic aluminum oxide.

20 In some embodiments, the substrate used can comprise any fiber or textile material, such as, but not limited to, a fiber or textile material of a continuous shape. In this regard, the shape of the fiber or textile material need not be limited to common cylindrical fibers or planar substrates. In some embodiments, the presently disclosed methods can be used to create a
25 conformal coating of individual fibers having complex shapes and surface topologies (e.g., corrugated substrate, non-woven web). For example, a woven cotton fabric comprising yarns made up of many cotton fibers of different sizes and shapes can be used as a substrate. In another example, the textile material can be formed from melt blown polyolefin (e.g. polypropylene)
30 nonwoven fiber mats, wherein molten polymer is drawn through a quenching medium and hot air causes attenuations and fibrillation, creating fibers having large variability in diameter (e.g., about 0.2 to about 20 microns). In yet another example, the textile material can be spun bond polyolefin nonwoven fiber mats,

e.g., where molten polymer is extruded through a spin pack, quenched by cold air, lengthened and tangled by warm air, and calendared and compacted by rollers. The fiber mats produced in this manner can have a more uniform size distribution, with fibers having diameters of approximately 12 to 50 microns.

5 Thus, in some embodiments, the substrate is a fiber-based substrate (e.g., a fiber or a substrate comprising a plurality of fibers, such as a fiber mat or a woven or non-woven fabric). The fiber-based substrate can comprise natural fibers, synthetic fibers or both natural and synthetic fibers. In some embodiments, the fiber-based substrate is selected from, but not limited to, 10 cotton fiber, cotton fabric, woven cotton fabric, non-woven cotton fabric, protein-based fiber, polyvinyl alcohol fiber, polyvinyl alcohol fabric, woven polyvinyl alcohol fabric, non-woven polyvinyl alcohol fabric, polyolefin polymer fiber, polyolefin fabric, woven polyolefin fabric, non-woven polyolefin fabric, polyethylene terephthalate fiber, polyethylene terephthalate fabric, woven 15 polyethylene terephthalate fabric, non-woven polyethylene terephthalate fabric, polyamide fiber, polyamide fabric, woven polyamide fabric, non-woven polyamide fabric, acrylic fiber, acrylic fabric, woven acrylic fabric, non-woven acrylic fabric, polycarbonate fiber, polycarbonate fabric, woven polycarbonate fabric, non-woven polycarbonate fabric, fluorocarbon fiber, fluorocarbon fabric, 20 woven fluorocarbon fabric, non-woven fluorocarbon fabric, glass fiber, glass fabric, woven glass fiber, and non-woven glass fabric. In some embodiments, the substrate comprises one or more nanofibers. Nanofibers can have average diameters that are between about 1 micron and about 100 nm.

The substrate can comprise a natural or synthetic polymer-based 25 surface. In some embodiments, the polymer-based surface can comprise a material selected from, but not limited to, polyimide, polyethersulfone, cellophane, polydimethylsiloxane, polytetrafluoroethylene, wood, cellulose, cotton, polyvinyl alcohol, polyvinyl chloride, polystyrene, polyacrylonitrile, polyethylene, polybutylene, and polyethylene terephthalate.

30 In some embodiments, the substrate is substantially stationary during the contacting steps. Thus, the method can be performed without moving the substrate between contacting it with the vapor-phase precursor and contacting it with the vapor-phase reactant. However, in some embodiments, it can be

advantageous to move the substrate after the contacting steps so that the contacting steps can be repeated when another portion of the substrate is in proximity to an outlet. In some embodiments, the substrate is moved between contacting steps.

5 In some embodiments, the flow of vapor-phase precursor, vapor-phase reactant, and non-reactive gas can be provided by an apparatus comprising one or more gas delivery units, each gas delivery unit comprising: a first input for the non-reactive gas; one or more gas delivery channels, wherein a first end of each gas delivery channel is in flow communication (e.g., gaseous flow 10 communication) with at least an input for receiving the vapor-phase precursor or the vapor-phase reactant, and wherein a second end of each gas delivery channel comprises an outlet for directing a flow of gas to the substrate; and an output face in flow communication with the outlet of each of the one or more gas delivery channels, with the first input for the non-reactive gas, and with the 15 exterior of the gas delivery unit. In some embodiments, the outlet or outlets of the gas delivery channel or channels can each be between about 0.1 mm and about 0.5 mm (e.g., about 0.1, about 0.2, about 0.3, about 0.4, or about 0.5 mm) in diameter.

The gas delivery units can also be referred to herein as "gas delivery 20 heads" "reactors" (e.g., "single point reactors"), or "manifolds." In some embodiments, the gas delivery unit can have a single channel or a dual channel configuration, i.e., depending upon how many channels the unit has for vapor delivery of reactive vapors (i.e., for vapor-phase precursor and vapor phase reactant). The delivery units can comprise inner outlets for vapor delivery of the 25 reactive vapors, surrounded by an inert gas flow sheath. Various gas delivery units that can be used in the presently disclosed methods are described further hereinbelow.

During the contacting steps one face or outer surface of a substrate, e.g., one face of a porous substrate (i.e., the "delivery surface"), can be placed 30 in proximity to the output face of a gas delivery unit. In some embodiments, the apparatus of the presently disclosed subject matter can also include an exhaust system, which can be positioned in proximity to the opposite face of a porous substrate being modified than the face in proximity to the gas delivery unit. The

use of the exhaust system can provide one or more of: (1) assist in controlling the flow direction of the vapors from the delivery head through a porous substrate without potential mixing on the delivery surface or perpendicular to the flow direction, (2) promote a more linear pathway or vapor penetration into the porous substrate, (3) increase purge gas velocity and/or materials growth rate, and (4) allow for containment of excess reactive vapors to prevent materials deposition on unwanted regions of the substrate and/or of non-substrate surfaces. In some embodiments, the exhaust system can be used to provide pressure differential.

In some embodiments, the outlet or outlets of the one or more gas delivery channels are coplanar with the output face. In some embodiments, the outlet or outlets are in an interior space of the gas delivery unit. Thus, in some embodiments, the outlet or outlets are recessed (e.g., by between about 1 mm and about 20 mm) within the gas delivery unit, but the output face of the gas delivery unit has at least one opening (e.g., that is between about 0.1 mm and about 0.5 mm in diameter or larger (e.g., is about the diameter of the output face as a whole)) such that the outlet or outlets of the delivery channel or channels are still in flow communication with the exterior of the gas delivery unit. Thus, the reactant gases can be directed to a deposition zone on a surface of the substrate from the output face.

In some embodiments, at least one gas delivery unit comprises a gas delivery channel wherein the first end of the gas delivery channel is in flow communication with one or more input for sequentially receiving the vapor-phase precursor, the non-reactive gas, and the vapor-phase reactant, such that the outlet of the gas delivery channel can sequentially direct a flow of vapor-phase precursor, the non-reactive gas, and the vapor-phase reactant to the substrate. In some embodiments, at least one gas delivery unit comprises at least two gas delivery channels, wherein said at least two gas delivery channels comprise: a first gas delivery channel, wherein said first gas delivery channel has a first end in flow communication with one or more inputs for the vapor-phase precursor or for the vapor-phase precursor and the non-reactive gas, and a second end comprising an outlet for delivering the vapor-phase precursor or for sequentially delivering the vapor-phase precursor and the non-reactive

gas; and a second gas delivery channel, wherein said second gas delivery channel has a first end in flow communication with one or more inputs for the vapor-phase reactant or for the vapor-phase reactant and the non-reactive gas, and a second end comprising an outlet for delivering the vapor-phase reactant
5 or for sequentially delivering the vapor-phase reactant and the non-reactive gas. In some embodiments, each of the one or more gas delivery units of the apparatus for the presently disclosed methods can comprise one or two gas delivery channels.

When the gas delivery unit comprises two gas delivery channels (i.e.,
10 when the gas delivery unit is a "dual channel" unit), the first and second gas delivery channels can be substantially parallel to one another. However, in some embodiments, the first and second gas delivery channels are not substantially parallel to one another. When the first and second gas delivery channels are not substantially parallel to one another, they can be oriented
15 relative to one another such that they join at or near their outlet ends to form a single combined outlet. For example, the single outlet can be at the vertex of an angle (e.g., a right or an acute angle) formed by a portion of the first and second gas delivery channels.

In some embodiments, the gas delivery unit comprises a first and a
20 second gas delivery channel (e.g., in substantially parallel orientation) and a partition between said first and second gas delivery channels. When the outlets of the first and second gas delivery channels are recessed in the delivery unit, the partition can extend from the outlets of the first and second gas delivery channels to the output face of the gas delivery unit (i.e., in a direction parallel to
25 the first and second gas delivery channels). In some embodiments, the partition can extend beyond the output face. In some embodiments, the gas delivery unit can comprise a second input for non-reactive gas such that the first input for the non-reactive gas is located on one side of the partition and the second input for the non-reactive gas is located on the other side of the
30 partition. Thus, both outlets (and their respective gas flows) can be surrounded by a sheath of non-reactive gas.

In some embodiments, providing the substrate comprises positioning an outer or external surface of the substrate between about 0.01 millimeters and

about 20 millimeters from an output face of a gas delivery unit. In some embodiments, an outer or external surface of the substrate can be positioned between about 0.02 millimeters and about 1.0 millimeters from an output face of a gas delivery unit. In some embodiments, an outer or external surface of the substrate can be positioned between about 0.02 millimeters and about 0.5 millimeters (e.g., about 0.02, 0.04, 0.06, 0.08, 0.1, 0.12, 0.14, 0.16, 0.18, 0.2, 0.22, 0.24, 0.26, 0.28, 0.3, 0.32, 0.34, 0.36, 0.38, 0.4, 0.42, 0.44, 0.46, 0.48, or 0.5 mm) from an output face of a gas delivery unit.

The output face can have any desired shape, such as, but not limited to, circular, oval, square, rectangular, etc. In some embodiments, an outlet for delivering the vapor-phase precursor and/or reactant is located substantially in the center of the output face or in flow communication with the center of the output face. In some embodiments, at least an outlet for the vapor-phase precursor is located such that it is substantially at, or can direct a flow of vapor-phase precursor through, the center of the output face. (e.g., through an opening located at or about at the center of the output face).

In some embodiments, a spacer can be extended from the output face (e.g., from an outer edge of the output face). The spacer can be useful in positioning the substrate relative to the gas delivery unit, in directing the flow of gases, and/or to prevent unwanted surface modification on portions of the substrate where no surface modification is desired.

In some embodiments, the apparatus comprises a plurality of gas delivery units (e.g., 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 100, 500, or more gas delivery units). The plurality of gas delivery units can be in a linear or two-dimensional array. In some embodiments, providing the substrate comprises positioning the substrate such that a plurality of portions of an outer or external surface of the substrate are in proximity to the output faces of a plurality of gas delivery units. Thus, the use of a plurality of gas delivery units can provide for simultaneous surface modification of a large continuous portion of a substrate or can provide for surface modification of a plurality of separate portions of a substrate. Thus, the use of an array of gas delivery units can provide a patterned modified substrate.

In some embodiments, the gas delivery unit or gas delivery units can be translated relative to the substrate between ALD cycles. This translation can be done manually or mechanically (e.g., via a robotic arm). Particularly as there is no need for an enclosed reaction chamber, the gas delivery unit or units (e.g., 5 an array of gas delivery units) can be provided as a portable or hand held ALD "gun", "pen", or "jet." The ALD gun can be used to modify the surfaces of large and/or complex geometry substrates (e.g., steel I-beams or ship hulls) by coating a plurality of portions of the outer surface of the substrate sequentially, moving the ALD gun from proximity to one portion of the surface into proximity 10 with another portion of the surface between ALD cycles.

In some embodiments, the vapor-phase precursor comprises a metal-containing compound, comprising a metal such as, but not limited to, aluminum, zinc, titanium, tungsten, or zirconium. In some embodiments, the vapor-phase precursor comprises, for example, trimethylaluminum (TMA), diethyl zinc (DEZ), 15 titanium tetrachloride ($TiCl_4$), tungsten hexafluoride, titanium isopropoxide, or zirconium tertbutoxide (ZTB). In some embodiments, the flow of the vapor-phase precursor is provided at a flow rate between about 0.001 and about 5.0 standard liters per minute (slm). Thus, the flow rate can be about 0.001, 0.005, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 2.0, 3.0, 4.0, or about 20 5.0 slm. In some embodiments, the flow of the vapor-phase precursor is provided at a flow rate between about 0.05 slm and about 0.2 slm (e.g., about 0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.11, 0.12, 0.13, 0.14, 0.15, 0.16, 0.17, 0.18, 0.19, or about 0.2 slm). In some embodiments, the flow of the vapor-phase precursor is provided at a flow rate between about 0.15 slm and about 0.3 slm. 25 In some embodiments, the first period of time (i.e., the first "dose" time) is between about 0.01 seconds and about 60 seconds. In some embodiments, the first period of time is between about 0.1 seconds and about 2.0 seconds (e.g., about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0. 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, or about 2.0 seconds).

30 Any suitable vapor-phase reactant can be used. In some embodiments, the vapor-phase reactant can comprise oxygen, nitrogen, carbon or silicon atoms, or combinations thereof. In some embodiments, the vapor-phase reactant is selected from the group including, but not limited to, H_2O (i.e., water

vapor), NH_3, ozone, O_2, CO_2, CO, NO, N_2O, NO_2, SiH_4, and Si_2H_6. In some embodiments, the vapor-phase reactant is provided at a flow rate between about 0.001 and about 5.0 slm. Thus, the flow rate for the vapor-phase reactant can be about 0.001, 0.005, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 2.0, 3.0, 4.0, or about 5.0 slm. In some embodiments, the vapor-phase reactant is provided at a flow rate between about 0.05 slm and about 0.2 slm (e.g., about 0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.11, 0.12, 0.13, 0.14, 0.15, 0.16, 0.17, 0.18, 0.19, or about 0.20 slm). In some embodiments, the vapor-phase reactant is provided at a low rate between about 0.15 slm and about 0.3 slm. In some embodiments, the second period of time (i.e., the second "dose" time) is between about 0.01 seconds and about 60 seconds. In some embodiments, the second period of time is between about 0.1 seconds and about 2.0 seconds (e.g., about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, or about 2.0 seconds). In some embodiments, the vapor-phase reactant is H_2O, the vapor-phase precursor is TMA and the method comprises modifying the substrate with aluminum oxide.

