Title: APPARATUS AND METHOD FOR CONTROLLED APPLICATION OF REACTIVE VAPORS TO PRODUCE THIN FILMS AND COATINGS

Abstract: A vapor phase deposition method and apparatus for the application of thin layers and coatings on substrates. The method and apparatus are useful in the fabrication of electronic devices, micro-electromechanical systems (MEMS), Bio-MEMS devices, micro and nano imprinting lithography, and microfluidic devices. The apparatus used to carry out the method provides for the addition of a precise amount of each of the reactants to be consumed in a single reaction step of the coating formation process. The apparatus provides for precise addition of quantities of different combinations of reactants during a single step or when there are a number of different individual steps in the coating formation process. The precise addition of each of the reactants in vapor form is metered into predetermined set volume at a specified temperature to a specified pressure, to provide a highly accurate amount of reactant.
Declaration under Rule 4.17:
— as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations

Published:
— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
[0001] APPARATUS AND METHOD FOR CONTROLLED APPLICATION
OF REACTIVE VAPORS TO PRODUCE THIN FILMS AND COATINGS

[0002] This application is related to Provisional Application Serial No. 60/482,861,
filed June 27, 2003 and entitled: "Method And Apparatus for Mono-Layer Coatings";
Provisional Application Serial No. 60/506,864, filed September 30, 2003, and entitled:
"Method Of Thin Film Deposition"; and, Provisional Application Serial No. 60/509,563,
filed October 9, 2003, and entitled: "Method of Controlling Monolayer Film Properties".

[0003]

BACKGROUND OF THE INVENTION

[0004] 1. Field of the Invention

[0005] The present invention pertains to apparatus and a method useful in the
deposition of a coating on a substrate, where the coating is formed from chemically
reactive species present in a vapor which is reacted with the substrate surface.

[0006] 2. Brief Description of the Background Art

[0007] Both integrated circuit (IC) device fabrication and micro-electromechanical
systems (MEMS) fabrication make use of layers or coatings of material which are
deposited on a substrate for various purposes. In some instances, the layers are deposited
on a substrate and then are subsequently removed, such as when the layer is used as a
patterned masking material and then is subsequently removed after the pattern is
transferred to an underlying layer. In other instances, the layers are deposited to perform
a function in a device or system and remain as part of the fabricated device. There are
numerous methods for depositing a thin film layer or a coating, such as: Sputter
deposition, where a plasma is used to sputter atoms from a target material (commonly a
metal), and the sputtered atoms deposit on the substrate. Chemical vapor deposition,
where activated (e.g. by means of plasma, radiation, or temperature, or a combination
thereof) species react either in a vapor phase (with subsequent deposition of the reacted
product on the substrate) or react on the substrate surface to produce a reacted product on
the substrate. Evaporative deposition, where evaporated material condenses on a
substrate to form a layer. And, spin-on, spray-on, or dip-on deposition, typically from a
solvent solution of the coating material, where the solvent is subsequently evaporated to
leave the coating material on the substrate.

[0008] In applications where the wear on the coating is likely to occur due to
mechanical contact or fluid flow over the substrate surface on which the layer of coating
is present, it is helpful to have the coating chemically bonded directly to the substrate
surface via reaction of the species with the surface in order to obtain particular surface
properties.

[0009] With respect to layers and coatings which are chemically bonded to the
substrate surface, areas of particular current interest are those of integrated circuitry, and a
combination of integrated circuitry with mechanical systems, which are referred to as
micro-electromechanical systems, or MEMS. Due to the nanometer size scale of some of
the electrical devices formed, and the use of MEMS in applications such as the biological
sciences, where the type and properties of the coating on the substrate surface is used to
provide a particular functionality to the surface, a need has grown for improved methods
of controlling the formation of the coating or layer on the substrate surface. Historically,
these types of coatings were deposited in the liquid phase, resulting in limited film
property control and loss of device yield due to capillary forces. More recently, vapor-
phase deposition has been used as a way to replace liquid processing and to improve
coating properties.

[0010] For purposes of illustrating a few of the many potential applications for vapor
phase coatings, which must either be deposited to have particular critical properties and/or
to have particular permanent structural orientation relative to the underlying substrate,
applicants would like to mention the following publications and patents which relate to
methods of coating formation. Applicants would like to make it clear that some of this
Background Art is not prior art to the present invention because it has been published at such a time that it is subsequent to the date of invention for applicants' invention. It is mentioned here because it is of interest to the general subject matter.

[0011] Product applications employing coatings deposited on a substrate surface from a vapor include the following, as examples and not by way of limitation. U.S. Patent 5,576,247 to Yano et al., issued November 19, 1996, entitled: "Thin layer forming method where hydrophobic molecular layers preventing a BPSG layer from absorbing moisture". U.S. Patent No. 5,602,671 of Hornbeck, issued February 11, 1997, which describes low surface energy passivation layers for use in micromechanical devices. In particular, an oriented monolayer is used to limit the Van der Waals forces between two elements, reducing the attraction between the surfaces of the elements. An article by Steven A. Henck in Tribology Letters 3 (1997) 239–247, entitled "Lubrication of digital micromirror devices", describes nearly fifty lubricants which were investigated for use in a digital micromirror device. The lubricants included self-assembled monolayers (SAMs), fluids, and solid lubricants. The lubricants were used to reduce the adhesion between contacting surfaces within a microelectromechanical system (MEMS) device. In an article entitled "Vapor phase deposition of uniform and ultrathin silanes", by Yuchun Wang et al., SPIE Vol. 3258 - 0277-786X(98) 20 - 28, the authors describe uniform, conformal, and ultrathin coatings needed on the surface of biomedical microdevices such as microfabricated silicon filters, in order to regulate hydrophilicity and minimize unspecific protein adsorption. Jian Wang et al., in an article published in Thin Solid Films 327 - 329 (1998) 591 - 594, entitled: "Gold nanoparticulate film bound to silicon surface with self-assembled monolayers, discuss a method for attaching gold nanoparticles to silicon surfaces with a SAM used for surface preparation".

