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(54) Title: IN SITU MODIFICATION OF GROUP IV NANOPARTICLES USING GAS PHASE NANOPARTICLE REACTORS

(57) Abstract: A method for creating an organically capped Group IV semiconductor nanoparticle is disclosed. The method includes flowing a Group IV semiconductor precursor gas into a chamber. The method also includes generating a set of Group IV semiconductor precursor radical species from the Group IV semiconductor precursor gas with a laser pyrolysis apparatus, wherein the set of the Group IV semiconductor precursor radical species nucleate to form the Group IV semiconductor nanoparticle; and flowing an organic capping agent precursor gas into the chamber. The method further includes generating a set of organic capping agent radical species from the organic capping agent precursor gas, wherein the set of organic capping agent radical species reacts with a surface of the Group IV semiconductor nanoparticle and forms the organically capped Group IV semiconductor nanoparticle.

IN SITU MODIFICATION OF GROUP IV NANOPARTICLES USING GAS PHASE NANOPARTICLE REACTORS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Pat. No. 60/881,869 filed January 1, 2007, entitled *IN SITU MODIFICATION OF GROUP IV NANOPARTICLES USING GAS PHASE NANOPARTICLE REACTORS,* the entire disclosure of which is incorporated by reference.

FIELD OF DISCLOSURE

[0002] This disclosure relates to methods for the in situ modification of Group IV nanoparticles.

BACKGROUND

[0003] Group IV nanoparticles have proven useful in a variety of applications for a wide selection of optoelectronic devices. However, due to problems associated with the reactivity of Group IV nanoparticle, and hence the stability of Group IV nanoparticle materials, effort has been taken in the art to address the issue of stabilizing Group IV nanoparticles for real world applications.

[0004] One example of an approach to increasing the surface stability and hence the quality of photoluminescence of silicon nanoparticles (*i.e.,* nanoparticles that are about 1.0 nm to about 4.0 nm in diameter that emit in the visible portion of the electromagnetic spectrum) has been to passivate the surfaces of the nanoparticles. For some applications, thermal oxidation of the silicon nanoparticle surfaces has proven effective at passivating the nanoparticles. However, for many optoelectronic applications, passivation by oxidation is not appropriate.

[0005] An alternative to passivation by surface oxidation is the formation of an organic passivation layer. For example, an extensive review of formation of organic passivation layers on flat and porous bulk surfaces of silicon and germanium surfaces can be found in J.M. Buriak, *Chem. Rev.*, vol. 102, pp. 1271-1308 (2002). The insertion reaction of an unsaturated organic species, such as an alkene or alkyne at a hydrogen-terminated Group IV semiconductor surface site has been known for some time. As detailed in the Buriak review, when the Group IV semiconductor material is silicon, the reaction is referred to as hydrosilylation. In general, this reaction forms a Si-C bond and has been shown to date to provide bulk silicon semiconductor materials some level of protection against chemical attack from certain chemicals.

[0006] More specifically, with respect to Group IV nanoparticles, the passivation of colloidal dispersions of silicon nanocrystals harvested from porous silicon wafers using hydrosilylation has been demonstrated (Lars H. Lie, et. al., *Journal of Electroanalytical Chemistry*, **538-539**, pp. 183-190 (2002)). However, the surfaces of such Group IV nanomaterials do not have the integrity required for use in range of optoelectronic devices. This is apparent in that silicon nanoparticles so far reported with organic passivation layers have produced Group IV nanoparticles with poor quantum yields (~10% or less) and photoluminescent intensities that are not stable over substantial periods of time.

[0007] As covered in the above mentioned review, in the context of hydrosilylation using electrografting of porous bulk silicon surfaces, it has been suggested that oxygen in the solvents used during the hydrosilylation reaction may compete with the binding of alkynes to porous silicon solid. Still, even approaches taking the precaution of using oxygen-free solvents during hydrosilylation of silicon nanoparticles have not proven to overcome the surface stability problems associated with Group IV nanoparticles (see for example Swihart et al. US 2004/0229447, Nov. 8, 2004).

[0008] Still other approaches suggested for stabilizing Group IV nanoparticles includes a stable shell layer around a Group IV nanoparticle core. However, producing sizable quantities of quality core/shell material has proven to be difficult. Thus, there is a need in the art for approaches to stabilizing Group IV nanoparticles, and methods of producing such materials.

SUMMARY OF THE INVENTION

[0009] The invention relates, in one embodiment, to a method for creating an organically capped Group IV semiconductor nanoparticle. The method includes flowing a Group IV semiconductor precursor gas into a chamber. The method also includesgenerating a set of Group IV semiconductor precursor radical species from the Group IV semiconductor precursor gas with a laser pyrolysis apparatus, wherein the set of the Group IV semiconductor precursor radical species nucleate to form the Group IV semiconductor nanoparticle; and flowing an organic capping agent precursor gas into the chamber. The method further includes generating a set of organic capping agent radical species from the organic capping agent precursor gas, wherein the set of organic capping agent radical species reacts with a surface of the Group IV semiconductor nanoparticle and forms the organically capped Group IV semiconductor nanoparticle.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] **FIG. 1** shows a series of Fourier Transform Infrared (FTIR) spectra comparing silicon nanoparticles prepared using different conditions in a gas phase reactor, in accordance with the invention;

[0011] **FIG. 2** is a generalized schematic of an embodiment of an apparatus for the synthesis of embodiments of in situ modified Group IV nanoparticles, in accordance with the invention;

[0012] **FIG. 3** is a schematic of an embodiment of a two-stage RF plasma reactor for the synthesis of embodiments of in situ modified Group IV nanoparticles, in accordance with the invention;

[0013] **FIG. 4** is a schematic of an embodiment of a two-stage laser pyrolysis reactor for the synthesis of embodiments of in situ modified Group IV nanoparticles, in accordance with the invention; and

[0014] **FIG. 5** is a representation for the demonstration of factors impacting the synthesis of embodiments of in situ modified Group IV nanoparticles using an embodiment of a two-stage laser pyrolysis reactor, in accordance with the invention.

DETAILED DESCRIPTION

[0015] What is disclosed herein provides for embodiments of in situ modified Group IV nanoparticles prepared using gas phase nanoparticle reactors. In some embodiments, the in situ modified Group IV nanoparticle core materials are modified with a shell layer. As will be discussed in more detail subsequently, such core/shell nanoparticles may have cores of silicon, germanium, and alpha-tin Group IV material; or alloys thereof. The core/shell in situ modified Group IV nanoparticles may be doped. The shell may be of a variety of Group IV materials and combination thereof, or other materials, such as, for example, but not limited by, a variety of oxides, nitrides, carbides, and sulfides. In still other embodiments, a stable organic passivation layer may be formed in situ; either on a Group IV nanoparticle material, or on a core/shell nanoparticle.

[0016] It is contemplated that Group IV semiconductor nanoparticles may be used in a variety of applications. Due to the luminescent properties of small nanoparticles, silicon and germanium nanoparticles have been contemplated for use in light-emitting applications, including use as phosphors for solid-state lighting, luminescent taggants for biological applications, security markers and related anti-counterfeiting measures. Other potential applications include a variety of optoelectronic devices, such as light-emitting diodes, photodiodes, photovoltaic cells, and sensors that utilize their unique optical and semiconductor properties. Because of the ability to produce colloidal forms of semiconductor nanoparticles, these materials offer the potential of low-cost processing, such as printing, that is not possible with conventional semiconductor materials.