Any suitable non-reactive (e.g., chemically inert) gas can be used. In some embodiments, the non-reactive gas is nitrogen or argon. In some embodiments, the non-reactive gas is provided at a flow rate between about 1 and about 100 slm (e.g., about 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90 or 100 slm). In some embodiments, the non-reactive gas is provided at a flow rate between about 5 and about 20 slm (e.g., about 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 slm). In some embodiments, a flow of a non-reactive gas is provided for between about 1 second and about 300 seconds after the first period of time and before the second period of time and/or after the second period of time. In some embodiments, the flow of a non-reactive gas is provided for about 40 seconds after the first period of time and before the second period of time and/or after the second period of time. In some embodiments, the flow of a non-reactive gas is provided for about 10 seconds after the first period of time and before the second period of time and/or after the second period of time. In some embodiments, the flow of a non-reactive gas is provided for more than about 300 seconds after the first period of time and before the second period of time and/or after the second

period of time. In some embodiments, a flow of non-reactive gas is provided during the first and/or second periods of time. Thus, the methods can comprise one or more purge steps and/or can involve the use of a continuous flow of purge gas.

5 The methods described herein can provide modified dose and purge times based on the nature of the substrates used. Depending on the characteristics of the substrate, longer dose and purge times can be necessary to completely saturate the surface. For example, a dense, layered, nonwoven fiber web would require longer dose and purge times when compared to a 10 loosely knit fibrous structure. In addition, reactants generally require longer times to diffuse into the porous and/or fiber samples (such as cotton fiber samples), possibly leading to a change in the growth rate. Thus, surface modification in accordance with the presently disclosed subject matter can include adjusting the dose times to allow for penetration into the bulk of a 15 fibrous substrate and/or adjusting purge times to provide complete removal of reactive gases.

The presently disclosed methods can be performed at low temperatures ranging from 20 or 25 to 200°C, depending on the nature of the fiber or textile material being used. Synthetic fibers may have a range of melting 20 temperatures depending on the polymer they are constructed from. For example, polypropylene fibers have a melting point of 150°C. Natural fibers, such as cotton fiber, have a burning point rather than a melting point and start to degrade at temperatures over 100°C. Precursors and reactants of sufficient reactivity, such as trimethylamines, can be used in order to improve deposition 25 at low temperatures. The ALD process can be carried out at low temperatures in order to prevent degradation of the fiber and textile substrates. Fiber and textile materials are often very sensitive to temperature changes, resulting in changes to their performance capabilities. Therefore, it can be advantageous to keep reaction temperatures as low as possible. The reaction temperature 30 can be increased or decreased depending on the nature of the particular fiber or textile substrate being used.

In some embodiments, one or both contacting steps are conducted at a temperature between about 20°C and about 200°C (e.g., at about 20, 30, 40,

50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, or about 200°C). In some embodiments, one or both contacting steps are conducted at a temperature that is less than about 150°C or less than about 100°C. In some embodiments, the temperature is selected to limit thermal damage to the
5 substrate (e.g., to a temperature-sensitive substrate such as a textile or polymer fiber-based substrate). In some embodiments, one or both contacting steps are conducted at 120°C. In some embodiments, one or both contacting steps are conducted at a temperature of about 50°C. In some embodiments, reaction temperature can be controlled by heating or cooling the gas delivery units of the
10 presently disclosed subject matter or heating or cooling gas delivery lines running into the gas delivery units.

In some embodiments of the presently disclosed subject matter, a method is provided for depositing polymer films comprising providing a substrate (e.g., a fiber-based substrate); contacting the substrate with a vapor-
15 phase precursor comprising an organic monomer to create an atomic layer of the organic monomer on the substrate; and contacting the substrate with a vapor-phase reactant comprising a complementary organic monomer; wherein said method further comprises providing a flow of a non-reactive gas to the substrate surface during and/or after one or both contacting steps. The
20 contacting steps can be repeated until the desired thickness of polymer films is deposited. In some embodiments, the polymer films are deposited on fiber-based substrates using a precursor and reactant that have complementary end-groups to enable binary self-limiting reaction steps. In some embodiments, the complementary end-groups include but are not limited to end-groups such as
25 aldehyde, anhydride, amine, ethylene and sulfide. In some embodiments, the precursor comprising the organic monomer can be pyromellitic dianhydride and the reactant comprising the organic monomer can be phenylene diamine. In some embodiments, the precursor comprising the organic monomer can be phenylene diamine and the reactant comprising the organic monomer can be
30 phenylene dialdehyde. The examples provided above are a small representative subset of precursor and reactant molecules that can be used for deposition of polymer layers.

In some embodiments of the presently disclosed subject matter, the final structure of the thin film can comprise a combination of layers, such as but not limited to metal containing layers stacked on one another. For example, a film comprising alternating layers of Al_2O_3 and TiO_2 can be fabricated. Thus, in some embodiments, the contacting steps are repeated one or more times and then the substrate is subjected to one or more cycles of a method involving a different vapor-phase precursor and/or vapor-phase reactant.

In some embodiments of the presently disclosed subject matter, methods are provided for atomic layer deposition of a hybrid organic-inorganic film on a substrate. The method can include providing a fiber-based substrate, contacting the substrate with a vapor-phase reactant comprising a first component comprising an organic or an inorganic component, and contacting the substrate with a vapor-phase reactant comprising an organic or an inorganic component (i.e., depending on the first component), wherein said method further comprises providing a flow of a non-reactive gas to the substrate during and/or after one or both contacting steps, and repeating the pulsing and purging steps as necessary until the desired thickness of hybrid films is deposited. If the reactant is an organic component, the co-reactant can be an inorganic component (or vice versa). For instance, the presently disclosed method can be used for the step-wise deposition of ethylene glycol and diethyl zinc to provide a hybrid film.

In some embodiments of the presently disclosed subject matter, the surface energy of fiber-based substrates can be modified. For instance, the surface energy of the fiber-based structure can be modified to form a uniformly hydrophilic surface. A uniformly hydrophilic surface will demonstrate the same contact angle (<90°) over the surface of the sample.

In some embodiments of the presently disclosed subject matter, methods are provided for fabricating replica structures of both natural and synthetic fibrous systems. Replicate fiber structures can be created by performing ALD on various fiber formats (including cotton fiber formats), including single fibers, yarn bundles and woven fabrics, and subsequently removing the cotton fibers. With a sufficiently thick ALD coating, removal of the core fibers results in free-standing micro- and/or nanostructures (e.g., Al_2O_3 tubules) as fibers, "yarns"

and woven structures. The resulting yarns and woven structures are surprisingly flexible and robust, even after the fiber core is removed. Only a very small number of cycles are needed to obtain measurable free-standing micro- and/or nanostructures. Such templated structures, developed from
5 readily available woven or non-woven fiber and fabric materials can act as an inorganic base material for a range of advanced devices. Moreover, the ability to fabricate and manipulate free-standing materials that are less than 10 Å thick is a unique attribute of ALD that can be exploited for any of a variety of micro- and nanoscale applications. In other related embodiments, ALD processes can
10 be used to form porous micro- and/or nanostructures. The porous nanostructure can have a controlled porosity based on desired properties for the structure.

In some embodiments of the presently disclosed subject matter applications are provided for micro- and nano-fluidics. Microfluidics is an
15 enabling technology that makes possible the study of a range of biological and chemical systems. Typical applications include microliter to femtoliter chemical analysis and reaction, medical diagnostics, chemical and bio-chemical separation, and environmental monitoring. Moreover, microfluidics offers engineered structures with dimensions comparable to that of individual cells,
20 organelles, and single biomolecules. Laboratory microfluidic systems are typically fabricated by casting polydimethylsiloxane (PDMS) against a mold and affixing it to a suitable flat surface. PDMS has several advantages over other materials, particularly its low cost and ease of fabrication. However, PDMS has significant limitations, especially in contact with organic media. A key problem
25 with PDMS is that it is hydrophobic, so the channels are difficult to wet and they tend to bind hydrophobic bio-materials. The surface can be relatively inert, so that there is no available simple route for surface modification, although many methods to modify PDMS have been evaluated. Moreover, there is interest in moving from flat 2D system geometries to more complex 3D fluidic systems.
30 Accordingly, in some embodiments of the presently disclosed subject matter, methods are provided for preparing microfluidics structures. In some embodiments the methods involve material nucleation on a hydrophobic surface. In this manner, the ALD process can enable a structural characteristic

(e.g., a dimension of a microfluidic channel) to be controlled at the atomic monolayer level. In some embodiments, an ALD process is performed in micro- or nanostructures (e.g., microfluidic channels) inside a mold, such as a PDMS template. Starting with a mold, channels can be coated using ALD. Then the mold can be removed, resulting in a micro- or nanostructure. In some embodiments, the micro- or nanostructure can be an Al_2O_3 based microfluidic structure.

Representative micro- and nanoscale systems and uses, including microfluidic systems and uses, are disclosed in the following published documents, which are incorporated herein by reference in their entirety: WO2005/101466, WO2005/084191, WO2007/021755, WO2007/021809, WO2007/021810, WO2007/021811, WO2007/021812, WO2007/021813, WO2007/021815, WO2007/021816, WO2007/021817, and WO2007/024485.

IV. Apparatus for Atmospheric Surface Modification

In some embodiments, the presently disclosed subject matter provides an apparatus that allows chemical deposition (e.g., film deposition) on a substrate without a closed reaction chamber and without moving the substrate or apparatus (e.g., during a single ALD cycle or series of cycles). In some embodiments, the apparatus can be used to provide localized deposition on a particular portion or portions of a substrate (e.g., a portion with a dimension of about several centimeters or less). For example, the apparatus can provide localized pulsed and/or sequential gas flow of reactant gases. Non-reactive gases can also be delivered by the apparatus to provide a barrier to enhance uniform deposition of the reactant gases.

In some embodiments, the apparatus can provide an array of gas delivery units to provide deposition on a larger area of the substrate or to provide patterned deposition on a substrate. In some embodiments, the apparatus, whether an array or non-array, can be rastered over or around the substrate to provide a patterned modified substrate.

Figures 1-10 show various exemplary apparatus and/or gas delivery unit configurations that are suitable for the presently disclosed methods. For instance, Figures 1, 2, 5, 6, and 7 provide examples of single channel gas

delivery units. Figures 3, 4, 9 and 10 provide examples of dual channel gas delivery units.

Referring now to Figure 1, shown is apparatus **100** having a delivery valve design (i.e., including valves **V-1**, **V-2**, **V-3**, and **V-4**) suitable for vapor delivery from liquid vapor-phase precursor source **A** and high pressure vapor-phase reactant source **B**. An inert gas, **IG** (e.g., argon, nitrogen, or helium), can be used as a carrier and/or purge gas. For delivery of vapor **A**, gas lines **110** can be arranged such that inert gas **IG** is routed through liquid vapor-phase precursor source **A** and into delivery channel **140** of the delivery head **120**. For this delivery, valves **V-1** and **V-2** are opened and valve **V-3** is closed. Similar designs can be made with two-way and three-way valves and/or when the vapor-phase reactant is from a liquid source and/or when the vapor-phase precursor is from a high pressure source. From high pressure vapor-phase reactant source **B**, a three-way valve can inject gas into a stream leading to delivery channel **140** or stop the inert gas flow by opening valve **V-4**. Valve sequencing and timing can be varied to supply the gases in a particular sequence and/or to provide a desired materials growth rate.

Continuing with Figure 1, apparatus **100** further includes a separate input **150** for providing additional inert gas to delivery head **120**. Substrate **160** can be positioned relative to delivery head **120** such that a gas flow from a recessed outlet **170** of gas delivery channel **140** is directed to a surface of the substrate. Optional exhaust system **180** can be positioned on the opposite face of substrate **160** to direct or pull the flow of excess vapors away from the substrate, such as in the direction of the arrows.

Referring now to Figure 2, shown is an apparatus **200** which includes gas delivery unit **220** having single gas delivery channel **210** for the sequential pulsing of vapor-phase precursor **A**, non-reactive gas (“inert ‘purge’ gas”, **IG**), vapor-phase reactant **B**, and non-reactive gas. Vapor phase-precursor **A**, inert gas **IG**, vapor-phase reactant **B**, and inert gas **IG** enter channel **210** via inlet **212** and are sequentially pulsed to a surface of porous substrate **260** from outlet **270** of channel **210**, located near the center of output face **240** of unit **220**. Unit **220** also includes separate inlet **215** for inert gas **IG**. Thus, a sheath of inert gas **IG** surrounds the flow of gases from delivery channel **210**. Optional

exhaust system **280** can direct excess gas away from the side of substrate **260** opposite to output face **240**. Gas flow is indicated by thin arrows (dotted arrows for **IG** sheath and solid arrows for flow from channel **210** and for excess gas/exhaust). Substrate **260** can be optionally translated relative to unit **220** as
5 indicated by the heavy arrows.

Referring now to Figure 3, shown is a dual delivery channel apparatus **300** wherein outlets **322** and **342** of two gas delivery channels (i.e., channel **320** for vapor-phase precursor **A** and inert purge gas **IG**, and channel **340** for vapor-phase reactant **B** and inert purge gas **IG**) are joined in gas delivery unit **380**
10 (e.g., at the vertex of an angle, such as a right or acute angle formed by ends of the channels) to create single outlet **385** for reactive gases to be directed to substrate **395**. Channels **320** and **340** include inlets **318** and **338**, and gas delivery unit **380** also includes separate inlet **360** for inert gas **IG** to provide a flow of inert gas **IG** to surround outlet **385**. Outlet **385** is coplanar with output
15 face **390** of unit **380**, but could alternatively be recessed inside unit **380**. Optional exhaust system **397** can be positioned to direct the flow of excess gas away from substrate **395**. Gas flow is indicated by thin arrows (dotted arrows for **IG** from inlet **360** and solid arrows for flow from outlet **385** and for excess gas/exhaust). Substrate **395** can be optionally translated relative to unit **380** as
20 indicated by the heavy arrows.