[0012] Patrick W. Hoffmann et al., in an article published by the American Chemical Society, Langmuir 1997, 13, 1877 - 1880, describe the molecular orientation in monomolecular thin organic films and surface coverage on Ge/Si oxide. A gas phase
reactor was said to have been used to provide precise control of surface hydration and reaction temperatures during the deposition of monofunctional perfluorated alkysilanes. Although some process conditions are provided, there is no description of the apparatus which was used to apply the thin films. T.M. Mayer et al. describe a "Chemical vapor deposition of fluoroalkysilane monolayer films for adhesion control in microelectromechanical systems" in J. Vac. Sci. Technol. B 18(5), Sep/Oct 2000. This article mentions the use of a remotely generated microwave plasma for cleaning a silicon oxide substrate surface prior to film deposition, where the plasma source gas is either water vapor or oxygen. U.S. Patent No. 6,203,505 to Jalisi et al., issued March 20 2001 describes guide wires having a vapor deposited primer coating. The guide wires are an intraluminal device having an adhesive primer coat formed of a carbonaceous material and a lubricious top coat of a hydrophilic polymeric material. One preferred coating method for applying a carbon-based primer coating is chemical vapor deposition. The coating is a plasma polymerized coating, so that the resulting polymer is an amorphous structure having groups in the structure other than the monomer groups of the source materials. For example, plasma polymerized polyethylene may include a variety of functional groups, such a vinyl, in addition to the methylene groups. In their article entitled: "Amino-terminated self-assembled monolayer on a SiO2 surface formed by chemical vapor deposition", J. Vac. Sci. Technol. A 19(4), Jul/Aug. 2001, Atsushi Hozumi et al. describe the formation of self-assembled monolayers (SAMs) on n-type Si (100) wafers which were photochemically cleaned by a UV/ ozone treatment, whereby a thin SiO2 layer was formed on the silicon surface. The SAM coating was applied by placing a cleaned wafer together with a silane liquid precursor diluted with absolute toluene into a container having a dry nitrogen ambient atmosphere. The container was sealed with a cap and heated in an oven maintained at 373 °K. [0013] International Patent Application No. PCT/US01/26691, published on April 11, 2002, describes substrates having a hydrophobic surface coating comprised of the reaction
products of a chlorosilyl group compound and an alkylsilane. In a preferred embodiment, a hydrophobic coating is formed by the simultaneous aqueous vapor phase deposition of a chloroalkysilane and a chlorosilyl group containing compound to form an anchor layer, which may then be capped with a hydrophobic coating. The reactants are said to be vapor-deposited simultaneously in a closed humidity-controlled chamber. Dry air, humid air, or dry air saturated with coating precursor vapor was introduced at one end of the chamber and exhausted at the other. The reaction precursors are said to be introduced into the reaction chamber by flowing dry air over the precursor liquid and into the chamber. U.S. Patent No. 6,383,642 to Le Bellac et al., issued May 7, 2002 described formation of a hydrophobic/oleophobic coating on a substrate such as a glass or plastic material. The coating precursor is introduced into a chamber which employs a pulsed plasma, with the frequency of the plasma generation source ranging from 10 kHz to 10 GHz at a power from 100 to 2000W, where the substrate surface area to be coated is 0.4 M². The precursors are introduced into the chamber at various flow rates to establish and maintain a pressure in the chamber ranging from 0.1 to 70 Pa..

[0014] W. Robert Ashurst et al., discuss a method of applying anti-stiction coatings for MEMS from a vapor phase in an article published by Elsevier Science B.V., in Sensors and Actuators A 104 (2003) 213 - 221. In particular, silicon (100) samples cut from a P-doped, n-type test wafer are rinsed in acetone and then cleaned by exposure to UV light and ozone for 15 minutes. The samples are treated with concentrated HF for 10 minutes and then cleaned again as described above before introduction to a vapor deposition chamber. In the vapor deposition chamber, the silicon substrates are additionally cleaned of any organic contamination using an oxygen plasma which is generated in the coating chamber, but at a sufficient distance away from the samples that the samples can be contacted by plasma species without being inside the plasma discharge area. After O₂ plasma exposure was begun, water gas was dosed into the chamber and eventually displaced the oxygen. The water was added to form -OH surface terminations
on the substrate surface. The coating was applied by first admitting water vapor to the
chamber until the pressure in the chamber exceeded 5 Torr. Subsequently, the chamber
was evacuated down to the desired water vapor pressure between 1 and 1.3 Torr. Next a
dimethyl dichlorosilane (DDMS) precursor was introduced into the process chamber until
the total pressure was in the range of 2.5 - 3 Torr. The reaction was carried out for 10 - 15
minutes, after which time the chamber was pumped out and vented with nitrogen. It was
concluded that increasing substrate temperature during coating over a range of 20 °C to
50 °C, all other variables being equal, results in films that have decreasing water contact
angle. The main result of the temperature experiments is said to be that there is no need
to heat the sample. In a second article entitled: "Vapor Deposition of Amino-
Functionalized Self-Assembled Monolayers on Mems", Reliability, Testing, and
Characterization of MEMS MOEMS II", Rajeshuni Ramesham, Danelle M. Tanner,
Editors, Proceedings of SPIE Vol. 4980 (2003), authors Matthew G. Hankins et al.
describe microengine test devices coated with films made from amino-functionalized
silanes. The coatings were applied in a vapor-deposited self-assembled monolayer system
developed at Sandia National Laboratories. The process variables used to deposit the
coatings are not discussed in the article.

[U0015] U.S. Patent No. 6,576,489 to Leung et al., issued June 10, 2003 describes
methods of forming microstructure devices. The methods include the use of vapor-phase
alkylsilane-containing molecules to form a coating over a substrate surface. The
alkylsilane-containing molecules are introduced into a reaction chamber containing the
substrate by bubbling an anhydrous, inert gas through a liquid source of the alkylsilane-
containing molecules, to transport the molecules in the vapor phase into the reaction
chamber. The formation of the coating is carried out on a substrate surface at a
temperature ranging between about 15 °C and 100 °C, at a pressure in the reaction
chamber which is said to be below atmospheric pressure, and yet sufficiently high for a
suitable amount of alkylsilane-containing molecules to be present for expeditious
formation of the coating. The liquid source of alkylsilane molecules may be heated to
increase the vapor pressure of the alkylsilane-containing molecules.

[0016] While various methods useful in applying layers and coatings to semiconductor
devices and MEMS have been discussed above and there is some description of the kinds
of apparatus which may be employed to deposit the coatings, the apparatus description is
minimal. The following references deal more with apparatus. U.S. Patent Application
pertains to a method of sequential chemical vapor deposition which is used to deposit
layers of inorganic materials such as SiO₂, Al₂O₃, TiO₂, Si₃N₄, Si₅O₇N₉, and aluminum
2002/0076507 A1 of Chiang et al., published June 20, 2002, describes an atomic layer
deposition (ALD) process based on the sequential supply of at least two separate reactants
into a process chamber. A first reactant reacts (becomes adsorbed) with the surface of the
substrate via chemisorption. The first reactant gas is removed from the process chamber,
and a second reactant gas reacts with the adsorbed reactant to form a monolayer of the
desired film. The process is repeated to form a layer of a desired thickness. To reduce the
process time, there is no separate purge gas used to purge the first reactant gas from the
chamber prior to introducing the second gas, containing the second reactant. Instead, the
purge gas also includes the second reactant. Several valving systems for gas flow to
provide various mixtures of gases are described in detail.