[0017] Group IV nanoparticles have an intermediate size between individual atoms and macroscopic bulk solids. In some embodiments, Group IV nanoparticles have a size on the order of the Bohr exciton radius (*e.g.,* 4.9 nm for silicon), or the de Broglie wavelength, which allows individual Group IV nanoparticles to trap individual or discrete numbers of charge carriers, either electrons or holes, or excitons, within the particle. The Group IV nanoparticles may exhibit a number of unique electronic, magnetic, catalytic, physical, optoelectronic and optical properties due to quantum confinement and surface energy effects. For example, Group IV nanoparticles exhibit luminescence effects that are significantly greater than, as well as melting temperatures of nanoparticles substantially lower than the complementary bulk Group IV materials.

[0018] These unique effects vary with properties such as size and elemental composition of the nanoparticles. For instance, as will be discussed in more detail subsequently, the melting of germanium nanoparticles is significantly lower than the melting of silicon nanoparticles of comparable size. With respect to quantum confinement effects, for silicon nanoparticles, the range of nanoparticle dimensions for quantum confined behavior is between about 1 nm to about 15 nm, while for germanium nanoparticles, the range of nanoparticle dimensions for quantum confined behavior is between about 1 nm to about 35 nm, and for alpha-tin nanoparticles, the range of nanoparticle dimensions for quantum confined behavior is between about 1nm to about 40 nm. In another example, some embodiments of Group IV nanoparticles exhibit photoluminescence effects that are significantly greater than the photoluminescence effects of macroscopic materials having the same composition. Such these photoluminescence effects vary as a function of the size of the nanoparticle, so that light emitted, and hence color emitted in the visible portion of the electromagnetic spectrum is a quantum confinement effect that varies with nanoparticle size.

[0019] As used herein, the term "Group IV nanoparticle" generally refers to hydrogen terminated Group IV nanoparticles having an average diameter between about 1.0 nm to 100.0 nm, and composed of silicon, germanium, and alpha-tin, or combinations thereof. As will be discussed subsequently, some embodiments of Group IV nanoparticles are doped. With respect to shape, embodiments of Group IV nanoparticles include elongated particle shapes, such as nanowires, or irregular shapes, in addition to more regular shapes, such as spherical, hexagonal, and cubic nanoparticles, and mixtures thereof. Additionally, the nanoparticles may be single-crystalline, polycrystalline, or amorphous in nature. As such, a variety of types of Group IV nanoparticle materials may be created by varying the attributes of composition, size, shape, and crystallinity of Group IV nanoparticles. Exemplary types of Group IV nanoparticle materials are yielded by variations including, but not limited by: 1) single or mixed elemental composition; including alloys, core/shell structures, doped nanoparticles, and combinations thereof; 2) single or mixed shapes and sizes, and combinations thereof; and 3) single form of crystallinity or a range or mixture of crystallinity, and combinations thereof.

[0020] It is contemplated that suitable quality Group IV nanoparticles are used as starting materials for the uses and compositions disclosed herein. Particle quality includes, but is not limited by, particle morphology, average size and size distribution. For embodiments of disclosed in situ modified Group IV nanoparticles, suitable nanoparticle materials useful as starting materials have distinct particle morphology, with low incidence of particle clumping, agglomeration, or fusion. As mentioned previously, the properties that are imparted for Group IV nanoparticles are related closely to the particle size. In that regard, for many applications, a monodisperse population of particles of specific diameter is also indicated.

[0021] For the Group IV nanoparticles, the surface area to volume ratio, which is inversely proportional to radius, is in the range of a thousand times greater than for colloids in the 1.0 micron range. These high surface areas, as well as other factors, such as, for example, the strain of the Group IV atoms at curved surfaces, are conjectured to account for what the inventors have observed, which has not been generally reported in the literature, as the extraordinary reactivity of the Group IV nanoparticles. As a result of this observation, embodiments of the disclosed in situ modified Group IV nanoparticle materials are maintained in an inert environment until they are stably processed, so that for the target application the material so produced has the highest quality for the intended use.

[0022] For example, stabilized luminescence is observed for in situ modified Group IV nanoparticles that have been organically capped. Phenomena such as high quantum yield and intensity of photoluminescence emitted from such embodiments of organically capped

Group IV nanoparticles is observed. With respect to semiconductor properties, the inventors' have observed that by keeping embodiments of the native Group IV nanoparticles in an inert environment from the moment the particles are formed through the formation of Group IV semiconductor thin films, that such thin films so produced have properties characteristic of native bulk semiconductor materials. In that regard, such thin films are formed from materials for which the spectral absorbance, photovoltaic and photoconductive properties are well characterized. This is in contrast, for example, to the use nanoparticles mixed with organic modifiers. In some such modifications, the Group IV nanoparticle materials are significantly oxidized. The use of these types of nanoparticle materials produces hybrid thin films, which hybrid thin films do not have as yet the same desirable properties as traditional Group IV materials.

[0023] The first step for producing embodiments of the disclosed in situ modified Group IV nanoparticles is to produce quality nanoparticles in an inert environment. For the purposes of this disclosure, an inert environment is an environment in which there are no fluids (*i.e.*, gases, solvents, and solutions) that react in such a way that they would negatively affect properties such as the semiconductor, photoelectrical, and luminescent properties of the Group IV nanoparticles. In that regard, an inert gas is any gas that does not react with embodiments of in situ modified Group IV nanoparticles in such a way that it negatively affects the properties of the in situ modified Group IV nanoparticles for their intended use. Likewise, an inert solvent is any solvent that does not react with embodiments of in situ modified Group IV nanoparticles in such a way that it negatively affects the properties of the in situ modified Group IV nanoparticles for their intended use. Finally, an inert solution is a mixture of two or more substances that does not react with in situ modified Group IV nanoparticles in such a way that it that it negatively affects the properties of the in situ modified Group IV nanoparticles for their intended use.

[0024] Accordingly, the in situ Group IV nanoparticles may be made in any suitable gas phase reactor according to any suitable gas phase method provided they are formed in an environment that is substantially inert. Examples of suitable gas phase reactors include, for example, but not limited by RF plasma and laser pyrolysis reactors. Examples of inert gases that may be used to provide an inert environment include nitrogen and the rare gases, such as argon. Though not limited by defining inert as only oxygen-free, since other fluids may react in such a way that they negatively affect the semiconductor, photoelectrical, and luminescent properties of the in situ modified Group IV nanoparticles, it has been observed that a substantially oxygen-free environment is indicated for producing suitable Group IV nanoparticles. As used herein, the terms “substantially oxygen free” in reference to environments, solvents, or solutions refer to environments, solvents, or solutions wherein the oxygen content has been reduced in an effort to eliminate or minimize the oxidation of the in situ modified Group IV nanoparticles in contact with those environments, solvents, or solutions. As such, the in situ modified Group IV nanoparticles starting materials are fabricated in inert, substantially oxygen-free conditions until they are stably processed.

[0025] For some embodiments of in situ modified Group IV nanoparticles used for example in photoluminescent applications, substantially oxygen-free conditions will contain no more than about 100 ppm oxygen (O_2). This includes embodiments where the substantially oxygen-free conditions contain no more than about 1 ppm oxygen and further includes embodiments where the substantially oxygen-free conditions contain no more than about 100 ppb oxygen. For photovoltaic and photoconductive applications of in situ modified Group IV nanoparticles, “inert” refers to environments, solvents, or solutions wherein the oxygen content has been substantially reduced to produce, for example, Group IV semiconductor thin films having no more than 10^{17} to 10^{19} oxygen per cubic centimeter of Group IV semiconductor thin film. In that regard, if the in situ modified Group IV nanoparticle materials are reactive after preparation, such as for example a silicon/germanium core/shell nanoparticle material, such material should be maintained under vacuum or an inert, substantially oxygen-free atmosphere until it has been stably processed. In another example, some embodiments of inks formulated using such reactive in situ modified Group IV nanoparticle materials are made in anhydrous, deoxygenated solvents or solutions held under vacuum or inert gas to minimize the dissolved oxygen content in the liquid until the nanoparticle material is stably processed.