Dual delivery channel apparatuses can also be configured so that the outlets of the two channels are near or directly next to one another (e.g., in a plane parallel to or co-planar with the output face). Figure 4 shows dual delivery channel apparatus **400** having channels **410** and **415** with inlets **408**
25 and **413**. Each reactive gas (the vapor-phase precursor **A** and vapor-phase reactant **B**) is expelled from a separate outlet, **412** or **417**, such that the flows from outlets **412** and **417** are delivered in individual flow paths surrounded by inert gas **IG**. More particularly, apparatus **400** includes gas delivery unit **405** with two substantially parallel gas delivery channels (i.e., channel **410** for vapor-
30 phase precursor **A** and channel **415** for vapor-phase reactant **B**). Partition **420** extends between channels **410** and **415**, even extending beyond output face **440** of the delivery unit, which is coplanar with outlets **412** and **417** of channels **410** and **415**. Delivery unit **405** includes two separate inputs **430** and **435** for

inert gas **IG**, such that a sheath of inert gas **IG** can surround the flows of **A** and **B** from outlets **412** and **417** of channels **410** and **415**. Flows of gases (represented by thin arrows) are directed from unit **405** to porous substrate **460**. Optional exhaust system **480** can direct and/or pull excess gas away from substrate **460**. Substrate **460** can be optionally translated relative to unit **405** as indicated by the heavy arrows.

Figure 5 shows a bottom view of a single delivery channel apparatus **500** having a gas delivery unit **502** with a circular output face. Gas delivery unit **502** comprises a gas delivery channel for reactive gases (cross-hatching) with a circular outlet **506**, which has a diameter **d** and is surrounded by a ring **508** in flow communication with a flow of inert gas **IG** (stippling) which can enter (arrow) unit **502** via side inlet **504**. Figure 6 shows a bottom view of a single delivery channel apparatus **600** having a rectangular output face **602**. Outlet **604** of a gas delivery channel for reactive gases (cross-hatching) can have dimensions **l** and **w** and can be surrounded by an outer area **606** in flow communication with a non-reactive gas **IG** which can enter (arrows) apparatus **600** from a side inlet **608**. In some embodiments, a substrate sheet (not shown in Figure 6) can be moved past output face **602** at a constant rate to modify several continuous portions of the substrate.

Figure 7 shows how movement of apparatus **700** comprising a single point reactor (i.e., comprising single gas delivery unit **710**) can provide a patterned film **725** on substrate **720**. Single point reactor **710** is placed in proximity to, but not touching, an outer surface of substrate **720**. Single point reactor **710** includes a gas delivery channel **712** for sequentially pulsing vapor-phase precursor **A**, inert gas (**inert**), vapor-phase reactant **B**, and inert gas (**inert**) to a surface of substrate **720**, as well as a separate inlet **714** for inert gas (**inert**). Optional exhaust system **730** can be placed in proximity to an opposing outer surface of substrate **720** from the surface in proximity to reactor **710**, e.g., to enhance gas flow and/or remove excess gases (arrow). Between ALD cycles from the sequential pulsing of the gases, reactor **710** can be translated in the x and y directions in a plane over the surface of substrate **720** to create pattern **725** of a deposited film. The apparatus can be moved manually or via an electronically controlled and/or mechanized translation or

rastering system (not shown). Arrays (e.g., linear, square, rectangular, circular, or other shaped) of multiple gas delivery units can also be rastered or translated over a surface or surfaces of a substrate to provide a patterned modified substrate.

5 While more typically each gas delivery unit of the presently disclosed subject matter can deliver all the reactive gases for a desired surface modification (e.g., all of the reactive gases for a particular ALD modification cycle), Figure 8 shows an apparatus **800** that includes roller system **820** for moving substrate **840** (e.g., a length of fabric) past array **810**. Array **810** 10 includes a linear series of gas delivery units **812** wherein every other gas delivery unit delivers the vapor-phase precursor **A** and the non-reactive gas **I**. The remaining gas delivery units deliver the vapor-phase reactant **B** and the non-reactive gas **I**. Thus, in some embodiments, roller system **820** can be used to translate substrate **840** so that portions of the substrate that have been 15 contacted with precursor **A** are moved into proximity with a flow from a delivery unit that provides reactant **B** (e.g., to complete formation of an atomic layer of film). Flow of **A**, **B**, and **I** from units **812** is indicated by the thin straight arrows. Movement of roller system **820** is indicated by curved arrows. Alternatively, in some embodiments, the vapor flows from the individual delivery units can be 20 directed so that there is overlap between the deposition zones from the precursor and reactant delivery units. If there is overlap between the deposition zones, translation of the substrate is not necessary to complete formation of an atomic layer, but can be performed so that modification of a different portion of the substrate can be performed. In either case, the roller system can be used 25 to position the substrate at a particular distance from the array (e.g., 20 mm or less, but not directly in contact) to optimize surface modification. Also, in either case, optional exhaust system **860** can be provided in proximity to an opposing outer surface of substrate **840** from the outer surface in proximity to array **810**, to direct excess gas away from the substrate (indicated by the thick straight 30 arrow).

Figure 9 shows another embodiment of a multiple gas delivery unit apparatus. More particularly, Figure 9 shows an apparatus **900** comprising a linear array **902** of single point reactors **904** (i.e., gas delivery units), wherein

each single point reactor **904** includes delivery channels **906** for a vapor-phase reactant **R** (e.g., H_2O) and a vapor-phase precursor **P** (e.g., trimethylaluminum, TMA), and an inlet **908** for a non-reactive (nitrogen, N_2) gas **IG**. Thus, each reactor **904** shown in Figure 9 is a dual channel gas delivery unit. In alternative embodiments (not shown), one or more of the delivery units of Figure 9 could be a single channel unit that delivers both precursor **P** and reactant **R** (e.g., via sequential pulsing through a single delivery channel). As pictured in Figure 9, outlets **910** and **912** of the two delivery channels **906** are located at (i.e., are co-planar with) output face **914** of a single point reactor. In alternative embodiments (not shown), the outlets can be recessed in the body of the reactor (e.g., by about 1 to about 20 mm). A substrate **S** (e.g., a porous substrate), which can be movable or fixed, can be positioned in proximity to the output faces (e.g., within about 20 mm or less). For example, while not shown in Figure 9, a roller system such as that shown in Figure 8 could be added to the apparatus of Figure 9 to facilitate movement of substrate **S** between material deposition cycles. Alternatively, substrate **S** can be positioned by a frame or other type of support. Further, gases can be removed from the underside of the substrate (e.g., using an optional exhaust system).

As shown in Figure 9, each of reactors **904** is a tubular body (e.g., with a largest diameter of about 0.5 to about 1 cm) that tapers toward an end comprising circular output face **914**. However, larger diameter single point reactors can also be used. For example, although not shown in Figure 9, each of the reactors could have a tubular body that has a largest diameter of between about 0.5 cm and about 4 cm. Gas flow (as shown by arrows) from the outlets **910** and **912** can spread out from output face **914** to provide a conical area over substrate **S** where gas flows toward substrate **S**. This area can be referred to as the "deposition zone" **DZ** and is located over a portion of the substrate where, for example, an atomic layer is deposited by an ALD cycle or cycles to provide a coated substrate **CS**. Thus, the substrate surface area modified by each reactor can be somewhat larger in diameter than the output face of the gas delivery unit. If desired, the individual reactors in the array can be positioned such that there is a gap between the deposition zones and a patterned (e.g., dotted) and/or non-homogenous film is provided on the surface

of the substrate. In some embodiments, the delivery units are provided such that deposition zones **DZ** touch or overlap to provide a continuous and/or homogenous surface modification on substrate **S**. Thus, using linear array **902** shown in Figure 9, for example, a series of adjoining portions of substrate **S** can be modified to provide coated substrate **CS**. The shape of deposition zone **DZ** can vary depending upon the shape of output face **914**. In addition to the linear array shown in Figure 9, the array of multiple single point reactors can be provided as a two dimensional (e.g., square or rectangular) array.

Figure 10 shows apparatus **1000** comprising dual channel single point reactor **1010** with two satellite non-reactive gas delivery units **1090**. Single point reactor **1010** has two delivery channels (i.e., **1020** for delivery of vapor-phase precursor (**A**) and **1030** for delivery of vapor-phase reactant (**B**)) and side input **1040** for a non-reactive gas (**NRG**). Outlets **1050** of delivery channels **1020** and **1030** are in the interior of single point reactor **1010**, recessed from output face **1060**. Gas flow is directed from opening **1070** in output face **1060** to substrate **1080**, providing a deposition zone as indicated by the single headed arrows under reactor **1010**. Spacers **1075** are extended from the outer sides of output face **1060** toward substrate **1080**. Satellite non-reactive gas delivery units **1090** are positioned on either side of single point reactor **1010**. Satellite non-reactive gas delivery units can direct a flow of **NRG** to the surface of the substrate, thereby providing an area over the substrate that is substantially free of reactive gases **A** and **B** (see double headed arrows under each of the satellite non-reactive gas units). While satellite non-reactive gas delivery units **1090** as shown in Figure 10 are parallel to single point reactor **1010**, either or both could also be inclined at an angle (e.g., at an about 45 degree angle) from the axis of single point reactor **1010**. Referring again to Figure 10, exhaust **1095** from the process can exit from openings between spacers **1075** and satellite non-reactive gas delivery units **1090**. While Figure 10 shows two satellite non-reactive gas delivery units, additional satellite non-reactive gas delivery units can be provided to completely surround the single point reactor, if desired.

Thus, in some embodiments, the presently disclosed subject matter provides an apparatus for modifying a substrate, wherein the apparatus

comprises one or more gas delivery units, each gas delivery unit comprising: a first input for the non-reactive gas; one or more gas delivery channels, wherein a first end of each gas delivery channel is in flow communication with at least an input for receiving the vapor-phase precursor or the vapor-phase reactant, 5 and wherein a second end of each gas delivery channel comprises an outlet for directing a flow of gas to a substrate; and an output face in flow communication with the outlet of each of the one or more gas delivery channels and with the first input for the non-reactive gas, and is adapted for gaseous and/or flow communication with an exterior of the gas delivery unit.

10 In some embodiments, the outlet or outlets of the one or more gas delivery channels are coplanar with the output face. In some embodiments, the outlet or outlets are in an interior space of the gas delivery unit (e.g., recessed by a few millimeters or centimeters from the output face). In some embodiments, the outlet or outlets are recessed by about 1 to about 20 mm 15 (e.g., about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or about 20 mm) from the output face.

In some embodiments, the outlet for delivering a flow of the vapor-phase precursor (and/or the vapor-phase reactant) is at or near the center of the output face. In some embodiments, at least the outlet providing the vapor-20 phase precursor flow is at or near the center of the output face. In some embodiments, when the outlet is recessed in the gas delivery unit, the outlet for delivering a flow of the vapor-phase precursor (and/or the vapor-phase reactant) can be positioned such that gas flow is directed through or near to the center of the output face (e.g., through an opening in the center or near the 25 center of the output face).

The output face can have any shape, such as but not limited to, circular, square, rectangular, oval, etc. In some embodiments, the output face is square or rectangular. In some embodiments, the output face is substantially circular. In some embodiments, the output face has a diameter or other dimension (e.g., 30 length or width) that is about 0.5 cm or smaller. However, the output face can also be larger (e.g., be between about 0.5 cm and about 4 cm or larger). In some embodiments, the output face has an opening or a plurality of openings, wherein each opening is smaller in diameter than the output face as a whole,

for directing gas flow to the surface of a substrate. In some embodiments, one or more openings in the output face have a diameter between about 0.1 mm and about 0.5 mm (e.g., about 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 or 0.5 mm).

5 In some embodiments, the gas delivery unit comprises a tubular body comprising an input face at a first end of the tubular body adapted to receive one or more input ports and/or one or more gas delivery channels, and wherein the output face is at a second end of the tubular body. In some embodiments, the tubular body can be tapered such that the output face has a smaller 10 diameter than the input face. In some embodiments, the input face and/or main portion of the tubular body can have a diameter that is between about 0.5 and about 1.0 centimeters (e.g., about 0.5, 0.6, 0.7, 0.8, 0.9 or 1 cm). In some embodiments, the input face and/or main portion of the gas delivery unit body is larger than about 1 cm in diameter. In some embodiments, the input face 15 and/or main portion of the body is between about 1 cm and about 4 cm in diameter (e.g., about 1, 1.5, 2, 2.5, 3, 3.5, or 4 cm in diameter).

Each gas delivery unit can have one, two, three, four, five, ten, or more gas delivery channels. In some embodiments, the gas delivery units can each be single or dual channel gas delivery units (i.e., comprising one or two gas 20 delivery channels, respectively). Thus, in some embodiments, at least one gas delivery unit comprises a gas delivery channel wherein the first end of the gas delivery channel is in flow communication with one or more input for sequentially receiving the vapor-phase precursor, the non-reactive gas, and the vapor-phase reactant. See e.g., Figures 1 and 2. In some embodiments, at 25 least one gas delivery unit comprises at least two gas delivery channels, wherein said at least two gas delivery channels comprise: a first gas delivery channel, wherein said first gas delivery channel has a first end in flow communication with one or more inputs for the vapor-phase precursor or for the vapor-phase precursor and the non-reactive gas, and a second end comprising 30 an outlet for delivering the vapor-phase precursor or for sequentially delivering the vapor-phase precursor and the non-reactive gas; and a second gas delivery channel, wherein said second gas delivery channel has a first end in flow communication with one or more inputs for the vapor-phase reactant or for the

vapor-phase reactant and the non-reactive gas, and a second end comprising an outlet for delivering the vapor-phase reactant or for sequentially delivering the vapor-phase reactant and the non-reactive gas.