[0017] The background information above provides a number of methods for
generation of coatings which have considerable commercial applicability. The apparatus
described for producing layers or coatings for use in electronic devices and/or micro-
electromechanical systems devices enables application of the layers or coatings, but does
not provide sufficient accuracy and repeatability in terms of the amount of the vaporous
reactants provided to the substrate surface. As a result, the precise composition of the
layer or coating which is desired may not be available. At other times, because of the
improper ratio of various reactants relative to each other, or oversaturation by a precursor, reactants may polymerize and/or particulate agglomerations may be formed which act as surface contaminants. Further, the ability to reproduce the same coating reliably, time after time, is diminished due to lack of control over the precise amount of reactants supplied to the coating formation process. This decreases the product yield and affects the commercial viability of a coating process. It would be highly desirable to have a more accurate and reliable method of supplying precise quantities of the reactants to the process chamber and to the substrate surface for coating formation.

[0018]

SUMMARY OF THE INVENTION

[0019] We have developed an improved vapor-phase deposition method and apparatus for the application of layers and coatings on substrates. The method and apparatus are useful in the fabrication of electronic devices, micro-electromechanical systems (MEMS), Bio-MEMS devices, and microfluidic devices. The coating formation method employs a batch-like addition and mixing of all of the reactants to be consumed in a coating formation process. The coating formation process may be complete after one step, or may include a number of individual steps, where different or repetitive reactive processes are carried out in each individual step. The apparatus used to carry out the method provides for the addition of a precise amount of each of the reactants to be consumed in a single reaction step of the coating formation process. The apparatus may provide for precise addition of quantities of different combinations of reactants during a single step or when there are a number of different individual steps in the coating formation process. The precise addition of each of the reactants is based on a metering system where the amount of reactant added in an individual step is carefully controlled. In particular, the reactant in vapor form is metered into a vapor reservoir with a predetermined set volume at a specified temperature to a specified pressure to provide a highly accurate amount of reactant. The entire measured amounts(s) of each reactant is (are) transferred in batch
fashion into the process chamber in which the coating is formed. The order in which each reactant is added to the chamber for a given reaction step is selectable, and may depend on the relative reactivities of the reactants when there are more than one reactant, the need to have one reactant or the catalytic agent contact the substrate surface first, or a balancing of these considerations.

[0020] In some instances, it may be necessary to carry out a series of individual vapor delivery steps to provide a complete coating, rather than carrying out one continuous reaction process. For example, all of a precisely measured quantity of one reacting component may be added initially, followed by a series of precisely measured quantities of a second reacting component. In each case all of the measured quantity is added to the reaction chamber. This provides a precise, carefully measured quantity of reactant at a precise time for each reactant.

[0021] A computer driven process control system may be used to provide for a series of additions of reactants to the process chamber in which the layer or coating is being formed. This process control system typically also controls other process variables, such as, (for example and not by way of limitation), process time, chamber pressure, temperatures of the process chamber and the substrate to which the coating is applied, as well as temperatures of the vapor delivery lines and vapor reservoirs relative to the temperatures of the precursors.

[0022] The apparatus for vapor deposition of coatings is particularly useful for deposition of coatings having a thickness ranging from about 5 Å to about 1,000 Å, (and may be used for increased coating thicknesses), where at least one precursor used for formation of the coating exhibits a vapor pressure below about 150 Torr at a temperature of 25 °C. The apparatus includes at least one precursor container in which at least one precursor, in the form of a liquid or solid, is placed; at least one precursor vapor reservoir for holding vapor of the at least one precursor; at least one device which controls precursor vapor flow from the precursor container into the precursor vapor reservoir; a
pressure sensor in communication with the precursor vapor reservoir; a process controller
which receives data from the pressure sensor, compares the data with a desired nominal
vapor reservoir pressure, and sends a signal to a device which controls vapor flow from
the precursor container into the precursor vapor reservoir, to prevent further vapor flow
into the precursor vapor reservoir when the desired nominal pressure is reached; a device
which controls precursor vapor flow into the precursor vapor reservoir upon receipt of a
signal from the process controller; a process chamber for vapor deposition of the coating
on a substrate present in the process chamber; and a device which controls precursor
vapor flow into the process chamber upon receipt of a signal from the process controller.

[0023] In some instances, the apparatus includes a device which applies heat to the
precursor while it is in the container, to produce a vaporous phase of the precursor.
Typically the apparatus includes at least one catalyst container, in which a catalyst, in the
form of a liquid or a solid is placed; and a catalyst vapor reservoir for holding vapor of the
catalyst, with the same basic elements facilitating transfer of catalyst to the process
chamber at those described with reference to a precursor.

[0024] A method of the invention provides for vapor-phase deposition of coatings,
where at least one precursor used for formation of the coating exhibits a vapor pressure
below about 150 Torr at a temperature of 25 °C. The method includes the steps of: a)
providing a processing chamber in which the coating is vapor deposited; b) providing at
least one precursor exhibiting a vapor pressure below about 150 Torr at a temperature of
25 °C; c) transferring vapor of the precursor to a precursor vapor reservoir in which the
precursor vapor accumulates; d) accumulating a nominal amount of the precursor vapor
required for the vapor phase coating deposition; and e) adding the nominal amount of the
precursor vapor to the processing chamber in which the coating is being deposited.
Typically at least one catalyst vapor is added to the process chamber in addition to the at
least one precursor vapor, where the relative quantities of catalyst and precursor vapors
are based on the physical characteristics to be exhibited by the coating.
[0025] **BRIEF DESCRIPTION OF THE DRAWINGS**

[0026] Figure 1 shows a cross-sectional schematic of an apparatus 100 for vapor deposition of a coating, which apparatus employs the present invention for metering precise amounts of reactants to the coating formation process.

[0027] Figure 2 shows a cross-sectional schematic view of an apparatus 200 of the kind shown in Figure 1, where a number of substrates are processed simultaneously.