[0026] In one aspect of in situ modified Group IV nanoparticle materials using gas phase reactors, embodiments of core/shell particles can be prepared. For example, in the fabrication of photovoltaic thin films, it is desirable to adjust the band gap of embodiments of Group IV photoconductive thin films. For Group IV nanoparticle materials used to fabricate such thin films, the band gap of silicon is about 1.1 eV, while the band gap of germanium is about 0.7 eV, and for alpha-tin is about 0.05 eV. This may be done through formulations of single or mixed elemental composition of silicon; germanium and tin nanoparticles in core/shell structures, as well as alloys, doped nanoparticles, and combinations thereof. Embodiments of the in situ modified Group IV core/shell nanoparticle materials so formed can be specifically designed to provide the targeted thin film band property. As previously discussed, Group IV nanoparticle core materials can be prepared having a variety of shell materials, for example, but not limited by, carbide, nitride, sulfide, and oxide shell compositions.

[0027] In another aspect of in situ modified Group IV nanoparticle materials using gas phase reactors, embodiments of Group IV nanoparticles with a variety of organic passivation layers from a variety of organic capping agents is contemplated. One example of a reaction that is used for creating an organic passivation layer on Group IV nanoparticle materials is an insertion reaction between the hydrogen-terminated Group IV atoms at the nanoparticles surface and alkenes or alkynes. For the in situ modified Group IV nanoparticles of interest, which are silicon, germanium, and tin; and core/shell nanoparticle materials, as well as alloy nanoparticle material thereof, the reaction is referred to as hydrosilylation, hydrogermylation, and hydrostannylation, respectively. In solution, various suitable protocols for this class of insertion reaction are known. Such protocols include the use of a free-radical initiator, thermally induced insertion, photochemical insertion using ultraviolet or visible light, and metal complex mediated insertion. Descriptions of protocols for the above described insertion reaction, and other known reactions for forming Group IV element-carbon bonds may be found in J.M. Buriak, Chem. Rev., vol. 102, pp. 1271-1308 (2002), the entire disclosure of which is incorporated herein by reference.

[0028] However, embodiments of in situ Group IV nanoparticles disclosed herein are stably passivated with an organic capping agent in the gas phase, using for example, but not limited by, either RF plasma or laser pyrolysis reactors. Without limiting the scope of the invention, one possible explanation for the organic capping of Group IV nanoparticles is that the conditions in such reactors may be optimized to create radical species necessary for reactions such as hydrosilylation to occur between a Group IV atom on a nanoparticle surface, and an organic moiety. The inventors' observations of Group IV nanoparticle reactivity to organic moieties having terminal alkene or alkyne groups in the gas phase are consistent with such an explanation, as can be understood from the Fourier Transform Infrared (FTIR) spectra shown in **FIG. 1**.

[0029] In **FIG. 1**, the spectra of samples of Group IV nanoparticles subjected to different conditions in a two-stage RF plasma reactor comprised of an RF plasma reactor in the first stage, in series with a second RF reactor configured like the first stage, only without using RF source, as will be discussed in more detail subsequently. In the first-stage reactor, silicon nanoparticles were formed, and then flowed into the second-stage reactor for further modification in a set of experiments for producing core/shell Group IV nanoparticles. The optimization experiments produced some surprising results. In the second stage, ethylene gas was used as a precursor gas for creating silicon carbide. In **FIG. 1**, FTIR Spectra A is a control in which no ethylene gas or plasma is used in the second-stage reactor, but only a stream of hydrogen gas. FTIR Spectra A of **FIG. 1** is characteristic of hydrogen terminated silicon nanoparticles, having bands at 2140 cm^{-1} (Si-H stretching mode), as well as 950 cm^{-1} and 860 cm^{-1} (both Si-H wagging modes). In FTIR Spectra B of **FIG. 1**, ethylene was flowed into the second-stage reactor, but no plasma was actuated. It is known that ethylene may ethyl adducts in an insertion reaction with hydrogen terminated Group IV materials. In the mid-range of the infrared portion of the electromagnetic spectrum, bands at about 2850 cm^{-1} to about 3000 cm^{-1} are indicative of ethyl adducts to silicon, respectively. These bands are evident in FTIR Spectra B, indicative of conditions which are favorable for promotion of the gas phase insertion reaction of an organic moiety having a terminal alkene or alkyne group.

[0030] As will be discussed in more detail subsequently, some examples of organic species of interest for the in situ organic capping of Group IV nanoparticle materials include, but are not limited by, simple alkenes and alkynes in the C2-C18 series, as well as substituted alkenes and alkynes. It is contemplated that for some embodiments of Group IV organic-capped nanoparticle materials, more polar organic moieties such as those containing heteroatoms, or amine of hydroxyl groups are indicated, while in other, aromatic groups, such as phenyl, and benzyl groups are indicated.

[0031] As has been previously discussed, examples of reactors suitable for preparation of embodiments of in situ modified Group IV nanoparticles include RF plasma reactors and laser pyrolysis reactors.

[0032] **FIG. 2** depicts a generalized schematic of an embodiment of a gas phase reactor apparatus **100** suitable for the fabrication of doped Group IV nanoparticles. For gas phase reactors, a plurality of gas lines as shown in **FIG. 2** may be used. Gas line **5** is a generalized gas line for use with nanoparticle reactors, comprised of a gas source **7**, a gas line trap **11** for scrubbing oxygen and water from the gas, a gas line analyzer **13** for monitoring oxygen and water levels to ensure that they are effectively removed from the gas phase reactor lines, a gas line mass flow controller **15**, and a gas line valve **17**. All elements comprising the gas line **5** are in fluid communication with one another through gas line conduit **9**. Gas line **5** could be useful as, for example but not limited by, a dopant gas line. As a dopant gas line, then gas line trap **11** is optional for scrubbing oxygen and water from the dopant gas may be used in cases where the dopant gas is not aggressive and can be effectively filtered. Additionally, the gas line analyzer **13** for monitoring oxygen and water levels to ensure that they are effectively removed from the RF plasma reactor lines, may be also optional for the same reason. For example, gas line **25** may be useful for inert make-up gas, and is comprised of an inert gas source **27**, an inert gas line trap **31** for scrubbing oxygen and water from the inert gas, an inert gas line analyzer **33** for monitoring oxygen and water levels to ensure that they are effectively removed from the gas phase reactor lines, an inert gas line mass flow controller **35**, and an inert gas line valve **37**. All elements comprising the inert gas line **25** are in fluid communication with one another through inert gas line conduit **29**. In order to make Group IV nanoparticles, gas line **45** is comprised of Group IV semiconductor primary precursor gas source **47**, a Group IV primary precursor gas line trap **51** for scrubbing oxygen and water from the Group IV primary precursor gas, a Group IV primary precursor gas line analyzer **53** for monitoring oxygen and water levels to ensure that they are effectively removed from the gas phase reactor lines, a Group IV primary precursor gas line mass flow controller **55**, and a Group IV primary precursor gas line valve **57**. All elements comprising the Group IV primary precursor gas line **45** are in fluid communication with one another through inert gas line conduit **49**.