In some embodiments, the first and second gas delivery channels are substantially parallel to one another. See e.g., Figure 4. When the channels are substantially parallel to one another, the gas delivery unit can optionally comprise a partition between the first and second gas delivery channels, extending in a direction parallel to said channels, beyond the outlets of said channels toward and/or beyond the outlet face. The gas delivery unit can further comprise a second input for the non-reactive gas such that the first input for the non-reactive gas is located on one side of the partition and the second input for the non-reactive gas is located on the other side of the partition. Thus, the flow of gas from both gas delivery channels can be surrounded by sheath of non-reactive gas.

In some embodiments, the first and second gas delivery channels can join one another near or at their second ends to form a single outlet. See e.g., Figure 3. The single outlet can be formed, for example, at the vertex of a right (i.e., 90°) or acute (i.e., less than 90°) angle formed by portions of the bodies of the first and second gas delivery channels.

In some embodiments, each gas delivery channel outlet has a diameter of between about 0.1 mm and about 0.5 mm. For example, the outlet or outlets can have a diameter of about 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 or about 0.5 mm.

In some embodiments, the apparatus of the presently disclosed subject matter can comprise a substrate support. The support can aid in keeping the substrate positioned in proximity to, but not in direct contact with, the output face of the gas delivery unit. Suitable supports include, but are not limited to, stationary or adjustable platforms and frames, roller systems, and conveyor belts. Adjustable supports can be manually or mechanically adjustable. In some embodiments, supports can be adjusted via electronic control systems. In some embodiments, the support can support the substrate when the substrate is positioned about 20 mm or less from, but not in direct contact with, the output face. In some embodiments, the support can support the substrate

positioned about 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, or about 1 mm from the output face.

In some embodiments, the support is adapted to hold the substrate stationary. In some embodiments, the support is adapted to translate the substrate with respect to an output face. For example, the support can be adapted to translate the substrate in one or more directions in a plane parallel to the output face (between deposition cycles, e.g., to produce a patterned modified substrate) and/or can be adapted to adjust the distance of the substrate from the output face (e.g., to control the rate of deposition or the area size of the deposited film). In some embodiments, the apparatus can comprise a roller system for positioning and translating the substrate relative to one or more output faces.

In some embodiments, one or more gas delivery units of the presently disclosed apparatus can be translated with respect to a length, width, and/or height of a substrate. Thus, in some embodiments, one or more gas delivery units can be rastered over the substrate to provide a patterned modified substrate. In some embodiments, one or more gas delivery units can be provided as an ALD (or other modification process) "gun", which can be hand-held or robotically moved relative to a substrate surface.

In some embodiments, the apparatus comprises an array of gas delivery units. Thus, in some embodiments, the apparatus comprises a plurality of gas delivery units (e.g., 2, 3. 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 40, 45, 50, 75, 100, 200, 300, 400, 500, 1000 or more gas delivery units). The plurality of gas delivery units can be arranged in a single row to form a linear array of gas delivery units. The array can also be two-dimensional. Thus, the plurality of gas delivery units can be arranged in a plurality of rows to form a square or rectangular array of gas delivery units.

In some embodiments, the apparatus further comprises an exhaust system. For example, the exhaust system can create a pressure differential between the outlet or outlets of the one or more gas delivery channels and the substrate and/or to remove excess vapor-phase precursor, excess vapor-phase reactant, non-reactive gas, and/or any gaseous side products formed during

use of the apparatus. In some embodiments, the exhaust system can comprise a tube or manifold, a fan, and/or a vacuum.

Other optional features of the apparatus include, but are not limited to, one or more spacers, extending (e.g., perpendicularly) from the exterior of the
5 output face to assist in positioning the substrate; heating/cooling units (e.g., to control the temperature of the vapors and gases in the gas delivery units and/or in gas delivery lines leading into the gas delivery units), and one or more satellite gas delivery units, wherein each satellite gas delivery unit comprises a gas delivery channel for delivery of a flow of non-reactive gas to the substrate.
10 Each satellite gas delivery unit can be positioned adjacent to a gas delivery unit that delivers reactive gas to the substrate. Thus, in some embodiments, a gas delivery unit can be adjacent to one, two, three, or four satellite gas delivery units. The satellite gas delivery units can be used to localize the surface modification to one or more particular positions on the substrate and/or to
15 prevent undesirable gas-phase reactions. The satellite gas delivery unit can have its main axis parallel to that of a gas delivery unit or can be angled (e.g., have its main axis at an about 45 degree angle) relative to the main axis of the gas delivery unit.

In some embodiments, the apparatus can comprise a roller system and
20 an array of gas delivery units wherein each gas delivery unit delivers either a vapor-phase precursor or a vapor-phase reactant. Thus, in some embodiments, the apparatus comprises a roller system and an array of vapor-phase precursor delivery units and vapor-phase reactant delivery units, wherein each vapor-phase precursor delivery unit comprises a vapor-phase precursor
25 delivery channel, wherein a first end of the channel is in flow communication with one or more inputs for receiving the vapor-phase precursor or receiving the vapor-phase precursor and a non-reactive gas, and wherein a second end of the channel comprises an outlet for directing a flow of vapor-phase precursor and/or non-reactive gas to a substrate; wherein each vapor-phase reactant
30 delivery unit comprises a vapor-phase reactant delivery channel, wherein a first end of the channel is in flow communication with one or more inputs for receiving the vapor-phase reactant or receiving the vapor-phase reactant and a non-reactive gas, and wherein a second end of the channel comprises an outlet

for directing a flow of vapor-phase reactant and/or non-reactive gas to a substrate; and wherein the roller system can translate a substrate relative to the outlets of the array, e.g., such that a portion of the substrate is sequentially in contact with a flow from the outlet of a vapor-phase precursor delivery unit and 5 a flow from the outlet of a vapor-phase reactant delivery unit. An example of such an apparatus is shown in Figure 8. In some embodiments, the apparatus further comprises an exhaust system for creating a pressure differential between the outlets of the delivery channels and the substrate and/or to remove excess vapor-phase precursor, excess vapor-phase reactant, non-reactive gas, 10 and/or any gaseous side products formed during use of the apparatus.

V. Modified Substrates

In some embodiments, the presently disclosed subject matter provides a modified substrate (e.g., a modified porous and/or fiber substrate). In some 15 embodiments, the modified substrate is prepared by one of the presently disclosed methods and/or using one of the presently disclosed apparatuses. Thus, in some embodiments, the modified substrate is modified with a thin film (e.g., of aluminum oxide or another material that can be deposited by ALD or low temperature ALD), wherein the thin film has a thickness of less than 10 20 microns, less than 1 micron, less than 100 nm, less than 50 nm, less than 10 nm, or less than 1 nm. In some embodiments, the modified substrate is patterned with a thin film. Thus, for example, the modified substrate can be prepared using a method or apparatus wherein a gas delivery unit or units are rastered or otherwise translated over a surface of the substrate between ALD 25 cycles or wherein a substrate is moved relative to one or more gas delivery units for ALD between ALD cycles. In some embodiments, the modified substrate can be prepared wherein a roller or another support system translates the substrate relative to one or more gas delivery units between ALD cycles. In some embodiments, the presently disclosed apparatus or method provides a 30 modified fiber or porous substrate wherein the substrate is conformally modified. Thus, the presently disclosed subject matter can provide a fiber-based substrate (e.g., a fabric or fiber mat) wherein each fiber in the substrate is modified by a conformal and uniform thin film.

VI. Representative Embodiments

The presently disclosed subject matter relates generally to the production of thin films by atomic layer deposition (ALD) process or similar processes at atmospheric pressure and/or in the absence of a closed reaction chamber. Further, in some embodiments, the presently disclosed subject matter more particularly relates to the production of conformal, uniformly thin films with precise thickness and composition control over large scales. In some embodiments, the substrate modified using the presently disclosed method or apparatus is a fiber-based substrate.

In some embodiments, the presently disclosed subject matter can be used to coat and modify low-cost polymer fibers to produce a surface that can be readily functionalized. For instance, in some embodiments, the modification of the surface energy of the fiber-based substrate can entail atomic layer deposition for surface treatment for fiber-based filters by depositing a material with a strong surface charge, and thereby providing an efficient and durable approach to enable surface functionalization. In some embodiments, the substrate can be modified by ALD to provide a high-density amino-group functionalized surface. See U.S. Patent Application Publication No. 2009/0137043, incorporated herein by reference in its entirety. Referring to one specific example, a nonwoven fiber mat comprising a synthetic polymer such as polypropylene, after coating with ALD, can become a low-cost and easy to handle filtration platform to enable a chosen chemical functionality, such as affinity ligands, to be bound to the surface with very high density. Such novel device platform materials can result in a wide variety of new applications, including blood purification, water decontamination, specialty nanoparticle, and nanotube collection, as well as chemical and bio-hazard detection systems. A particular example is the production of precision modified low-cost nonwoven fibers for use in targeted protein filtration and separation devices, such as a blood filtration device. Such devices can be effective at removing transmissible spongiform encephalopathies caused by prion proteins in contaminated blood supplies. Experiments have shown that the surface energy of the coated fibers can depend on the material used for coating, as well as the thickness of the

ALD coating applied. The nonwoven fiber platform is an example of a complex surface topology, where the surface contour and appearance changes as one adjusts the scale of observation.

Other possible applications include, but are not limited to, new formats
5 and platforms for active electronic and energy conversion devices, as well as fuel cells, target-selective nano and biomolecule filtration and separation structures, tissue engineering scaffolds, and high performance engineered fibers and fabrics.

High surface area complex nanostructures are gaining interest in
10 electronic systems. Examples include organic-based photovoltaic structures and novel fuel cell designs where increased surface area enhances the overall device efficiency. (See, for example, U.S. Patent Nos. 3,969,163 and 7,160,424, the disclosures of which are incorporated herein by reference in their entirety.) In some embodiments of the presently disclosed subject matter,
15 highly uniform coating techniques such as ALD can allow modification of the surface functionality and composition within the complex nanostructure to broaden the applicability and reduce the fabrication cost of such device systems.

In some embodiments of the presently disclosed subject matter,
20 manufacturing techniques are of interest that can modify fiber surface functionality, as well as the bulk properties within a woven fabric to protect against mechanical, chemical, biological and thermal exposure, and effectively repel undesirable foreign substances, while maintaining the benefits of light-weight breathable fabrics. (See, for example, U.S. Patent Nos. 4,007,305,
25 4,623,574, 4,987,026, 5,298,303, and 6,187,391, the disclosures of which are incorporated herein by reference in their entirety.) Inorganic insulator and metallic coatings on engineered fabrics are capable of meeting at least some of these objectives. Extending reactive systems and components to fabric platforms to produce catalytic mantles is another area of application.

30 In some embodiments of the presently disclosed subject matter, methods are provided for reproducibly converting the surface of fiber systems into inorganic material forms to, for example, significantly change the wetting properties of filters and other separation media, or enable template fabrication

of hollow nanoscale needles, spheres, or other structures for bio-medical or tissue engineering applications. Also, in addition to surface chemistry, the wettability of a surface can be affected by the surface topography and roughness. For example a large contact angle observed for coated fibers can be ascribed to an increase in the fiber rigidity by the more incompliant inorganic coating, effectively reducing the total contract area between the fiber and the water droplet. For a super-hydrophobic material, a contact angle of greater than 120° is desired. Accordingly, the ability to conformally modify woven textile materials with near monolayer precision can provide new multifunctional textiles with properties and performance that deviate radically from current structured fabrics. As noted above, these multifunctional textiles can be used for a number of different tasks, for example in such industries as medical, geotextiles and construction, upholstery, and filtration, to name a few. In addition, these modified textile materials can still meet consumer demand in regards to comfort, ease of care, and health issues, and the modified textile materials can protect against mechanical, thermal, chemical, and biological attacks and offer improved durability and performance.

In some embodiments of the presently disclosed subject matter, methods are provided for surface modification of fiber webs using biocompatible materials such as TiN as a coating for implant materials including, for example, heart valves and orthopedics, due to the superior mechanical properties, corrosion resistance, and low cytotoxicity of TiN. TiN is often used as a hard, wear-resistant surface treatment, and it has been investigated as an antibacterial coating. The self-limiting film growth mechanism that is characteristic of ALD provides a technique to coat a wide range of substrates using conditions more favorable than other methodologies such as physical vapor deposition or plasma immersion ion implantation. Due to the nature of the process, self-limiting reactions allow for high precision of metallic and metal oxide deposition on the nano-scale. In addition, the use of ALD offers an environmentally friendly method for the formation of biocompatible materials. As a result, ALD processing can provide a valuable approach to control surface properties of fibers and other implant materials to promote preferred extracellular protein interactions for healthy cell adhesion and proliferation.

EXAMPLES

The following Examples have been included to provide guidance to one of ordinary skill in the art for practicing representative embodiments of the presently disclosed subject matter. In light of the present disclosure and the general level of skill in the art, those of skill can appreciate that the following Examples are intended to be exemplary only and that numerous changes, modifications, and alterations can be employed without departing from the scope of the presently disclosed subject matter.

EXAMPLE 1

Atmospheric ALD was performed using nitrogen (N_2) as the inert/purge gas, trimethylaluminum (TMA) as the vapor-phase precursor, and water as the vapor-phase reactant, forming a layer of Al_2O_3 on a substrate. The nitrogen, TMA, and water were provided via a dual channel gas delivery unit which could direct a flow of the precursor, reactant and purge gas to a surface of the substrate. In general, the N_2 flow rate for the water and TMA lines could be varied between about 0.5 and 1.0 slm and the N_2 flow rate for the purge line could be varied between 4 and 10 slm.

The effects of providing or not providing a continuous flow of inert gas via the purge line was determined as follows. Substrates were treated to 10 cycles of ALD, each cycle comprising a 1.0 second TMA dose (0.3 slm), a 40 second N_2 purge, a 1.0 second water dose (0.65 slm), and a 40 second N_2 purge. N_2 was provided at a flow rate of 4 slm. Some substrates received a continuous flow of inert gas while other substrates received inert gas only during the 40 second purge steps. The gas delivery unit was heated to 50°C. Without continuous purging, the modified substrate appeared to have particles on its surface. In contrast, the surface of the substrate modified using a continuous inert gas purge appeared to have no particles.