[0028] Figure 3 is a schematic illustrating a system 300 of the kind which could be used for production of a MEMS device where there are moving parts which are formed by a release-etching process in system 304 and where, subsequent to the release-etch process, the MEMS device is transferred through a pressure controlled passageway 306 to a coatings application chamber 302 of the kind described with reference to Figure 1.

[0029] **DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS**

[0030] As a preface to the detailed description, it should be noted that, as used in this specification and the appended claims, the singular forms "a", "an", and "the" include plural referents, unless the context clearly dictates otherwise.

[0031] We have developed an improved vapor-phase deposition method and apparatus for application of a thin (typically 5 Å to 1,000 Å thick, in and in some instances up to about 2,000 Å thick) film or coating to a semiconductor device substrate or a micro-electromechanical systems device. The method and apparatus are employed when at least one of the reactants or a catalyst used in coating formation must be vaporized prior to use, and where the amount of each reactant must be carefully controlled in terms of quantity available to react, in terms of time available for reaction at a given process pressure, or a combination of both. The method is particularly useful in the deposition of thin films or coatings where the thickness of the film or coating ranges from about 5 Å to about 500 Å,
and provides excellent results for coatings having a thickness in the range of about 300 Å.

[0032] As previously discussed herein, there are a multitude of applications for such thin layers or coatings. For purposes of illustration, applicants will describe the method and apparatus of the present invention in terms of the tunable deposition of an organic monolayer; however, one skilled in the art of deposition of layers and coatings will be able to use the concepts described for coatings which are not organic, and/or not monolayers.

[0033] There is a particular interest at this time in anti-stiction layers and coatings which are needed to enable reliable, long-term performance of the micro-electromechanical systems. Stiction (adhesion) of compliant micromechanical parts is one of the key reliability issues that has proven difficult to overcome. Conventionally, solution-based antistiction monolayers have been used; however, more recently, due to capillary stiction, particulation problems, and unsatisfactory quality, scalability, and reproducibility of the films produced by relatively lengthy wet processing, efforts are underway to develop vapor deposition methods for the antistiction coatings. The vacuum processing and vapor phase deposition of antistiction coatings, including self-assembled monolayers (SAMs) has provided higher quality films in general. An integrated vapor deposition process (including surface plasma treatment in the same chamber) typically offers better control of surface reactivity, while avoiding the potential for stiction between micromechanical parts during application of the antistiction coating.

[0034] The embodiments described in the examples below are with reference to the application of organic SAM coatings which are applied using vapor deposition techniques over the surface of a single crystal silicon substrate. The apparatus used for deposition of the coatings is available from Applied Microstructures, Inc. of San Jose, California. This apparatus is specifically designed to provide a high degree of control in terms of quantity of reactants provided to the coating application processing chamber for each individual process step, and in terms of the time and order at which these reactants are made.
available for the reaction.

[0035] The properties of the deposited films were evaluated using standard surface analysis methods, cantilever-beam-array test structures, and performance analysis of working MEMS devices.

[0036] I. AN APPARATUS FOR VAPOR DEPOSITION OF THIN COATINGS

[0037] Figure 1 shows a cross-sectional schematic of an apparatus 100 for vapor deposition of thin coatings. The apparatus 100 includes a process chamber 102 in which thin (typically 5 Å to 1,000Å thick) coatings are vapor deposited. A substrate 106 to be coated rests upon a substrate holder 104, typically within a recess 107 in the substrate holder 104. Depending on the chamber design, the substrate 106 may rest on the chamber bottom (not shown in this position in Figure 1). Attached to process chamber 102 is a remote plasma source 110, connected via a valve 108. Remote plasma source 110 may be used to provide a plasma which is used to clean and/or convert a substrate surface to a particular chemical state prior to application of a coating (which enables reaction of coating species and/or catalyst with the surface, thus improving adhesion and/or formation of the coating); or may be used to provide species helpful during formation of the coating (not shown) or modifications of the coating after deposition. The plasma may be generated using a microwave, DC, or inductive RF power source, or combinations thereof. The process chamber 102 makes use of an exhaust port 112 for the removal of reaction byproducts and is opened for pumping/purging the chamber 102. A shut-off valve or a control valve 114 is used to isolate the chamber or to control the amount of vacuum applied to the exhaust port. The vacuum source is not shown in Figure 1.

[0038] The apparatus 100 shown in Figure 1 is illustrative of a vapor deposited coating which employs two precursor materials and a catalyst. One skilled in the art will understand that one or more precursors and from zero to multiple catalysts may be used during vapor deposition of a coating. A catalyst storage container 116 contains catalyst
154, which may be heated using heater 118 to provide a vapor, as necessary. It is
understood that precursor and catalyst storage container walls, and transfer lines into
process chamber 102 will be heated as necessary to maintain a precursor or catalyst in a
vaporous state, minimizing or avoiding condensation. The same is true with respect to
heating of the interior surfaces of process chamber 102 and the surface of substrate 106 to
which the coating (not shown) is applied. A control valve 120 is present on transfer line
119 between catalyst storage container 116 and catalyst vapor reservoir 122, where the
catalyst vapor is permitted to accumulate until a nominal, specified pressure is measured
at pressure indicator 124. Control valve 120 is in a normally-closed position and returns
to that position once the specified pressure is reached in catalyst vapor reservoir 122. At
the time the catalyst vapor in vapor reservoir 122 is to be released, valve 126 on transfer
line 119 is opened to permit entrance of the catalyst present in vapor reservoir 122 into
process chamber 102 which is at a lower pressure. Control valves 120 and 126 are
controlled by a programmable process control system of the kind known in the art (which
is not shown in Figure 1).

[0039] A Precursor 1 storage container 128 contains coating reactant Precursor 1,
which may be heated using heater 130 to provide a vapor, as necessary. As previously
mentioned, Precursor 1 transfer line 129 and vapor reservoir 134 internal surfaces are
heated as necessary to maintain a Precursor 1 in a vaporous state, avoiding condensation.
A control valve 132 is present on transfer line 129 between Precursor 1 storage container
128 and Precursor 1 vapor reservoir 134, where the Precursor 1 vapor is permitted to
accumulate until a nominal, specified pressure is measured at pressure indicator 136.
Control valve 132 is in a normally-closed position and returns to that position once the
specified pressure is reached in Precursor 1 vapor reservoir 134. At the time the
Precursor 1 vapor in vapor reservoir 134 is to be released, valve 138 on transfer line 129
is opened to permit entrance of the Precursor 1 vapor present in vapor reservoir 134 into
process chamber 102, which is at a lower pressure. Control valves 132 and 138 are
controlled by a programmable process control system of the kind known in the art (which
is not shown in Figure 1).