[0033] The gas phase reactor assembly **60** is composed of a gas phase reactor **62**, a reactor inlet line **64**, a reactor inlet line valve **66**, and a reactor outlet line **66**. Downstream from the gas phase reactor assembly **60** is the particle collector assembly **70**. The particles are collected on a mesh material of a variety of configurations; for example, either as a flat screen or net-shaped. The particles come into the particle collector **72** from particle collector inlet line **71**, which has particle collector inlet valve **73**. The effluent gas flows from the particle collector **72** out through the particle collector outlet line **75**, which has particle outlet valve **77**. The pressure control system for particle collector **70** is composed of a pressure sensor **74**, controller **76**, and a throttle valve, for example, such as a butterfly valve **78**. During typical operation, inlet valve **73** and outlet valve **77** are open, but butterfly valve **78** is partially open. As particles are collected in particle collector **72**, pressure builds up, and is detected by pressure sensor **74**, which through a controller **76** opens butterfly valve **78** to keep the pressure constant. Downstream from the particle collector assembly **70** is the exhaust assembly **80**, which of an exhaust line **80**, a dust collector **82** and pump **86** with a mist trap **88**.

[0034] Unless otherwise designated, all valves indicated for the generalized gas phase reactor apparatus **100** are positive shut-off valves, such as ball, diaphragm, bellows, toggle, and plug valves, and all gas line conduits and fittings used are steel. For example, the but not restricted by, the gas lines to the reactor; *i.e.,* up to gas phase reactor inlet line **62** may be

0.250"OD/0.152" ID stainless steel tubing, while all gas lines from gas phase reactor outlet line **66** to the exhaust are QF40 stainless steel piping.

[0035] Where embodiments of gas phase reactor **60** as shown in **FIG. 2** are used for doping, a variety of dopant gases are possible for use for creating doped Group IV nanoparticles. For example, n-type Group IV nanoparticles may be prepared using a plasma phase method in the presence of well-known dopant gases such as phosphine, or arsine. Alternatively, p-type semiconductor nanoparticles may be prepared in the presence of dopant gases such as boron diflouride, trimethyl borane, or diborane. With respect to an inert gas sources, noble gases for example, such as argon, helium, and neon and combinations thereof may be used. With respect to the primary precursor gases used for Group IV nanoparticle preparation, primary precursor gases such as silane, disilane, germane, digermane, any of their halide analogs and combinations thereof, are contemplated for use.

[0036] **FIG. 3** is a schematic of an embodiment of a two-stage RF plasma reactor assembly **160**, which is an embodiment of reactor **60** of **FIG. 1**. The two-staged RF plasma reactor assembly **160** is composed of a first RF reactor assembly **200**, and a second RF plasma assembly **210**. The first RF reactor assembly **200** is comprised of a first gas phase reactor chamber **202**. The first gas phase reactor chamber **202** has an inlet end **201**, which is in fluid communication with a gas reactor inlet line, such as gas reactor inlet line **64** of **FIG. 1**. The first gas phase reactor chamber has an outlet end **203**, which is in fluid communication with the second RF reactor assembly **210** via a first RF reactor assembly line **208**. The first RF plasma reactor assembly **200** has a first RF source **206**, having a first RF plasma reactor assembly first electrode **205** and a first RF plasma reactor assembly second electrode **207**. The first electrode **205** and the second electrode **207** of the first RF plasma reactor assembly **200** are mounted onto the first RF plasma reactor assembly **200** chamber **202** using a ring electrode configuration.

[0037] Similarly, second RF reactor assembly **210** is comprised of a second gas phase reactor chamber **212**. The second gas phase reactor chamber **212** has an inlet end **211**, which is in fluid communication via a first RF reactor assembly line **208**. The first gas phase reactor chamber has an outlet end **213**, which is in fluid communication with both a particle collector assembly **70** and an exhaust system, such as the exhaust assembly **80** of **FIG. 1** via second RF reactor line **218**. The second RF plasma reactor assembly **210** has a second RF source **216**, having a second RF plasma reactor assembly first electrode **215** and a second RF plasma reactor assembly second electrode **217**. As will be discussed in more detail subsequently, for embodiments of Group IV nanoparticles modified with organic capping agents, the RF source **216** is not typically used, so that a dedicated system for organic capping of Group IV nanoparticles may be designed without RF plasma source **216**. The first electrode **215** and the second electrode **217** of the second RF plasma reactor assembly **210** are mounted onto the second RF plasma reactor assembly chamber **212** using a ring electrode configuration.

[0038] Desirable attributes for the gas phase reactor chambers **202, 212** include, but are not limited by a dielectric material having high transmission of RF frequency with mechanical and chemical stability under plasma conditions. Some examples of such materials include quartz, sapphire, and fumed silica. In some embodiments of RF reactor assemblies **200** and **210**, the chambers **202, 212** may be about 0.375" OD, while in other embodiments the chambers **202, 212** may be about 1.5". As shown the electrodes **205, 207, 215, 217** are on the exterior of the gas phase reactor chambers **202, 212**. A number of metallic materials are suitable for the electrodes, for example, but not limited by copper and stainless steel. The spacing of the electrodes **205, 207, 215, 217** may be about 5 mm to about 30 mm apart for 0.375" diameter gas phase reactor chambers **202, 212**, and may be about 5 mm to about 50 mm apart for 1.5" diameter gas phase reactor chambers **202, 212**. The pressure in the gas phase reactor chambers **202, 212** is kept at between about 0.5 Torr to about 20 Torr. RF reactor sources **206, 216** are sources capable of delivering up to 300W in power at 13.56 MHz. The power delivered to RF reactor chambers **202, 212** is between about 20W to about 150W.

[0039] Secondary precursor delivery assembly **220** of **FIG. 3** is composed of a secondary precursor assembly gas source **221**, and optionally, for some embodiments of in situ modified Group IV nanoparticles, such as Group IV nanoparticles prepared with organic capping, a fluid reservoir **222**, which is in fluid communication with secondary precursor assembly gas source **221** through optional fluid reservoir line **223**. Both the secondary precursor assembly gas source **221** and fluid reservoir **222** are in fluid communication with secondary RF reaction chamber **216** through secondary precursor assembly gas source line **224**, having secondary precursor assembly gas source valve **225**.

[0040] Optionally, an online analysis assembly **230** of **FIG. 3** may also be a component of embodiments of a two-stage RF plasma reactor assembly, such as two-stage RF plasma reactor assembly **160**. An analyzer **232**, such as a particle counter, or mass spectrometer may be plumbed inline through lines 234 and 236, having analysis assembly valves **235** and **237**, respectfully. As shown in **FIG. 3**, the valving can be two-way to ensure that the analyzer can analyze nanoparticles from both the first stage RF reactor **200** and second stage RF reactor **210**.

[0041] An example of the preparation of an embodiment of Group IV nanoparticles prepared in a two-stage RF reactor, such as two-stage RF reactor **160** of **FIG. 3** is given for doped Group IV nanoparticles prepared in a first stage reactor, such as first stage reactor **200** of **FIG. 3**, which are subsequently organically capped with a short chained terminal alkene, C2-C9 for example, in a second RF reactor, such as second reactor **210** of **FIG. 3**. The doped particles may be prepared in an RF reactor described by the combination of the generalized reactor of **FIG. 2** and the two-stage RF reactor of **FIG. 3**. A dopant gas line **5** of **FIG. 2** may be a p-type dopant gas line, for the delivery of diborane, while primary precursor gas line **45** of **FIG. 2** would be used for a primary precursor gas, such silane. For example, 100 ppm diborane in argon would be in gas source **7** of **FIG. 2**, while 10% silane in argon would be in source **47** of **FIG. 2**. The flow rate of the dopant gas may be, for example, between about 60sccm to about 150 sccm, while the flow rate of the Group IV precursor gas may be between about 15 sccm to about 30 sccm. The first RF plasma reactor chamber, such as first RF reactor chamber **202 FIG. 3** may be quartz tube of about 0.375" OD, and the electrodes **205, 207** may be copper with a spacing of about 11mm. Between about 40W to about 50W was delivered to the first RF plasma reactor chamber using an RF plasma source, such as first

RF plasma source **206** of **FIG. 3**. The pressure in the first RF plasma reactor chamber **202** may be maintained at between about 5 Torr to about 10 Torr.