The effect of temperature was also studied. Using a gas temperature of either room temperature (about 20°C) or 50°C, substrates were exposed to 10 cycles of ALD using 1 second dosing times for TMA (0.3 slm) and water (0.65

slm). The purge gas flow rate was 4 slm. The modified substrate treated with gases heated to 50°C appeared slightly more homogenous.

In addition to the observations above, it was noted that orienting the TMA (vapor-phase precursor) line so that the flow of TMA was directed to the
5 surface of the substrate from the center or near the center of the output face of the gas delivery unit improved homogeneity of the modified surface.

EXAMPLE 2

As an outlet or output face opening of a gas delivery reactor of the
10 presently disclosed subject matter approaches a substrate, high gas flow rate (e.g., of the inert/purge gas) can create a low pressure region between the outlet or output face and the substrate. Without being bound to any one theory, it is believed that this phenomenon can be explained by Bernoulli's principal. More particularly, it has been observed that a low pressure region can be
15 created when there is a gap size of less than about 5 mm between the reactor output face and the substrate. As a result of the low pressure region, the substrate can be sucked up and become self-positioned relative to the output face without any physical bottom support. As the substrate floats at the reactor output face, the upward force exerted at atmospheric pressure balances with
20 downward force exerted by the high gas flow (e.g., of the carrier gas) out of the reactor. This can be attributed mainly to the high gas velocity coming out of the reactor structure (e.g., the tapered structure) at the reactor output face. After the substrate becomes self-floating at the reactor output face, the gas flow dynamics between the reactor output face and the substrate can resemble that
25 of a confined impinging jet at high velocities and low flow gap relative to orifice diameter.

Atmospheric ALD was performed on 12 mm x 12 mm silicon pieces using nitrogen (N_2) as the inert/purge gas, trimethylaluminum (TMA) as the vapor-phase precursor, and water as the vapor-phase reactant, thus forming a
30 layer of Al_2O_3 on a substrate. The nitrogen, TMA, and water were provided via a dual channel gas delivery unit which could direct a flow of the precursor, reactant and purge gas to a surface of the substrate. In general, the N_2 flow rate for the water and TMA lines could be varied between about 0.05 and 0.5

slm and the N_2 flow rate for the purge line could be varied between about 2 and about 20 slm and heated up to about 200°C. Figure 11 shows the growth rate of the Al_2O_3 film on the surface of the substrate as a function of number of ALD cycles.

5 To further show that the ALD process was the cause of film deposition, a control run was performed in which only TMA was dosed, followed by an inert purge step without any water doses. This TMA only dosing cycle was repeated 300 times. As shown in Figure 11, no significant deposition of Al_2O_3 occurred as the result of TMA only dosing at atmospheric pressure conditions, further 10 indicating that the film deposition with the TMA/water dosing cycle was the result of a true ALD process. While some film growth was found after the multiple TMA doses, this is believed to be most likely due to a small fraction of residual water that is commonly found in the inert carrier gas.

15 EXAMPLE 3

The film formed after 300 ALD deposition cycles as described above in Example 2 showed a three region (or zone) deposition pattern (e.g., within the deposition zone as a whole). See Figure 12. This deposition pattern is also represented schematically in Figure 13. The pattern is believed to be due to 20 changes in gas velocity along the substrate surface as the carrier (inert) gas exits an ALD point reactor and interacts with a substrate (i.e., a flat, non-porous substrate). See Figure 14, top view. Referring to the top view of Figure 14, gas flow (indicated by arrows) is directed from opening **1410** in output face **1415** of a single point reactor **1400** toward flat substrate **1420**. The gas flow that initially 25 impinges substrate **1420** at a point directly beneath opening **1410** is perpendicular to substrate **1420**, but then spreads radially outward. Under experimental conditions, it was determined that the size of the deposition regions of Figures 12 and 13 could be controlled and understood based on fluid flow dynamics.

30 For example, when operating with a high gas velocity and a low gap size between the exit (e.g., output face) of the ALD point reactor and the substrate, a confined turbulent flow develops outside the central ALD deposition zone (**Z1** in Figures 12 and 13), and the turbulent flow shows a small region (see the circular ring labeled **Z2** in Figures 12 and 13) of chemical vapor deposition

(CVD) Al_2O_3 outside of the central ALD deposition zone. The ring of **Z2** is relatively light in color in Figure 12 and black in Figure 13. The orthogonal jet profile and jet exit velocity is conserved up to the substrate surface. At the impinging point on the surface, the axial velocity is equal to the jet exit velocity and the radial gas velocity is almost zero. This results in a stagnant zone (i.e., **SP** of Figures 12 and 13) with a size equivalent to the orifice diameter (e.g., the outlet of the gas delivery channel or the diameter of an opening in the output face). The flow deviates from the stagnant point radially into what can be referred to as the "wall jet".

Outside of **SP**, the axial gas velocity drops considerably with increasing radial distance from **SP**, while radial gas velocity increases. As a result, the gas pressure decreases and the gas flow starts accelerating away from the stagnant point. As the gas flow accelerates, the Reynolds number continues increasing in the radial direction away from **SP** until the gas flow eventually undergoes transition to a turbulent flow region (**Z2** of Figures 12 and 13). This is equivalent to a development of the thin laminar boundary layer in the acceleration region until it develops to a turbulent boundary layer (refer to middle view of Figure 14, labeled boundary layer). Due to gas spreading, the turbulent flow does not sustain the gas flow for a long radial distance. Then the gas begins to decelerate and move back to a laminar flow region (**Z3** of Figures 12 and 13). The radial gas flow velocity is represented schematically in the bottom view of Figure 14.

Thus, more particularly, the regions/zones of Figures 12 and 13 can be described as follows:

SP (Stagnant point): maximum axial velocity, zero radial velocity, difficult gas purging.

Z1 (Zone 1, true ALD deposition zone): accelerating flow with a laminar boundary layer and low radial turbulence intensity.

Z2 (Zone 2, transition-small CVD zone): turbulent flow with maximum radial turbulence intensity and velocity. The position and size of this zone depends on the ALD reactor orifice to substrate separation distance, Reynolds number and orifice geometry.

Z3 (Zone 3, ALD like deposition zone): Decelerating flow of a likely laminar boundary layer depending on the jet exit velocity and outer surface pressure.

The size of the regions/zones can be controlled by decreasing the inert/purge gas flow rate. For example, 300 cycles of ALD deposition was performed on a silicon substrate as described above in Example 2, only changing the inert (N_2) gas flow rate from 10 to 7 slm. See Figure 15. When the inert gas flow was reduced, the diameter of **Z1** decreased from about 7.5 mm to about 5 mm. Thus, Figure 15 illustrates that the size of **Z1**, where the laminar flow region exists and true ALD deposition occurs, can be ultimately controlled by changing the impinging flow gas dynamics (e.g. inert gas flow rate, dose times, purge times) and by modifying the reactor deposition head dimensions.

It will be understood that various details of the presently disclosed subject matter can be changed without departing from the scope of the presently disclosed subject matter. Furthermore, the foregoing description is for the purpose of illustration only, and not for the purpose of limitation.

CLAIMS

What is claimed is:

1. A method for modifying a substrate, the method comprising:
5 providing a substrate;
contacting the substrate with a vapor-phase precursor comprising an organic or an inorganic component for a first period of time to create a partial atomic layer of the organic or inorganic component on the substrate, wherein the contacting comprises placing the substrate in proximity to an outlet directing
10 a flow of the vapor-phase precursor to the substrate; and
contacting the substrate with a vapor-phase reactant for a second period of time to complete the formation of an atomic layer on the substrate, wherein the contacting comprises placing the substrate in proximity to an outlet directing a flow of the vapor-phase reactant to the substrate;
15 wherein said method further comprises providing a flow of a non-reactive gas to the substrate during and/or after one or both of the contacting steps; and wherein said method is performed at atmospheric pressure, wherein the contacting is performed in the presence or absence of a closed reaction chamber, and wherein the method can be performed in the absence of
20 substrate or outlet movement.

2. The method of claim 1, wherein the contacting steps are repeated one or more times to provide a thin film of a desired thickness on the substrate.

25 3. The method of claim 2, wherein the contacting steps are repeated to provide a thin film having a thickness of between about 1 nanometer and about 10 microns.

4. The method of claim 1, wherein the substrate is a porous
30 substrate.

5. The method of claim 4, wherein the substrate is a fiber-based substrate, a metal organic framework, a zeolite, or anodic aluminum oxide.

6. The method of claim 5, wherein the substrate is a fiber-based substrate comprising natural fibers, synthetic fibers, or both natural and synthetic fibers.

5

7. The method of claim 6, wherein the fiber-based substrate is selected from the group consisting of cotton fiber, cotton fabric, woven cotton fabric, non-woven cotton fabric, protein-based fiber, polyvinyl alcohol fiber, polyvinyl alcohol fabric, woven polyvinyl alcohol fabric, non-woven polyvinyl
10 alcohol fabric, polyolefin polymer fiber, polyolefin fabric, woven polyolefin fabric, non-woven polyolefin fabric, polyethylene terephthalate fiber, polyethylene terephthalate fabric, woven polyethylene terephthalate fabric, non-woven polyethylene terephthalate fabric, polyamide fiber, polyamide fabric, woven polyamide fabric, non-woven polyamide fabric, acrylic fiber, acrylic fabric,
15 woven acrylic fabric, non-woven acrylic fabric, polycarbonate fiber, polycarbonate fabric, woven polycarbonate fabric, non-woven polycarbonate fabric, fluorocarbon fiber, fluorocarbon fabric, woven fluorocarbon fabric, non-woven fluorocarbon fabric, glass fiber, glass fabric, woven glass fiber, and non-woven glass fabric.

20

8. The method of claim 1, wherein the substrate comprises nanofibers.

9. The method of claim 1, wherein the substrate comprises a natural
25 or synthetic polymer-based surface.

10. The method of claim 9, wherein said polymer-based surface comprises a material selected from polyimide, polyethersulfone, cellophane, polydimethylsiloxane, polytetrafluoroethylene, wood, cellulose, cotton, polyvinyl
30 alcohol, polyvinyl chloride, polystyrene, polyacrylonitrile, polyethylene, polybutylene, and polyethylene terephthalate.

11. The method of claim 1, wherein the substrate is substantially stationary.

12. The method of claim 1, wherein the substrate is non-planar.

13. The method of claim 1, wherein the flow of vapor-phase
5 precursor, vapor-phase reactant, and non-reactive gas are provided by an apparatus comprising one or more gas delivery units, each gas delivery unit comprising:

a first input for the non-reactive gas;

one or more gas delivery channels, wherein a first end of each gas
10 delivery channel is in flow communication with at least an input for receiving the vapor-phase precursor or the vapor-phase reactant, and wherein a second end of each gas delivery channel comprises an outlet for directing a flow of gas to the substrate; and

an output face in flow communication with the outlet of each of the one
15 or more gas delivery channels, with the first input for the non-reactive gas, and with a deposition zone exterior to the gas delivery unit.

14. The method of claim 13, wherein the outlet or outlets of the one or more gas delivery channels are coplanar with the output face.

20

15. The method of claim 13, wherein the outlet or outlets of the one or more gas delivery channels are in an interior space of the gas delivery unit.

16. The method of claim 13, wherein at least one gas delivery unit
25 comprises a gas delivery channel wherein the first end of the gas delivery channel is in flow communication with one or more input for sequentially receiving the vapor-phase precursor, the non-reactive gas, and the vapor-phase reactant, such that the outlet of the gas delivery channel can sequentially direct a flow of vapor-phase precursor, the non-reactive gas, and the vapor-
30 phase reactant to the substrate.

17. The method of claim 13, wherein at least one gas delivery unit comprises at least two gas delivery channels, wherein said at least two gas delivery channels comprise:

a first gas delivery channel, wherein said first gas delivery channel has a first end in flow communication with one or more inputs for the vapor-phase precursor or for the vapor-phase precursor and the non-reactive gas, and a second end comprising an outlet for delivering the vapor-phase precursor or for
5 sequentially delivering the vapor-phase precursor and the non-reactive gas; and

a second gas delivery channel, wherein said second gas delivery channel has a first end in flow communication with one or more inputs for the vapor-phase reactant or for the vapor-phase reactant and the non-reactive gas,
10 and a second end comprising an outlet for delivering the vapor-phase reactant or for sequentially delivering the vapor-phase reactant and the non-reactive gas.

18. The method of claim 17, wherein the first and second gas delivery
15 channels are substantially parallel to one another.

19. The method of claim 18, wherein the gas delivery unit comprises a partition between the first and second gas delivery channels extending in a direction parallel to said first and second gas delivery channels and at or
20 beyond the outlets of the first and second gas delivery channels toward the outlet face, and further wherein the gas delivery unit comprises a second input for the non-reactive gas such that the first input for the non-reactive gas is located on one side of the partition and the second input for the non-reactive gas is located on the other side of the partition.

25

20. The method of claim 17, wherein the first and second gas delivery channels join one another near their second ends to form a single outlet.

21. The method of claim 13, wherein providing the substrate
30 comprises positioning an outer or external surface of the substrate between about 0.01 millimeters and about 20 millimeters from an output face of a gas delivery unit.

22. The method of claim 13, wherein providing the substrate comprises positioning an outer or external surface of the substrate between about 0.02 millimeters and about 1.0 millimeters from an output face of a gas delivery unit.

5

23. The method of claim 13, wherein providing the substrate comprises positioning an outer or external surface of the substrate between about 0.02 millimeters and about 0.5 millimeters from an output face of a gas delivery unit.

10

24. The method of claim 13, wherein an outlet for delivering the vapor-phase precursor is located substantially in the center of the output face.

25. The method of claim 13, wherein providing the substrate
15 comprises positioning the substrate such that a plurality of portions of an outer or external surface of the substrate are in proximity to the output faces of a plurality of gas delivery units.