[0040] A Precursor 2 storage container 140 contains coating reactant Precursor 2,
which may be heated using heater 142 to provide a vapor, as necessary. As previously
mentioned, Precursor 2 transfer line 141 and vapor reservoir 146 internal surfaces are
heated as necessary to maintain Precursor 2 in a vaporous state, avoiding condensation.
A control valve 144 is present on transfer line 141 between Precursor 2 storage container
146 and Precursor 2 vapor reservoir 146, where the Precursor 2 vapor is permitted to
accumulate until a nominal, specified pressure is measured at pressure indicator 148.
Control valve 144 is in a normally-closed position and returns to that position once the
specified pressure is reached in Precursor 2 vapor reservoir 146. At the time the
Precursor 2 vapor in vapor reservoir 146 is to be released, valve 150 on transfer line 141
is opened to permit entrance of the Precursor 2 vapor present in vapor reservoir 146 into
process chamber 102, which is at a lower pressure. Control valves 144 and 150 are
controlled by a programmable process control system of the kind known in the art (which
is not shown in Figure 1).

[0041] During formation of a coating (not shown) on a surface 105 of substrate 106, at
least one incremental addition of vapor equal to the vapor reservoir 122 of the catalyst
154, or the vapor reservoir 134 of the Precursor 1, or the vapor reservoir 146 of Precursor
2 may be added to process chamber 102. The total amount of vapor added is controlled
by both the adjustable volume size of each of the expansion chambers (typically 50 cc up
to 1,000 cc) and the number of vapor injections (doses) into the reaction chamber.
Further, the process control system (not shown) may adjust the set pressure 124 for
catalyst vapor reservoir 122, or the set pressure 136 for Precursor 1 vapor reservoir 134,
or the set pressure 148 for Precursor 2 vapor reservoir 146, to adjust the amount of the
catalyst or reactant added to any particular step during the coating formation process.
This ability to fix precise amounts of catalyst and coating reactant precursors dosed
(charged) to the process chamber 102 at any time during the coating formation enables the
precise addition of quantities of precursors and catalyst at precise timing intervals,
providing not only accurate dosing of reactants and catalysts, but repeatability in terms of
time of addition.

[0042]  This apparatus provides a very inexpensive, yet accurate method of adding
vapor phase precursor reactants and catalyst to the coating formation process, despite the
fact that many of the precursors and catalysts are typically relatively non-volatile
materials. In the past, flow controllers were used to control the addition of various
reactants; however, these flow controllers may not be able to handle some of the
precursors used for vapor deposition of coatings, due to the low vapor pressure and
chemical nature of the precursor materials. The rate at which vapor is generated from
some of the precursors is generally too slow to function with a flow controller in a manner
which provides availability of material in a timely manner for the vapor deposition
process.

[0043]  The present apparatus allows for accumulation of the vapor into an adequate
quantity which can be charged (dosed) to the reaction. In the event it is desired to make
several doses during the progress of the coating deposition, the apparatus can be
programmed to do so, as described above. Additionally, adding of the reactant vapors
into the reaction chamber in controlled aliquots (as opposed to continuous flow) greatly
reduces the amount of the reactants used and the cost of the coating process.

[0044]  Figure 2 shows a cross-sectional schematic of an embodiment of a vapor
deposition processing apparatus 200 which provides for the application of a thin coating to
a plurality of substrates 206 simultaneously. The apparatus 200 includes a process chamber
202 in which thin (5 Å to 1,000 Å thick) coatings are vapor deposited. A plurality of
substrates 206 to be coated rest upon a substrate holder 204, which can be moved within
process chamber 202 using a device 209. Attached to process chamber 202 is a remote
plasma source 210, connected via a valve 208. Remote plasma source 210 may be used to
provide a plasma which is used to clean or to react with (activate) a substrate surface prior
to application of a coating or may be used to provide species helpful during or after formation
of the coating (not shown). As previously described, the plasma may be generated using a
microwave, DC, or inductive RF power source, or may be generated using a combination of
power sources. The process chamber 202 makes use of an exhaust port 212 for the removal
of reaction byproducts and for pumping/purging of the process chamber 202. A control valve
214 is used to control the speed of vacuum pumping and evacuation (vacuum generator not
shown).

[0045] The apparatus 200 shown in Figure 2 is illustrative of a vapor deposited coating
which employs two precursor materials and a catalyst. One skilled in the art will
understand that one or more precursors and from zero to multiple catalysts may be used
during vapor deposition of a coating. Catalyst for use during the coating deposition
process enters process chamber 202 from a catalyst vapor reservoir (not shown) through
line 219 through control valve 220. Precursor 1 for use during the coating deposition
process enters process chamber 202 from a Precursor 1 vapor reservoir (not shown)
through line 217 through control valve 218, and Precursor 2 enters process chamber 202
from a Precursor 2 vapor reservoir (not shown) through line 215 through control valve
216. As previously mentioned transfer lines for the Catalyst, Precursor1, and Precursor 2
are heated as necessary to maintain these materials in a vaporous state, avoiding
condensation. The Catalyst, Precursor 1 and Precursor 2 may be distributed within
process chamber 202 through a baffling system 205 which typically contains separate
distribution paths for the catalyst and each precursor used in the coating deposition
process. The baffling system helps ensure even distribution of each reaction component
material throughout process chamber 202. Process chamber 202 typically uses a swing
door or a load lock 226. Upon completion of the reaction, process byproducts exit
process chamber 202 through exhaust port 212, which is connected to a vacuum pump
(not shown). The interior surfaces of process chamber 200 and other apparatus such as
baffling system 205 are typically heated to prevent condensation of the Catalyst, Precursor 1, and Precursor 2 upon these apparatus surfaces. The reaction pressure is typically determined by the amount of reactants injected into chamber 202. The processing chamber pressure is monitored by pressure sensing device 224, which is coordinated with the vapor delivery system previously described through a computerized control system (not shown). A flow control valve 214 is used to remove vapor and byproducts in general from the interior of process chamber 202. The operation of flow control valve 214 may be coordinated, through the computerized control system, to function in combination with the pressure sensing device, to maintain the desired pressure during pumping/purging steps.