[0042] As previously mentioned, and in light of the discussion of **FIG. 1**, for the purpose of modifying Group IV nanoparticles with an organic capping agent, a second reactor without an RF source is typically not used. Therefore, the doped silicon nanoparticles so formed are then passed into a chamber, such as chamber **212** of a second RF reactor **210** of **FIG. 3**, where the second reactor for organic passivation typically does not have RF plasma source **216**, or first and second electrodes **215**, **217**. Chamber **212** may be quartz tube of about 0.375" OD. For the gas phase insertion reaction, an inert gas, such as argon would be the secondary precursor assembly gas source, such as secondary precursor assembly gas source **221** of **FIG. 3**. In this example, secondary gas source would be used to bubble inert gas into a short chain (C5-C9) terminal alkene liquid held in reservoir **222**, in order to volatilize the alkene so that it can be passed into secondary RF reactor chamber **212**. In the case of C2-C4 alkenes, since these exist as gases, there is no need for reservoir **222**. The flow rates of the alkene going into secondary RF reactor chamber **212** may be between about 10 sccm to about 1000 sccm. The stoichiometry of the insertion reaction between the alkene and doped silicon nanoparticle reactants can be controlled by controlling the pressure head of alkene in through controlling the pressure coming from secondary precursor assembly gas source **221**. Additionally, an inert solution of an alkene can be prepared using a non-reactive solvent, such as low molecular weight alkanes, such as hexane.

[0043] As discussed in the above, given the results discussed for **FIG. 1**, the second RF source **216** may not be required to activate the reactants for the reaction of the insertion reaction between organic modifier and reactive silicon atoms at the surface of the nanoparticles to proceed, but may be useful for some embodiments of modified Group IV nanoparticles with organic capping agents. Moreover, a second RF reactor **210** of **FIG. 3** is required for the formation of core/shell Group IV nanoparticles.

[0044] In **FIG. 4**, a schematic showing the cross-section of an embodiment of a two-stage laser pyrolysis reactor assembly **260**, which is another embodiment of reactor **60** of **FIG. 2** is shown. The laser pyrolysis reactor body **305** is composed of a casing **300**, a bottom plate **310**, and top plate **320**. The primary precursor conduit or tube **330** is composed of a first inner conduit or tubing **332**, and a second outer conduit or tubing **334**. The concentric arrangement of inner conduit **332** and outer conduit **334** is maintained by spacer **336**, which is made of a porous stainless steel material, and also functions as a filter. The primary precursor conduit **330** has an inlet end **336**, which is in fluid communication with a gas reactor inlet line, such as gas reactor inlet line **64** of **FIG. 2** and an outlet end **338**, which is in fluid communication with laser pyrolysis reactor outlet port **324**. A first secondary precursor conduit assembly **340** is composed of secondary precursor conduit of tubing **342**, having an inlet end **341**, and an outlet end **343**. Inlet end **341** may be in fluid communication with a gas source line, such generalized gas line **5** of **FIG. 2**, or secondary precursor assembly **220** of **FIG. 3**. Outlet end **343** is in fluid communication with a first secondary precursor nozzle tubing **342**, and second secondary precursor nozzle tubing **344**. The first secondary precursor nozzle tubing **342** is in fluid communication with a first secondary precursor nozzle **346**, while the second secondary precursor nozzle tubing **344** is in fluid communication with a second secondary precursor nozzle **348**. A second secondary precursor conduit assembly **350**, not shown, and identical with respect to the elements described for first secondary precursor conduit assembly **340** is mounted in an axis orthogonal to the axis in which secondary precursor conduit assembly **340** is mounted, yielding a total of four nozzles symmetrically distributed in the vicinity of particle formation. In this fashion, the secondary precursor gas flow of the secondary precursor gas is evenly distributed around the area in which the particles are formed, which is indicated in the cross-section by the hatched circle. Though two secondary precursor nozzle assembles are disclosed, higher order assemblies and nozzle designs are possible, as would be apparent to one of ordinary skill in the art.

[0045] Referring to **FIG. 5**, the height adjustment of the secondary precursor gas nozzles is important for optimizing the conditions for in situ modification of Group IV nanoparticles. In **FIG. 5**, two heights are indicated. The first height, H_1 is the height between the secondary precursor nozzles, such as **346, 348**, and the center of laser beam, which laser beam is indicated by the arrowed line. It should be noted that this height may also be affected by the adjustment of the laser beam position, as well. The second height, H_2 is the height between the outlet end **338** of primary precursor conduit or tube **330**, and the tips of the secondary precursor nozzles, such as **346, 348**. In order to adjust the secondary precursor nozzle with great precision and accuracy, secondary precursor nozzle height adjustment assembly **360** is used. Secondary precursor nozzle stage assembly **360** is comprised of stage **362**, in which the nozzles, such as **346, 348**. Stage **362** is mounted on shaft **364**, which is connected to handle **366** and adjustment knob **368**. As one of ordinary skill in the art is apprised, such stage assemblies are capable of controlling height adjustments to fractions of a mil, providing highly precise and accurate adjustment of both height, H_1 and height, H_2.

[0046] The optical assembly **370** of laser pyrolysis reactor assembly **260** of **FIG. 4** is composed of a laser **372**, optionally a focusing lens **374** a first optical port **376**, and a second optical port **378**. The dark line indicates the direction of the laser beam through the laser pyrolysis reactor assembly **260**. Orthogonal to the line of sight through first and second optical ports **376, 378** are third and forth optical ports **375, 377** (not apparent in the plane the cross-section of **FIG. 4**), which are used for operator viewing. The laser needs to have wavelength and power specification suitable for the decomposition of the primary precursor gases in order to form the Group IV nanoparticles. A carbon dioxide (CO_2) laser, having a wavelength of 10.59 microns, and capable of delivering between about 30W to about 250W; operating either in the continuous wave or pulsed beam mode, and having an unfocused beam diameter of between about 4 mm to about 8 mm is an example of a laser suitable for use for the laser pyr`olysis preparation of Group IV nanoparticles. The window material for the optical ports **375, 376, 377, 378** and other optical material, such as the focusing lens **374** should be durable both chemically and mechanically, and capable of transmission of the light from the laser light source. An example of a suitable window material for use with a CO_2 laser is zinc selenide.

[0047] Finally, top plate **320** has particle collector conduit **324**, which accumulates and guides the nanoparticles produced towards the laser pyrolysis reactor outlet port **324**. The laser pyrolysis reactor outlet port **324** with is in fluid communication with both a particle collector assembly **70** of **FIG. 2** and finally, an exhaust system, such as the exhaust assembly **80** of **FIG. 2**.

Example

[0048] A set of grafted Group IV nanoparticles was produced by the two-stage laser pyrolysis reactor assembly 260 as shown in FIG. 4, in which a silicon nitride surface layer was deposited on silicon nanoparticles, in accordance with the invention. In this example, a silane primary precursor gas (at a flow rate of about 40 sccm) was combined with a helium purge gas (at a flow rate of 2500 sccm) and then flowed into two-stage laser pyrolysis reactor assembly 260, in order to form the core. In addition, an ammonia secondary precursor gas (at a flow rate of about 300 sccm) was also flowed in order to form the shell. The chamber pressure was maintained at about 650 Torr. The laser power was 104W, with a beam height (H_1 as shown in **FIG. 5**) of 1.5 mm.