26. The method of claim 1, wherein the vapor-phase precursor
20 comprises a metal-containing compound.

27. The method of claim 26, wherein the vapor-phase precursor comprises trimethylaluminum (TMA), diethyl zinc (DEZ), titanium tetrachloride ($TiCl_4$), tungsten hexafluoride, titanium isopropoxide, or zirconium tertbutoxide
25 (ZTB).

28. The method of claim 1, wherein the flow of the vapor-phase precursor is provided at a flow rate between about 0.001 and about 5.0 standard liters per minute (slm).

30 29. The method of claim 28, wherein the flow of the vapor-phase precursor is provided at a flow rate between about 0.05 slm and about 0.2 slm.

30. The method of claim 1, wherein the first period of time is between about 0.1 seconds and about 2.0 seconds.

31. The method of claim 1, wherein the vapor-phase reactant is selected from the group comprising H_2O, NH_3, ozone, O_2, CO_2, CO, NO, N_2O, NO_2, SiH_4, and Si_2H_6.

32. The method of claim 1, wherein the vapor-phase reactant is provided at a flow rate between about 0.001 and about 5.0 standard liters per minute (slm).

33. The method of claim 32, wherein the vapor-phase reactant is provided at a flow rate between about 0.05 slm and about 0.2 slm.

34. The method of claim 1, wherein the second period of time is between about 0.1 seconds and about 2.0 seconds.

35. The method of claim 1, wherein the vapor-phase reactant is H_2O, the vapor-phase precursor is TMA and the method comprises modifying the substrate with aluminum oxide.

36. The method of claim 1, wherein the non-reactive gas is selected from nitrogen and argon.

37. The method of claim 1, wherein the non-reactive gas is provided at a flow rate between about 1 and about 100 standard liters per minute (slm).

38. The method of claim 37, wherein the non-reactive gas is provided at a flow rate between about 5 and about 20 slm.

39. The method of claim 1, wherein the method comprises providing a flow of a non-reactive gas for between about 1 second and about 300 seconds after the first period of time and before the second period of time and/or after the second period of time.

40. The method of claim 1, wherein the method comprises providing a flow of a non-reactive gas for about 10 seconds after the first period of time and before the second period of time and/or after the second period of time.

5

41. The method of claim 1, wherein the method comprises providing a flow of a non-reactive gas during the first and/or second periods of time.

42. The method of claim 1, wherein one or both contacting steps are
10 conducted at a temperature between about 20°C and about 200°C.

43. The method of claim 42, wherein one or both contacting steps are conducted at a temperature of about 120°C.

15 44. An apparatus for modifying a substrate, wherein the apparatus comprises one or more gas delivery units, each gas delivery unit comprising:

a first input for the non-reactive gas;

one or more gas delivery channels, wherein a first end of each gas delivery channel is in flow communication with at least an input for receiving the
20 vapor-phase precursor or the vapor-phase reactant, and wherein a second end of each gas delivery channel comprises an outlet for directing a flow of gas to a substrate; and

an output face in flow communication with the outlet of each of the one or more gas delivery channels and with the first input for the non-reactive gas,
25 and is adapted for gaseous and/or flow communication with an exterior of the gas delivery unit.

45. The apparatus of claim 44, wherein the outlet or outlets of the one or more gas delivery channels are coplanar with the output face.

30

46. The apparatus of claim 44, wherein the outlet or outlets of the one or more gas delivery channels are in an interior space of the gas delivery unit.

47. The apparatus of claim 44, wherein an outlet for delivering a flow of the vapor-phase precursor is at or near the center of the output face.

48. The apparatus of claim 44, wherein the output face is square or rectangular.

49. The apparatus of claim 44, wherein the output face is substantially circular.

50. The apparatus of claim 49, wherein the output face has a diameter that is about 0.5 cm or smaller; and/or wherein an opening in the output face and/or a gas delivery channel outlet for directing a flow of gas to a substrate has a diameter that is between about 0.1 millimeters and about 0.5 millimeters.

51. The apparatus of claim 44, wherein the gas delivery unit comprises a tubular body comprising an input face at a first end of the tubular body adapted to receive one or more input ports and/or one or more gas delivery channels, and wherein the output face is at a second end of the tubular body.

52. The apparatus of claim 51, wherein the tubular body is tapered such that the output face has a smaller diameter than the input face.

53. The apparatus of claim 51, wherein the input face has a diameter that is between about 0.5 and about 1.0 centimeters.

54. The apparatus of claim 44, wherein at least one gas delivery unit comprises a gas delivery channel wherein the first end of the gas delivery channel is in flow communication with one or more input for sequentially receiving the vapor-phase precursor, the non-reactive gas, and the vapor-phase reactant.

55. The apparatus of claim 44, wherein at least one gas delivery unit comprises at least two gas delivery channels, wherein said at least two gas delivery channels comprise:

a first gas delivery channel, wherein said first gas delivery channel has a
5 first end in flow communication with one or more inputs for the vapor-phase precursor or for the vapor-phase precursor and the non-reactive gas, and a second end comprising an outlet for delivering the vapor-phase precursor or for sequentially delivering the vapor-phase precursor and the non-reactive gas; and

10 a second gas delivery channel, wherein said second gas delivery channel has a first end in flow communication with one or more inputs for the vapor-phase reactant or for the vapor-phase reactant and the non-reactive gas, and a second end comprising an outlet for delivering the vapor-phase reactant or for sequentially delivering the vapor-phase reactant and the non-reactive
15 gas.

56. The apparatus of claim 55, wherein the first and second gas delivery channels are substantially parallel to one another.

20 57. The apparatus of claim 56, wherein the gas delivery unit comprises a partition between the first and second gas delivery channels extending in a direction parallel to said first and second gas delivery channels and extending beyond the outlets of first and second gas delivery channels toward the outlet face, and further wherein the gas delivery unit comprises a
25 second input for the non-reactive gas such that the first input for the non-reactive gas is located on one side of the partition and the second input for the non-reactive gas is located on the other side of the partition.

58. The apparatus of claim 55, wherein the first and second gas
30 delivery channels join one another near their second ends to form a single outlet.

59. The apparatus of claim 44, further comprising a support for supporting a substrate when the substrate is positioned about 20 mm or less from, but not in direct contact with, the output face.

5 60. The apparatus of claim 59, wherein the support is adapted to hold the substrate stationary.

61. The apparatus of claim 59, wherein the support is adapted to translate the substrate with respect to an output face.

10

62. The apparatus of claim 44, wherein one or more gas delivery units can be translated with respect to a length, width, and/or height of a substrate.

63. The apparatus of claim 44, further comprising a roller system for
15 positioning a substrate sheet relative to the apparatus.

64. The apparatus of claim 44, comprising a plurality of gas delivery units.

20 65. The apparatus of claim 64, wherein the plurality of gas delivery units are arranged in a single row to form a linear array of gas delivery units.

66. The apparatus of claim 64, wherein the plurality of gas delivery units are arranged in a plurality of rows to form a square or rectangular array of
25 gas delivery units.

67. The apparatus of claim 44, further comprising an exhaust system.

68. The apparatus of claim 44, further comprising one or more
30 spacers extending from the exterior of the output face to assist in positioning the substrate.

69. The apparatus of claim 44, further comprising one or more satellite gas delivery units, wherein each satellite gas delivery unit comprises a gas delivery channel for delivery of a flow of non-reactive gas to the substrate.

5 70. A modified substrate created by the method of claim 1.

71. The modified substrate of claim 70, wherein the modified substrate is patterned with a thin film.

10 72. A modified substrate produced using an apparatus of claim 44.

73. The modified substrate of claim 72, wherein the modified substrate is patterned with a thin film.

15 74. An apparatus for modifying a substrate, wherein the apparatus comprises a roller system and an array of vapor-phase precursor delivery units and vapor-phase reactant delivery units,

wherein each vapor-phase precursor delivery unit comprises a vapor-phase precursor delivery channel, wherein a first end of the channel is in flow
20 communication with one or more inputs for receiving the vapor-phase precursor or receiving the vapor-phase precursor and a non-reactive gas, and wherein a second end of the channel comprises an outlet for directing a flow of vapor-phase precursor and/or non-reactive gas to a substrate;

wherein each vapor-phase reactant delivery unit comprises a vapor-
25 phase reactant delivery channel, wherein a first end of the channel is in flow communication with one or more inputs for receiving the vapor-phase reactant or receiving the vapor-phase reactant and a non-reactive gas, and wherein a second end of the channel comprises an outlet for directing a flow of vapor-phase reactant and/or non-reactive gas to a substrate; and

30 wherein the roller system can translate a substrate relative to the outlets of the array, such that a portion of the substrate is sequentially in contact with a flow from the outlet of a vapor-phase precursor delivery unit and a flow from the outlet of a vapor-phase reactant delivery unit.

75. The apparatus of claim 74, further comprising an exhaust system for creating a pressure differential between the outlets of the delivery channels and the substrate and/or to remove excess vapor-phase precursor, excess
5 vapor-phase reactant, non-reactive gas, and/or any gaseous side products formed during use of the apparatus.

76. A modified substrate produced using the apparatus of claim 74.

10 77. The method of claim 1, wherein an inner surface or both an outer surface and an inner surface of the substrate are modified.

78. The method of claim 13, wherein directing a flow of gas to the substrate comprises directing the flow of gas to the outer and/or inner surface
15 of the substrate.

79. An apparatus or process for modifying a substrate as described in the accompanying description and/or figures.

20

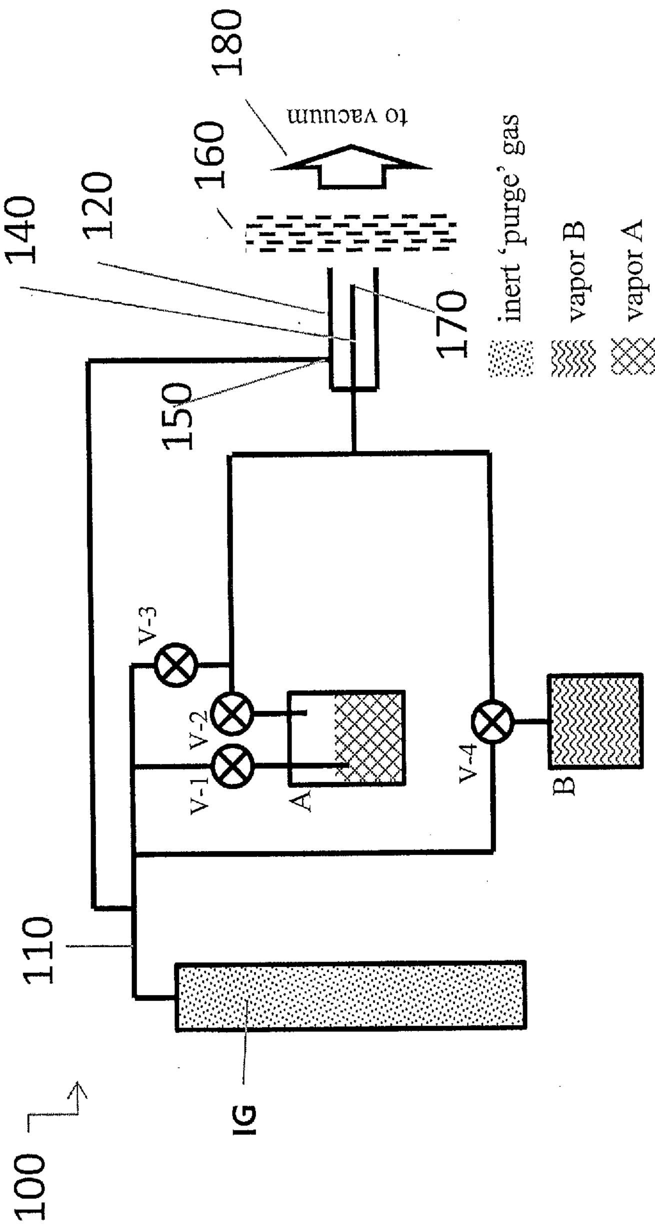


FIG. 1

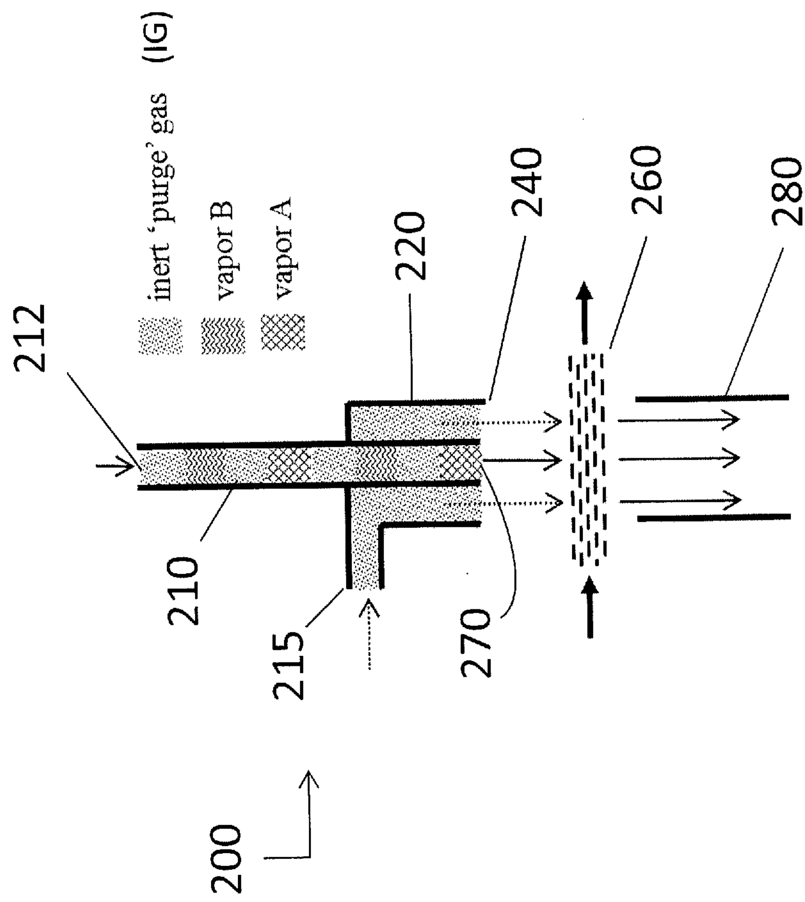


FIG. 2

inert 'purge' gas (IG)
vapor B
vapor A
0-90 deg
300
318
320
322
338
340
342
360
380
385
390
395
397