[0046] Figure 3 shows a cross-sectional schematic of a MEMS processing system 300 which employs a release-etch processing chamber 310 (of the type used to produce moveable elements of a mechanical nature in a MEMS device) and a vapor deposition coating application system 312 of the kind previously described with reference to Figures 1 and 2. The release-etch process chamber 310 includes apparatus for reagent entry 324 (shown as a single line for convenience, but which may be a plurality of lines); a pressure sensing and monitoring device 326; an exhaust port 334, with flow control valve 332; a recirculation loop 331 with pump 330 is optional, but can be used to provide important processing advantages. The vapor deposition coating apparatus process chamber 308 includes apparatus for reagent (catalyst and precursor) entry 312 (shown as a single line for convenience, but which is a plurality of lines as previously discussed); a pressure sensing and monitoring device 314; and an exhaust port 322, with a control valve 320. The release-etch process chamber 310 and vapor deposition coating process chamber 308 are joined to each other through an isolation valving system 306.

[0047] II. EXEMPLARY METHODS OF THE INVENTION:

[0048] As discussed with respect to the apparatus, there have been problems in
providing accurately measured quantities of reactants on a repeatable basis to a vapor
deposition coating system. This is because many of the precursor materials for coating
formation have a low vapor pressure or are not compatible with mass flow controllers. In
addition, for many of the vapor deposition coatings, water acts as a catalyst to the coating
formation, and the amount of water present in the coating deposition chamber is not
precisely controlled.

[0049] When the surfaces of features to be coated are in the nanometer size range, it is
critical that the coating deposition be carefully controlled to provide the desired thickness
of coating (typically about 5 Å to 1,000 Å, and in some instances up to 2,000 Å) over the
entire surface area, and that there be no formation of particulate or agglomerations within
the depositing coating. In order to meet these critical requirements for thin vapor
deposited coatings, it is necessary to provide accurately measured quantities of reactants
and catalysts and to control the time period over which these accurately measured
quantities are delivered to the surface of the substrate or the deposition chamber.
Delivery to the surface of the substrate depends on interior design of the processing
chamber, and there are techniques which are well known in the art of chemical vapor
deposition which apply to delivery of reagents to the substrate surface. The present
method addresses the problem of providing accurately measured quantities of reactants
and catalysts which are delivered in the proper order and at the proper time to the coating
deposition chamber.

[0050] By way of example and not by way of limitation, the provision of accurate
quantities of reactants and catalysts will be illustrated with respect to monolayer coatings
of chloro-silanes and alkyl-silanes which are used in many applications such as MEMS,
BioMEMS, and micro-fluidics. Organic precursor materials such as (and not by way of
limitation) silanes, chlorosilanes, fluorosilanes, methoxy silanes, alkyl silanes, and amino
silanes are useful in general. Some of the particular precursors used to produce coatings
are, by way of example and not by way of limitation, perfluorodecylnitriclorosilanes
(FDTS), undecyltrichlorosilanes (UTS), vinyl-trichlorosilanes (VTS),
decyltrichlorosilanes (DTS), octadecyltrichlorosilanes (OTS), dimethyl dichlorosilanes
(DDMS), dodecyltrichlorosilanes (DDTS), fluoro-tetrahydrooctydime-thylchlorosilanes
(FOTS), perfluoroocetyldimethylchlorosilanes, aminopropylmethoxy silanes (APTMS),
fluoropropylmethyldichlorosilanes, and perfluorodecyldimethylchlorosilanes. The OTS,
DTS, UTS, VTS, DDTS, FOTS, and FDTS are all trichloro silane precursors. The other
end of the precursor chain is a saturated hydrocarbon with respect to OTS, DTS, and
UTS; contains a vinyl functional group, with respect to VTS and DDTS; and contains
fluorine atoms with respect to FDTS (which also has fluorine atoms along the majority of
the chain length). Other useful precursors include 3-aminopropyltrimethoxysilane
(APTMS), which provides amino functionality, and 3-glycidoxypropyltrimethoxysilane
(GPTMS). One skilled in the art of organic chemistry can see that the vapor deposited
coatings from these precursors can be tailored to provide particular functional
characteristics for a coated surface. The surface to be coated may be silicon, glass,
organic (plastic) or metal, for example.

[0051] Most of the silane-based precursors, such as commonly used di- and tri-
chlorosilanes, for example and not by way of limitation, tend to create agglomerates on
the surface of the substrate during the coating formation. These agglomerates can cause
structure malfunctioning or stiction. Such agglomerations are produced by partial
hydrolysis and polycondensation of the polychlorosilanes. This agglomeration can be
prevented by precise metering of moisture in the process ambient which is a source of the
hydrolysis, and by carefully controlled metering of the availability of the chlorosilane
precursors to the coating formation process.

[0052] Those working in the MEMS field have recognized the advantages of vapor
deposited coatings over coatings applied using liquid-based immersion, spray-on and
spin-on techniques. Some of those advantages include: elimination of stiction induced by
capillary forces; control of the coating environment (particularly the amount of moisture
present); uniform coating properties on micron and nanometer size patterns such as microchannels and pores; solvent free process with no contamination; and, a faster process which is compatible with MEMS clean room processing protocols, for example.

[0053] In a vapor deposition process which employs one precursor and a catalyst, a DDTS precursor may be used in combination with a water catalyst, for example. In a vapor deposition process which employs two precursors and a catalyst, a DDTS precursor, a UTS precursor, and a water catalyst may be used in combination, for example and not by way of limitation. The relative quantities of the DDTS and UTS precursors can be adjusted to provide different overall functional properties for the coated surface.

However, the ability to control the coated surface properties and to reliably reproduce the properties depends on the ability to control the relative quantities of the DDTS and UTS precursors supplied to the coating formation process. This ability depends on provision of accurately controlled quantities of the kind which are possible when the present method of invention is used.

[0054] When the precursors used to form the initial vapor deposited coating have potentially reactive functional groups on the exposed surface of the coating, these functional groups can be further reacted with other chemical compounds to modify the functionality of the surface of the coating.

[0055] In addition to organo-silanes, poly(ethylene glycol) (PEG) is used separately or in combination with other film-forming compounds such as the silanes to provide biotechnology functional surfaces. One portion of the coated surface may be coated with the reaction product of an organo-silane, while another is coated with a PEG reaction product. In the alternative, the organo-silane may include a functional group on the distal end of the polymer chain, away from the substrate surface, which functional group can be reacted with a PEG reactant, to place a PEG functional group at the distal end of the polymer chain, affecting coating surface functionality. For example, PEG films are known to reduce protein adsorption in micro-fluidic applications. PEG 3 films include 6
carbons, while PEG 2 films include 4 carbons. The length of the polymer chain can also
be adjusted to provide the desired film properties.