[0049] Consequently, it was shown in transmission electron micrograph (TEM) images that adjusting the nozzle height (H_2 of **FIG. 5**) to about 4 mm produced grafted Group IV nanoparticles that did not significantly dissolve in 1M KOH. In contrast, adjusting the nozzle height (H_2 of **FIG. 5**) to about 5.25 mm produced grafted Group IV nanoparticles that did significantly dissolve in 1M KOH. This example demonstrates the significance of factors such as the height adjustment of the nozzles and the laser beam in producing high quality Group IV nanoparticle materials.

[0050] Organically capped material can be prepared using the two-stage laser pyrolysis reactor apparatus described for this example, in combination with a secondary precursor delivery assembly, such as the secondary precursor delivery assembly **220** of **FIG. 3**, and described in the example given in the above for the preparation of Group IV nanoparticles with organic capping using a two-stage RF reactor. In preparing stably passivated Group IV nanoparticles with an organic capping agent using the laser pyrolysis reactor described in this section for the preparation of the silicon core/ silicon nitride shell nanoparticles, instead of using ammonia in the secondary precursor gas stream, a gas stream of short chain (C2-C9) terminal alkene could be used at between about 10 sccm to about 1000 sccm of organic vapor.

[0051] While principles of the disclosed in situ modification of Group IV nanoparticles using gas phase reactors have been described in connection with specific embodiments, it should be understood clearly that these descriptions are made only by way of example and are not intended to limit the scope of what is disclosed. In that regard, what has been disclosed herein has been provided for the purposes of illustration and description. It is not intended to be exhaustive or to limit what is disclosed to the precise forms described. Many modifications and variations will be apparent to the practitioner skilled in the art. What is disclosed was chosen and described in order to best explain the principles and practical application of the disclosed embodiments of the art described, thereby enabling others skilled in the art to understand the various embodiments and various modifications that are suited to the particular use contemplated. It is intended that the scope of what is disclosed be defined by the following claims and their equivalence.

WHAT IS CLAIMED IS:

1. A method for creating an organically capped Group IV semiconductor nanoparticle, comprising:

flowing a Group IV semiconductor precursor gas into a chamber;

generating a set of Group IV semiconductor precursor radical species from the Group IV semiconductor precursor gas with a laser pyrolysis apparatus, wherein the set of the Group IV semiconductor precursor radical species nucleate to form the Group IV semiconductor nanoparticle;

flowing an organic capping agent precursor gas into the chamber;

generating a set of organic capping agent radical species from the organic capping agent precursor gas, wherein the set of organic capping agent radical species reacts with a surface of the Group IV semiconductor nanoparticle and forms the organically capped Group IV semiconductor nanoparticle.

2. The method of claim 1, wherein the Group IV semiconductor precursor gas is one of silane, disilane, germane, and digermane.

3. The method of claim 1, wherein the organic capping agent precursor gas includes at least one of an alkene, an alkyne, an amine, a phenyl, and a benzyl.

4. The method of claim 1, wherein the organically capped Group IV semiconductor nanoparticle has a diameter of between about 1 nm and about 100 nm.

5. The method of claim 1, wherein the organically capped Group IV semiconductor nanoparticle is one of a single-crystalline nanoparticle, a polycrystalline nanoparticle, and an amorphous nanoparticle.

6. A method for creating an organically capped Group IV semiconductor nanoparticle, comprising:

flowing a Group IV semiconductor precursor gas into a chamber;

flowing a dopant precursor gas into the chamber;

generating a set of Group IV semiconductor precursor radical species from the Group IV semiconductor precursor gas and the dopant precursor gas with a laser pyrolysis apparatus, wherein the set of the Group IV semiconductor precursor radical species nucleate to form a Group IV semiconductor nanoparticle;

flowing an organic capping agent precursor gas into the chamber;

generating a set of organic capping agent radical species from the organic capping agent precursor gas, wherein the set of organic capping agent radical species reacts with a surface of the Group IV semiconductor nanoparticle and forms the organically capped Group IV semiconductor nanoparticle.

7. The method of claim 6, wherein the Group IV semiconductor precursor gas is one of silane, disilane, germane, and digermane.

8. The method of claim 6, wherein the dopant precursor gas is one of boron diflouride, trimethyl borane, and diborane.

9. The method of claim 6, wherein the organic capping agent precursor gas includes at least one of an alkene, an alkyne, an amine, a phenyl, and a benzyl.

10. The method of claim 6, wherein the organically capped Group IV semiconductor nanoparticle has a diameter of between about 1 nm and about 100 nm.

11. The method of claim 6, wherein the organically capped Group IV semiconductor nanoparticle is one of a single-crystalline nanoparticle, a polycrystalline nanoparticle, and an amorphous nanoparticle.

12. An organically capped Group IV semiconductor nanoparticle, created by the method comprising:

flowing a Group IV semiconductor precursor gas into a chamber;

generating a set of Group IV semiconductor precursor radical species from the Group IV semiconductor precursor gas with a laser pyrolysis apparatus, wherein the set of the

Group IV semiconductor precursor radical species nucleate to form a Group IV semiconductor nanoparticle;

flowing an organic capping agent precursor gas into the chamber;

generating a set of organic capping agent radical species from the organic capping agent precursor gas, wherein the set of organic capping agent radical species reacts with a surface of the Group IV semiconductor nanoparticle and forms the organically capped Group IV semiconductor nanoparticle.

13. The organically capped Group IV semiconductor nanoparticle of claim 12, wherein the Group IV semiconductor precursor gas is one of silane, disilane, germane, and digermane.

14. The organically capped Group IV semiconductor nanoparticle of claim 12, wherein the organic capping agent precursor gas includes at least one of an alkene, an alkyne, an amine, a phenyl, and a benzyl.

15. The organically capped Group IV semiconductor nanoparticle of claim 12, wherein the organically capped Group IV semiconductor nanoparticle has a diameter of between about 1 nm and about 100 nm.

16. The organically capped Group IV semiconductor nanoparticle of claim 12, wherein the organically capped Group IV semiconductor nanoparticle is one of a single-crystalline nanoparticle, a polycrystalline nanoparticle, and an amorphous nanoparticle.

17. An organically capped Group IV semiconductor nanoparticle, created by the method comprising:

flowing a Group IV semiconductor precursor gas into a chamber;

flowing a dopant precursor gas into the chamber;

generating a set of Group IV semiconductor precursor radical species from the Group IV semiconductor precursor gas and the dopant precursor gas with a laser pyrolysis apparatus, wherein the set of the Group IV semiconductor precursor radical species nucleate to form a Group IV semiconductor nanoparticle;

flowing an organic capping agent precursor gas into the chamber;

generating a set of organic capping agent radical species from the organic capping agent precursor gas, wherein the set of organic capping agent radical species reacts with a surface of the Group IV semiconductor nanoparticle and forms the organically capped Group IV semiconductor nanoparticle.