FIG. 3

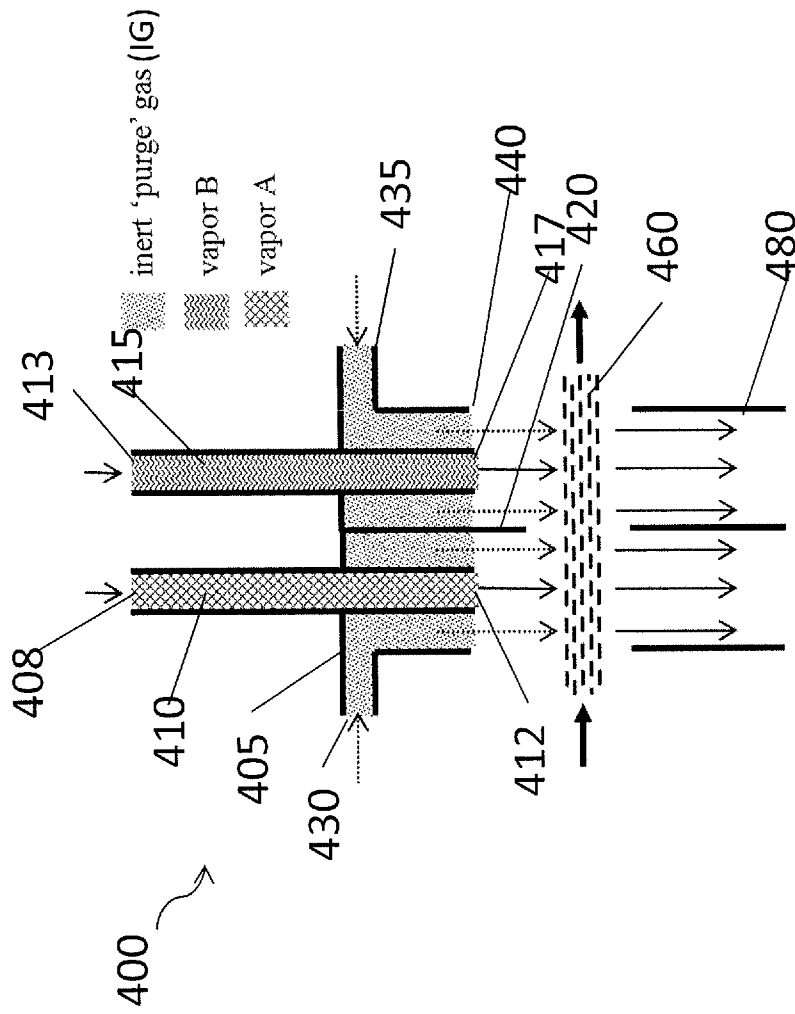


FIG. 4

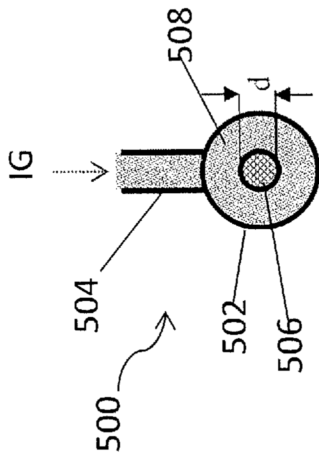


FIG. 5

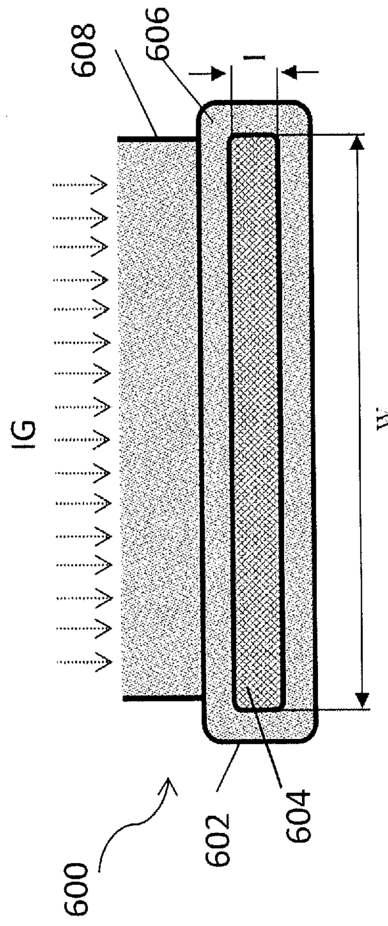


FIG. 6

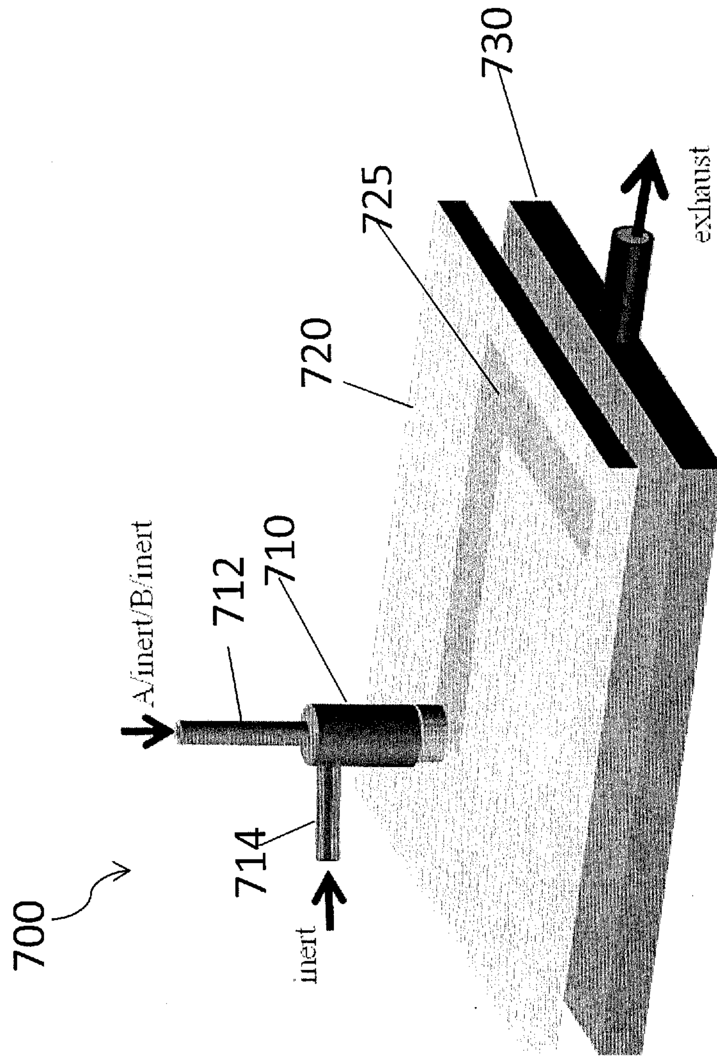


FIG. 7

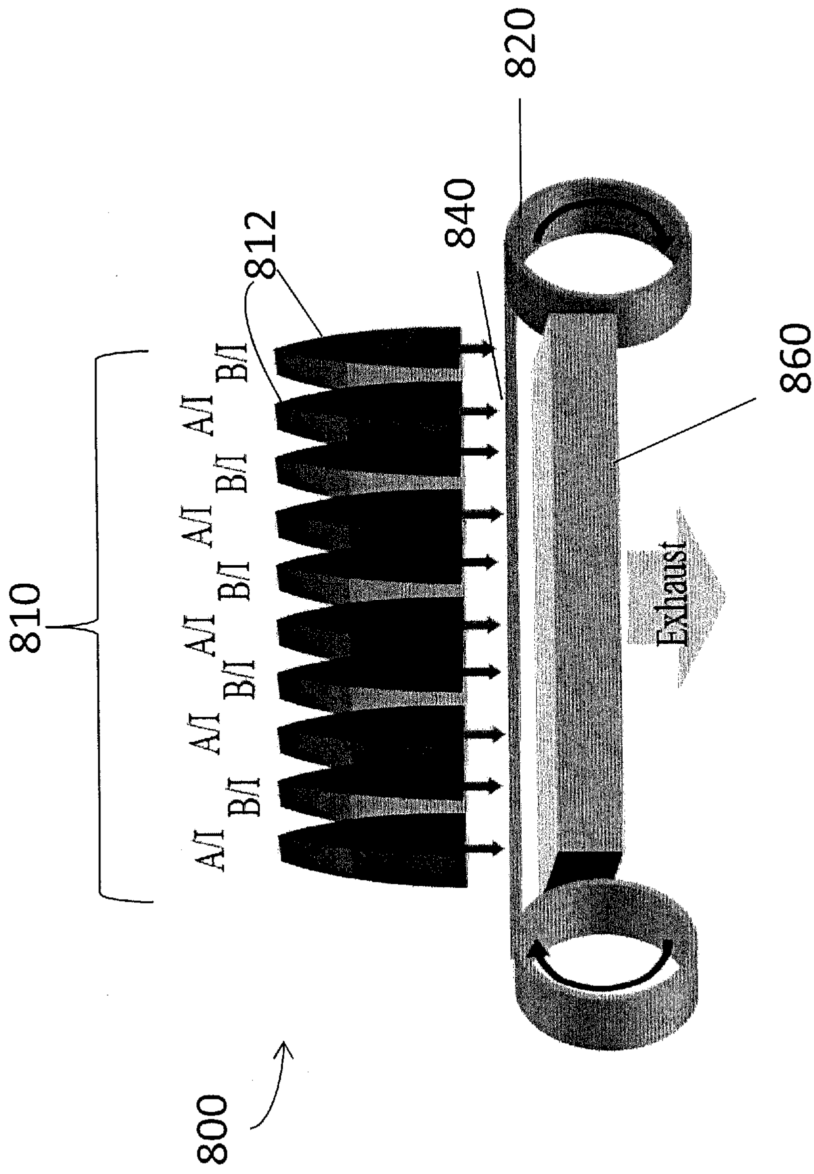


FIG. 8

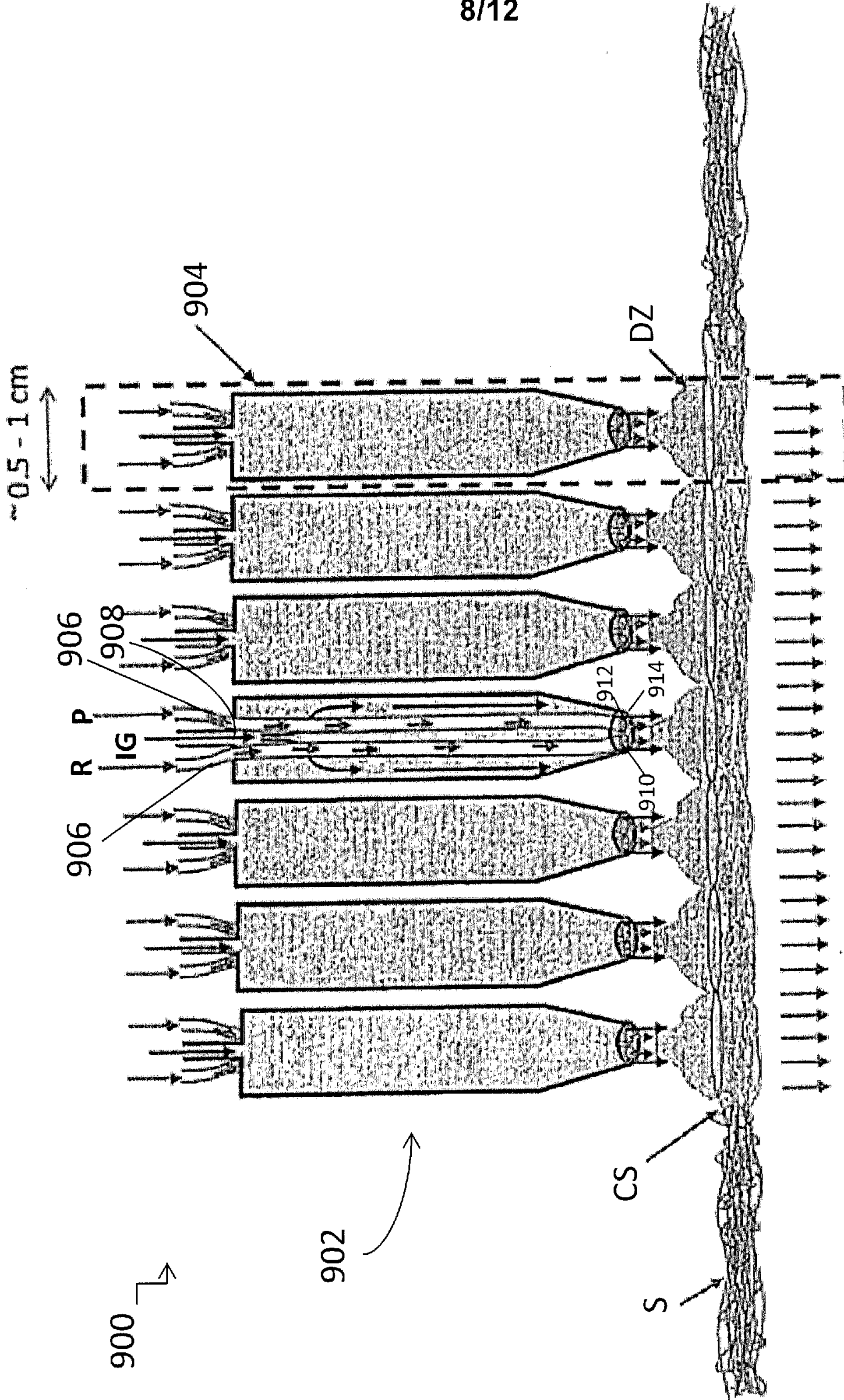


FIG. 9

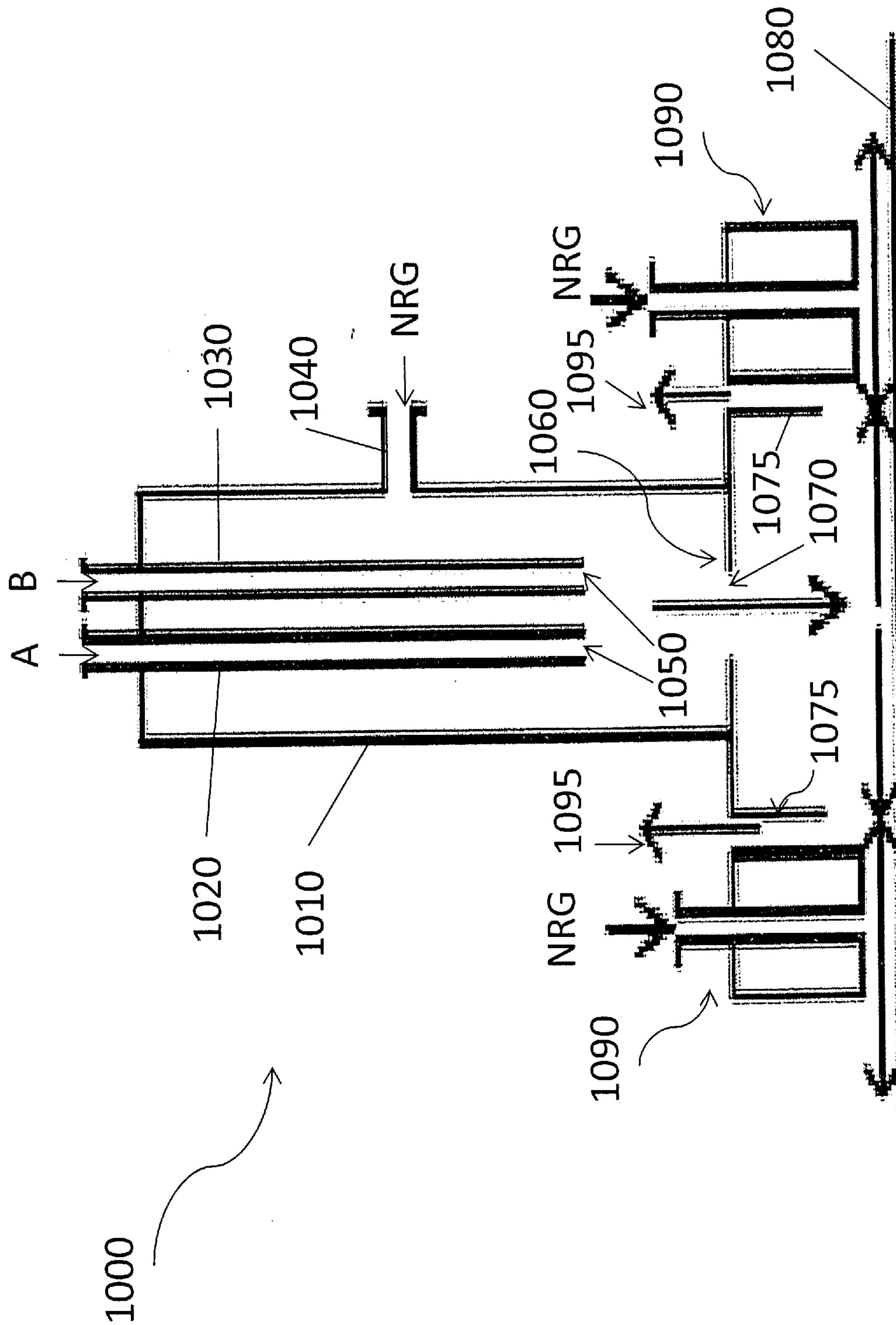


FIG. 10

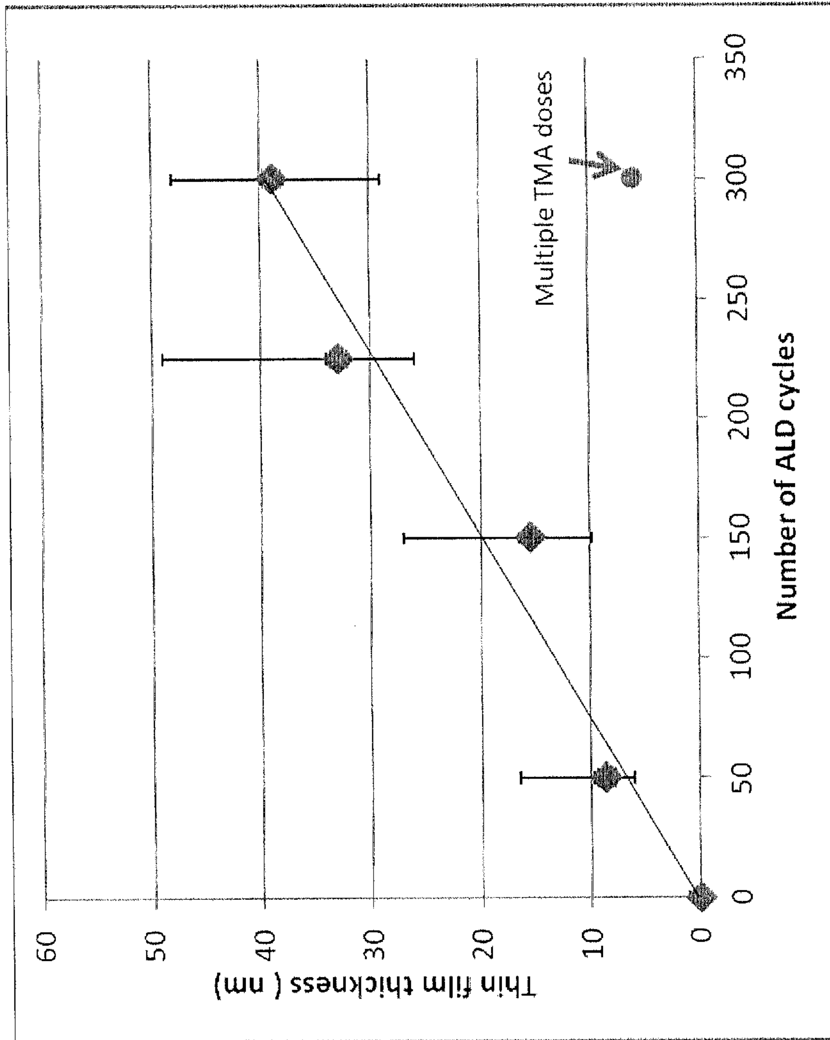


FIG. 11

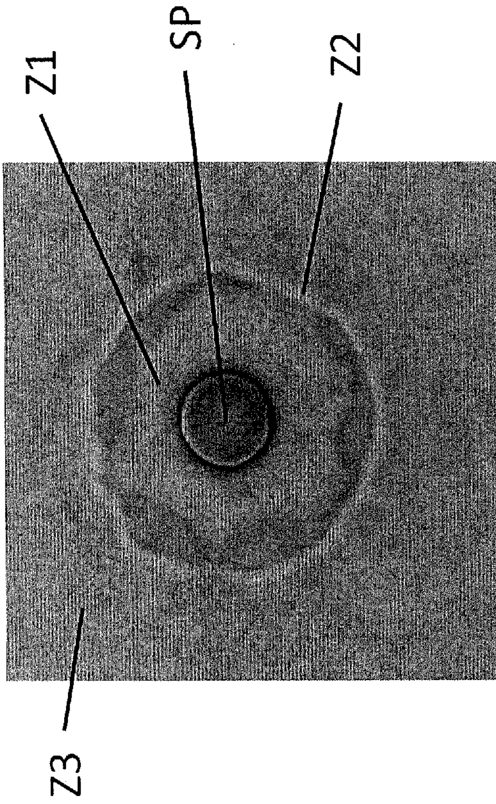


FIG. 12

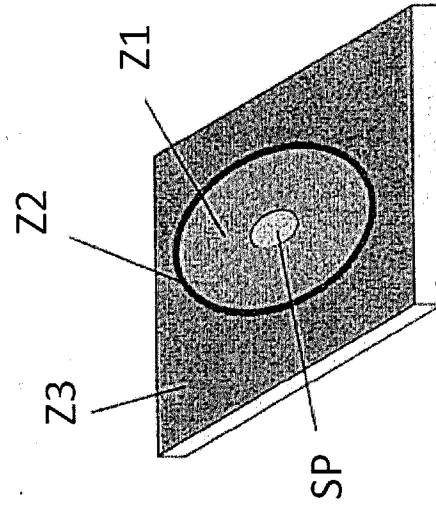


FIG. 13

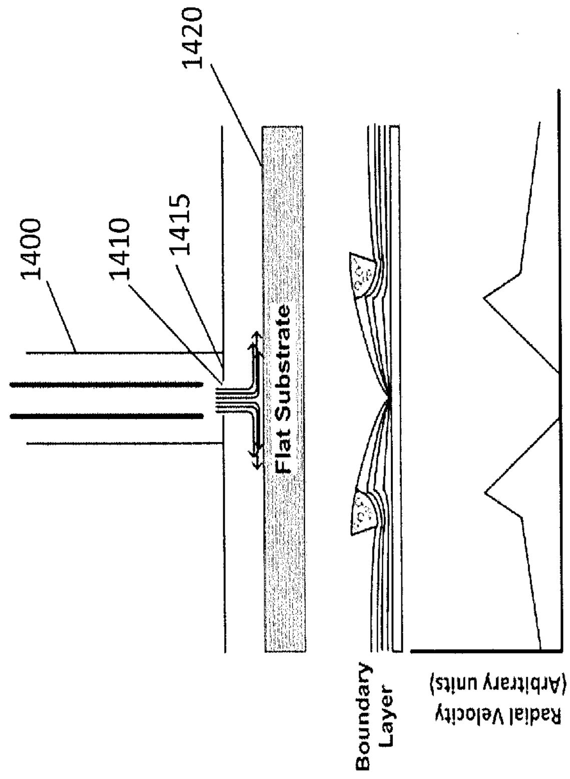


FIG. 14

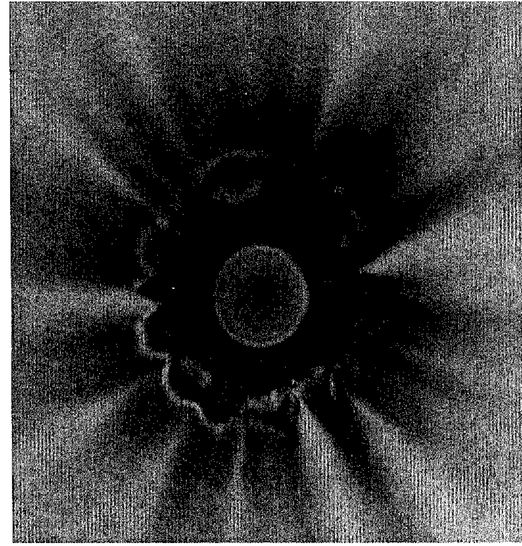


FIG. 15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/032203

A. CLASSIFICATION OF SUBJECT MATTER

C23C 16/448(2006.01)i, C23C 16/44(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C 16/448; C23C 16/54; H01L 21/205; C23C 14/54; H01L 31/18; H01L 21/31; C23C 16/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords:gas delivery, atomic layer, atmospheric pressure, deposit, and exhaust

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010-0255625 A1 (DE VRIES, HINDRIK WILLEM) 7 October 2010 See paragraphs [0060]-[0079] and figure 5a.	1-12,26-43,70,71
A		13-25,44-69,72-78
Y	US 2010-0018463 A1 (YU, CHEN-HUA et al.) 28 January 2010 See paragraphs [0036],[0037] and figures 5,6.	1-12,26-43,70,71
A	US 4843029 A (JOYCE, BRUCE A. et al.) 27 January 1989 See column 4, line 49 - column 5, line 22 and figure 1.	1-78
A	US 2011-0124204 A1 (OTA, YOSUKE et al.) 26 May 2011 See paragraphs [0056],[0057] and figure 1.	1-78