[0056] The present method for vapor deposition of coatings provides a number of
advantages. Typically a remote plasma source is used to generate a cleaning plasma
(typically oxygen-containing) which can be used to remove contaminants from the
substrate surface. When the substrate is silicon, the cleaning process is useful in the
formation of -OH functional groups which serve as binding sites for a number of coating
precursors such as the trichloro silanes. Precise control of the amount of precursors is
ensured through the direct measurement of the vapor pressure of the precursor at a given
temperature in a known volume. Process control is provided by varying the partial
pressure and the amount of the precursors employed in the vapor phase reaction.

[0057] III. GENERAL PARAMETER DESCRIPTIONS FOR VAPOR
DEPOSITION OF A MOLECULAR COATING:

[0058] Surfaces to be coated are typically pretreated in the same chamber. To obtain
bonding of a chloro- functional group to a substrate surface, it is necessary to create OH-
terminated sites on the surface. This can be done in the deposition chamber by treating a
silicon surface with an oxygen plasma in the presence of moisture. The plasma may be
produced using a remote power source of the kind previously described. The pressure in
the processing chamber during exposure of a substrate to the oxygen plasma typically
ranges from about 0.2 Torr to about 2 Torr, more typically from about 0.5 Torr to about 1
Torr. For a process chamber having a volume of about 2 liters, the plasma source gas
oxygen flow rate ranges from about 50 sccm to about 300 sccm, more typically from
about 100 sccm to 200 sccm. The substrate processing time is typically about 1 minute to
about 10 minutes, and more typically from about 1 minute to about 5 minutes.

[0059] The coating deposition is typically carried out in the deposition chamber at a
pressure ranging from about 100 mTorr to about 10 Torr, more typically at a pressure
ranging from about 0.5 Torr to about 5 Torr, and most typically at a pressure ranging from
about 0.1 Torr to about 3 Torr. The deposition temperature of the substrate depends on
the particular coating precursors and on the substrate material. For a silicon substrate,
where the coating precursor is FOTS or DDMS, used in combination with a water
catalyst, the substrate temperature is typically in the range of about 20 °C to about 60 °C.
To maintain these coating precursors in a vaporous state prior to reaction, the interior
surfaces of the coating deposition process chamber are typically maintained at a
temperature ranging from about 30 °C to about 60 °C. The time period required to
produce a continuous monolayer coating over the entire surface of the silicon substrate
using these coating precursors and the specified reaction temperature ranges from about 1
minute to about several hours, depending on precursor chemistry and substrate material,
typically the reaction time period is in the range of 5 minutes to 30 minutes, where the
coating precursor is FOTS or DDMS.

[0060] For deposition of an antistiction MEMS coating from chlorosilane precursors,
the following recipe and process conditions were used. In each case, a single precursor,
selected from the group consisting of dimethyldichlorosilane (DDMS), tridecafluoro-
1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS), and heptadecafluoro-1,1,2,2-
tetrahydrodecyltrichlorosilane (FDTS), was vaporized and used in combination with water
vapor as a catalyst. In each instance, the precursor and the water were degassed under
vacuum to remove dissolved gases prior to introduction into the system. The conditions
for degassing vary, depending on the precursor and catalyst, but one skilled in the art can
easily determine proper degassing conditions.

[0061] With reference to Figure 1, the degassed water was placed in catalyst storage
container 116 and was heated to a temperature of about 30 °C to produce a vapor which
was passed through transfer line 119 to accumulate in vapor reservoir 122, which had a
volume of 300 cc, and which was held at a pressure of 16 Torr. A DDMS precursor was
placed in Precursor 1 storage container 128 and was heated to a temperature of 30 °C to
produce a vapor which was passed through transfer line 129 to accumulate in vapor
reservoir 134, which had a volume of 50 cc, and which was held at a pressure of 50 Torr.
There was no precursor in Precursor 2 storage container 140.

[0062] A silicon substrate 106, having a surface 105 was manually loaded onto the
substrate holder 104. The process chamber 102, having a volume of about 2 liters, was
pumped down to about 20 mTorr and purged with nitrogen gas prior to and after the
coating reaction, which consisted of oxygen plasma treatment followed by coating
deposition. The process chamber 102 was vented to atmosphere. The process chamber
102 was then purged using nitrogen (filled with nitrogen to 10 Torr/pumped to 0.7 Torr,
five times). The surface 105 was treated with a remotely generated oxygen plasma from
plasma source 110 in the manner described above. Oxygen was directed into a plasma
generation source 110 through a mass flow controller (not shown). The oxygen flow rate
for plasma generation, based on the desired plasma residence time for process chamber
102, was about 200 sccm. The pressure in process chamber 102 was about 0.6 Torr.
The surface 105 of silicon substrate 106 was treated with the oxygen plasma at a pressure
of about 0.6 Torr for a time period of about 5 minutes. The plasma treatment was
discontinued, and the process chamber 102 was pumped down to the base pressure of
about 30 mTorr.

[0063] The water vapor reservoir 122 was charged with water vapor to a pressure of 16
Torr, as described above. The valve 126 between water vapor reservoir 122 and process
chamber 102 was opened until both pressures equalized (a time period of about 5
seconds) to about 0.8 Torr. The water vapor reservoir 122 was charged with vapor to 16
Torr a second time, and this volume of vapor was also dumped into the process chamber,
bringing the total water vapor pressure in process chamber 102 to about 1.6 Torr. The
DDMS vapor reservoir 134 had been charged with the precursor vapor to 50 Torr, as
described above, and the DDMS vapor was added immediately after completion of the
water vapor addition. The valve 138 between the DDMS vapor reservoir 134 and
process chamber 102 was opened until both pressures were equalized (a time period of
about 5 seconds) to about 4 Torr. The water and DDMS vapors were maintained in
process chamber 102 for a time period of 15 minutes. The process chamber was then
pumped back to the base pressure of about 30 mTorr.

[0064] The process chamber 102 was then purged (filled with nitrogen to
10 Torr/pumped to 0.7 Torr) five times. The process chamber was then vented to
atmosphere, and the silicon substrate 106 was manually removed from the process
chamber.

[0065] The resulting coated surface is typically very hydrophobic, as measured by
water contact angle, which is typically about 103° for DDMS films. The surface was
particularly smooth, having an RMS of 0.2 nm, with no visible particulation or defects.
The measured work of adhesion was reduced up to 3,000 times depending on the specific
process/chemistry. Under the conditions provided above, the measured work of adhesion
was reduced to about 30 µJ m⁻². The properties of the vapor deposited films are equivalent
to or better than those reported for liquid-phase deposited films. In addition, use of vapor
deposition prevents the stiction which frequently occurs during wet processing of the
substrate.