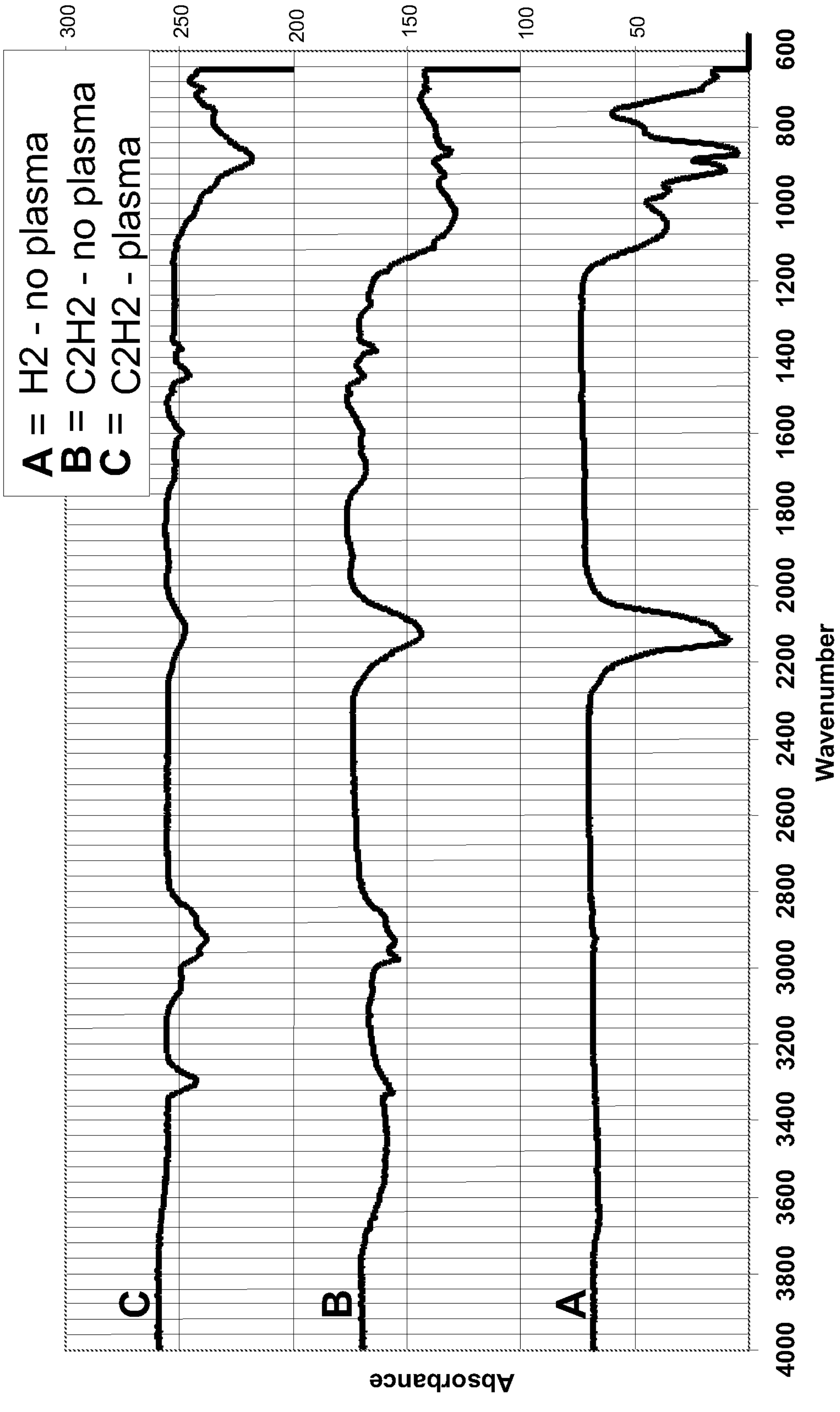
18. The organically capped Group IV semiconductor nanoparticle of claim 17, wherein the Group IV semiconductor precursor gas is one of silane, disilane, germane, and digermane.

19. The organically capped Group IV semiconductor nanoparticle of claim 17, wherein the dopant precursor gas is one of boron diflouride, trimethyl borane, and diborane.

20. The organically capped Group IV semiconductor nanoparticle of claim 17, wherein the organic capping agent precursor gas includes at least one of an alkene, an alkyne, an amine, a phenyl, and a benzyl.

21. The organically capped Group IV semiconductor nanoparticle of claim 17, wherein the organically capped Group IV semiconductor nanoparticle has a diameter of between about 1 nm and about 100 nm.