A	JP 2003-324070 A (SUZUKI MOTOR CORP.) 14 November 2003 See paragraphs [0016],[0017] and figure 1.	1-78

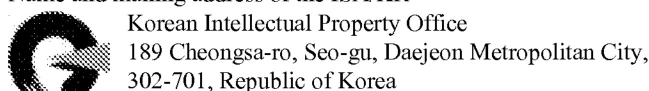
☐ Further documents are listed in the continuation of Box C.

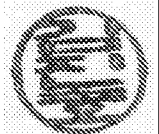
☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
24 June 2013 (24.06.2013)

Date of mailing of the international search report
25 June 2013 (25.06.2013)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer
KIM, Jin Ho

Telephone No. 82-42-481-8699

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/032203

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 79
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 79 relies on reference to the accompanying description or drawings, so does not clearly define the matter for which protection is sought in the claim..

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/032203

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2010-0255625 A1	07.10.2010	JP 2010-538165 A	09.12.2010
		WO 2009-031886 A2	12.03.2009
		WO 2009-031886 A3	04.06.2009
US 2010-0018463 A1	28.01.2010	CN 101634013 A	27.01.2010
		CN 101634013 B	20.04.2011
		TW 201005198 A	01.02.2010
US 04843029 A	27.06.1989	EP 0286181 A3	20.03.1991
		EP 0286181 B1	15.09.1993
		JP 63-261832 A	28.10.1988
		KR 10-1988-0013224 A	30.11.1988
US 2011-0124204 A1	26.05.2011	JP 2011-129879 A	30.06.2011
		KR 10-1074684 B1	18.10.2011
		KR 10-2011-0056234 A	26.05.2011
		TW 201126607 A	01.08.2011
		US 8202809 B2	19.06.2012
JP 2003-324070 A	14.11.2003	JP 04158139 B2	01.10.2008