[0066] The above described exemplary embodiments are not intended to limit the
scope of the present invention, as one skilled in the art can, in view of the present
disclosure expand such embodiments to correspond with the subject matter of the
invention claimed below.
CLAIMS

[0068] We claim:

1. An apparatus for vapor deposition of coatings having a thickness ranging from
   about 5 Å to about 1,000 Å, where at least one precursor used for formation of said coating
   exhibits a vapor pressure below about 150 Torr at a temperature of 25 °C, the apparatus
   comprising:
      at least one precursor container in which said at least one precursor, in the
      form of a liquid or a solid, is placed;
      at least one precursor vapor reservoir for holding vapor of said at least one
      precursor;
      at least one device which controls precursor vapor flow from said
      precursor container into said precursor vapor reservoir;
      a pressure sensor in communication with said precursor vapor reservoir;
      a process controller which receives data from said pressure sensor,
      compares said data with a desired nominal vapor reservoir pressure, and sends a signal to
      a device which controls vapor flow from said precursor container into said precursor
      vapor reservoir, to prevent further vapor flow into said precursor vapor reservoir when
      said desired nominal pressure is reached;
      a device which controls precursor vapor flow into said precursor vapor
      reservoir upon receipt of a signal from said first process controller;
      a process chamber for vapor deposition of said coating on a substrate
      present in said process chamber; and
      a device which controls precursor vapor flow into said process chamber
      upon receipt of a signal from said process controller.
2. An apparatus in accordance with Claim 1, including a device which applies heat to said precursor while it is in said container, to produce a vaporous phase of said precursor.

3. The apparatus in accordance with Claim 1, or Claim 2, wherein a plurality of precursor containers, and a corresponding plurality of vapor reservoirs are present.

4. The apparatus in accordance with Claim 1, wherein the following additional elements are present:

   at least one catalyst container in which said catalyst, in the form of a liquid or a solid is placed;

   at least one catalyst vapor reservoir for holding vapor of said at least one catalyst;

   at least one device which controls vapor flow from said catalyst container into said catalyst vapor reservoir;

   a pressure sensor in communication with said catalyst vapor reservoir;

   a process controller which receives data from said pressure sensor,

   compares said data with a desired nominal catalyst vapor reservoir pressure, and sends a signal to a device which controls catalyst vapor flow from said catalyst container into said catalyst vapor reservoir, to prevent further vapor flow into said catalyst vapor reservoir when said desired nominal pressure is reached;

   a device which controls catalyst vapor flow into said catalyst vapor reservoir upon receipt of a signal from said process controller; and

   a device which controls catalyst vapor flow into said process chamber upon receipt of a signal from said fourth process controller.

5. An apparatus in accordance with Claim 4, wherein all process controllers reside in a single process controller.
6. An apparatus in accordance with Claim 4 or Claim 5, including a device which applies heat to said at least one precursor while it is in said precursor container, to produce a vaporous phase of said precursor.

7. An apparatus in accordance with Claim 4 or Claim 5, including a device which applies heat to said at least one catalyst while it is in said catalyst container, to produce a vaporous phase of said catalyst.

8. An apparatus in accordance with Claim 4 or Claim 5, wherein a plurality of precursor containers, and a corresponding plurality of vapor reservoirs are present.

9. An apparatus in accordance with Claim 1 or Claim 2, or Claim 4, or Claim 5, wherein said coating thickness ranges from about 5 Å to about 500 Å.

10. An apparatus in accordance with Claim 9, wherein said coating thickness ranges from about 5 Å to about 300 Å.

11. A method for vapor-phase deposition of coatings, where at least one precursor used for formation of said coating exhibits a vapor pressure below about 150 Torr at a temperature of 25 °C, the method comprising:
   a) providing a processing chamber in which said coating is vapor deposited;
   b) providing at least one precursor exhibiting a vapor pressure below about 150 Torr at a temperature of 25 °C;
   c) transferring vapor of said precursor to a precursor vapor reservoir in which said precursor vapor accumulates;
d) accumulating a nominal amount of said precursor vapor required for said vapor phase coating deposition; and
e) adding said nominal amount of said precursor vapor to said processing chamber in which said coating is being deposited.

12. A method in accordance with Claim 11, wherein a plurality of precursors are used, and wherein a plurality of precursors are accumulated in a plurality of precursor vapor reservoirs.

13. A method in accordance with Claim 12, wherein at least two of said precursor vapors are added to said processing chamber essentially simultaneously.

14. A method in accordance with Claim 12, wherein at least two of said precursor vapors are added to said processing chamber in sequence.

15. A method in accordance with Claim 11, wherein at least one catalyst vapor is added to said processing chamber to facilitate vapor deposition of said coating.

16. A method in accordance with Claim 15, wherein said catalyst vapor is accumulated in a vapor reservoir prior to transfer to said processing chamber.

17. A method in accordance with Claim 16, wherein said catalyst vapor is added to said processing chamber essentially simultaneously with at least one of said at least one precursor vapors.

18. A method in accordance with Claim 16, wherein said catalyst vapor is added to said processing chamber in sequence with at least one of said precursor vapors.
19. A method in accordance with Claim 18, wherein said catalyst vapor is added to said processing chamber prior to the addition of a precursor vapor to said processing chamber.

20. A method in accordance with Claim 11 or Claim 12, wherein at least one of said at least one precursor vapors is added to said process chamber from said vapor reservoir more than once, by repeating steps c), d), and e).

21. A method in accordance with Claim 15, or Claim 16, wherein at least one of said at least one catalyst vapor is added to said process chamber from said vapor reservoir more than once, by repeated filling of a nominal vapor reservoir volume, followed by repeated adding of said vapor catalyst to said process chamber from said vapor reservoir.

22. A method in accordance with Claim 11 or Claim 12, wherein a plurality of precursor vapors are added to said process chamber and wherein said precursor vapors are added in relative quantities required to produce coating physical characteristics.

23. A method in accordance with Claim 15, or Claim 16, wherein at least one catalyst vapor is added to said process chamber in a quantity relative to said at least one precursor vapor to produce a coating having specific physical characteristics.

24. A method in accordance to Claim 23, wherein a volumetric ratio of a precursor to a catalyst ranges from about 1 : 6 to about 6 : 1.

25. A method in accordance with Claim 24, wherein said volumetric ratio ranges from about 1 : 3 to about 3 : 1.