22. The organically capped Group IV semiconductor nanoparticle of claim 17, wherein the organically capped Group IV semiconductor nanoparticle is one of a single-crystalline nanoparticle, a polycrystalline nanoparticle, and an amorphous nanoparticle.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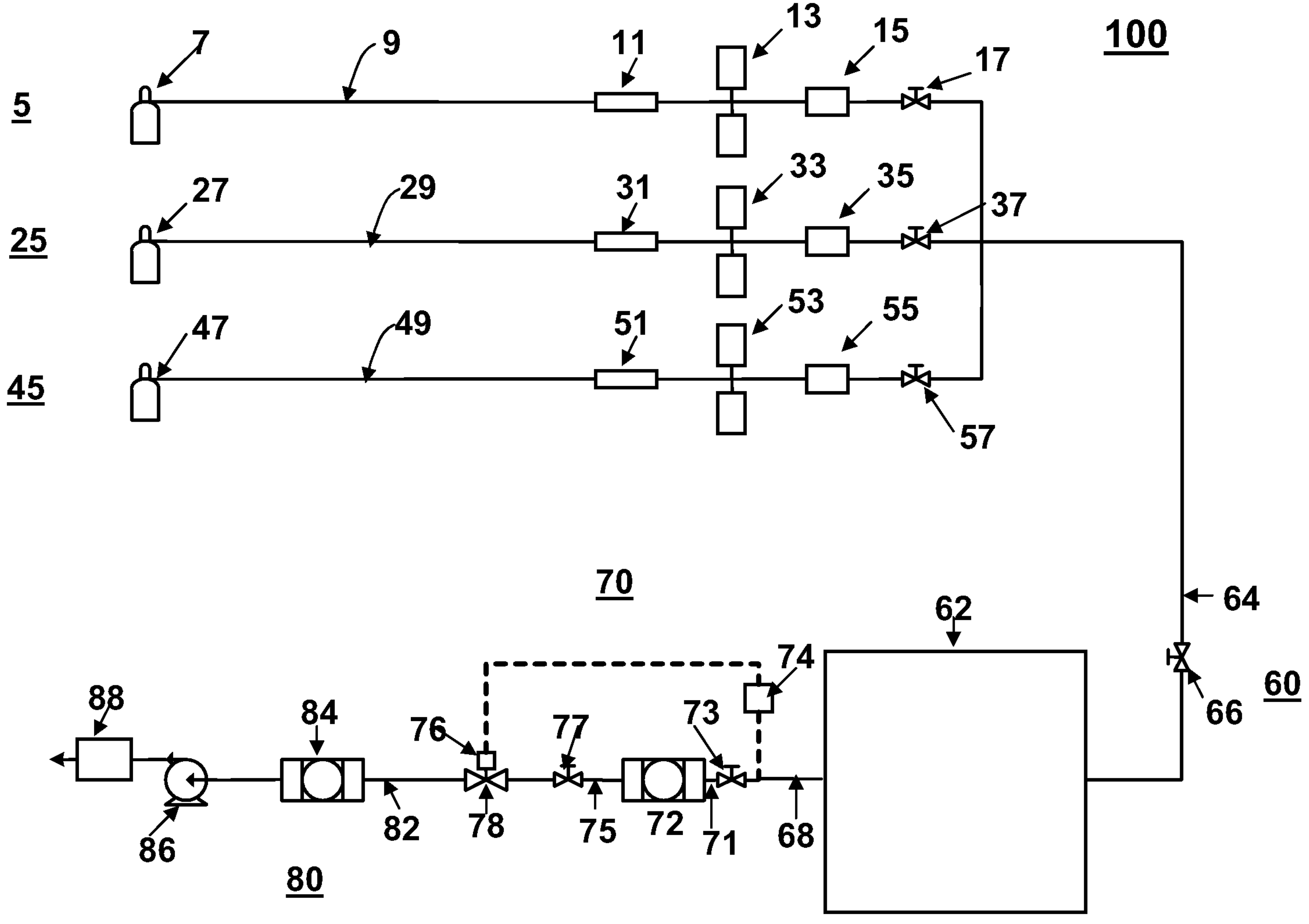
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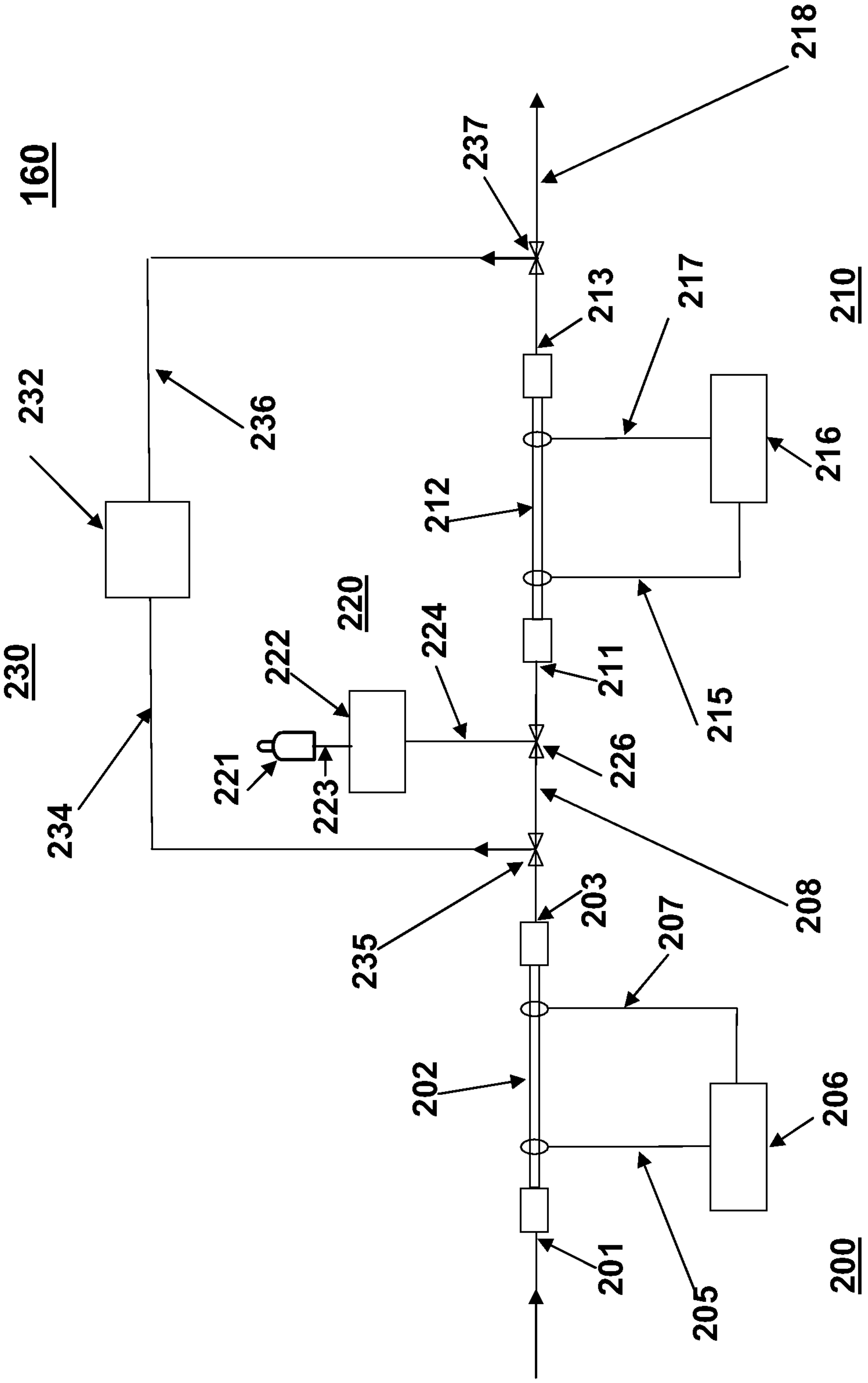
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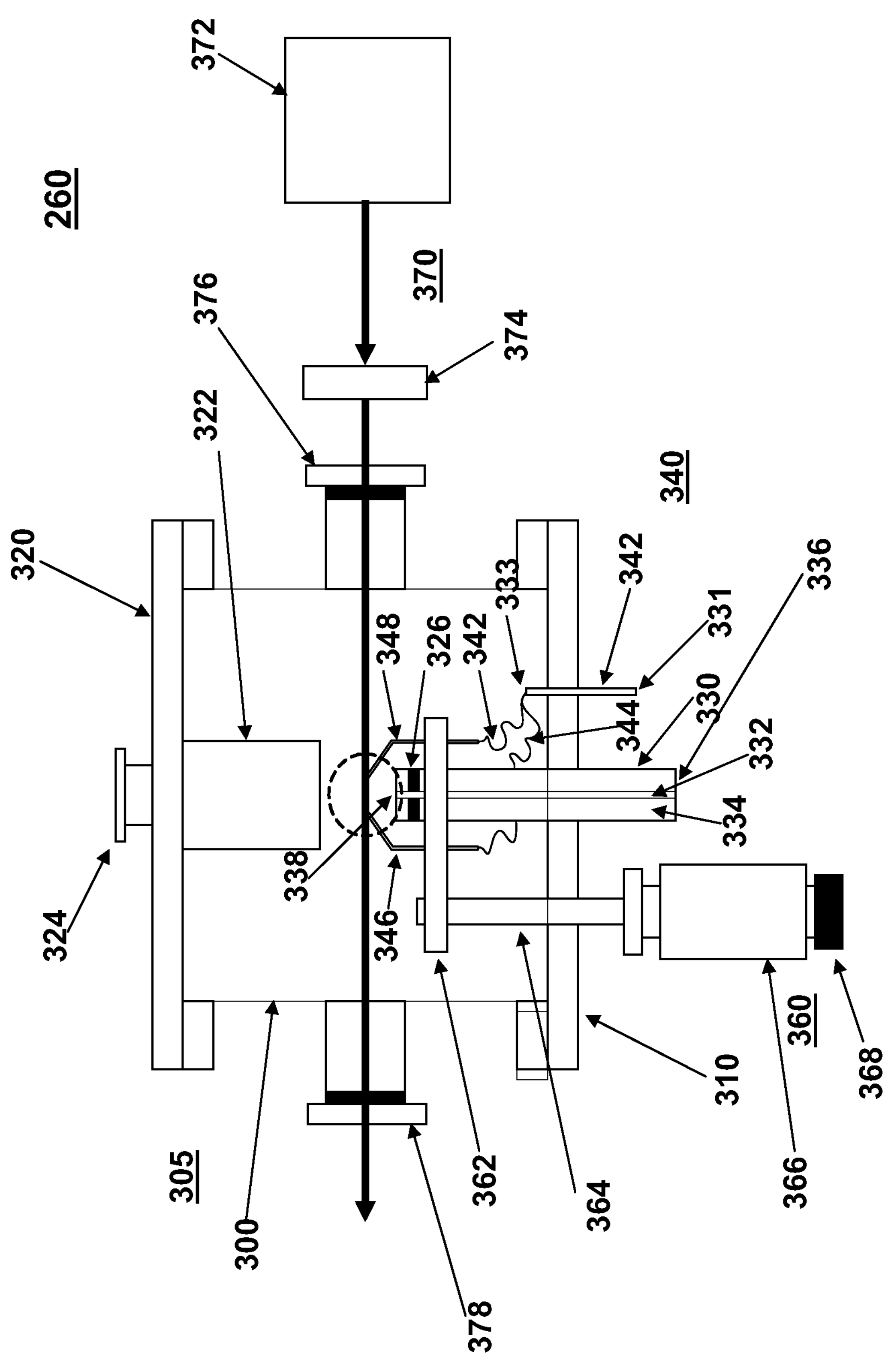
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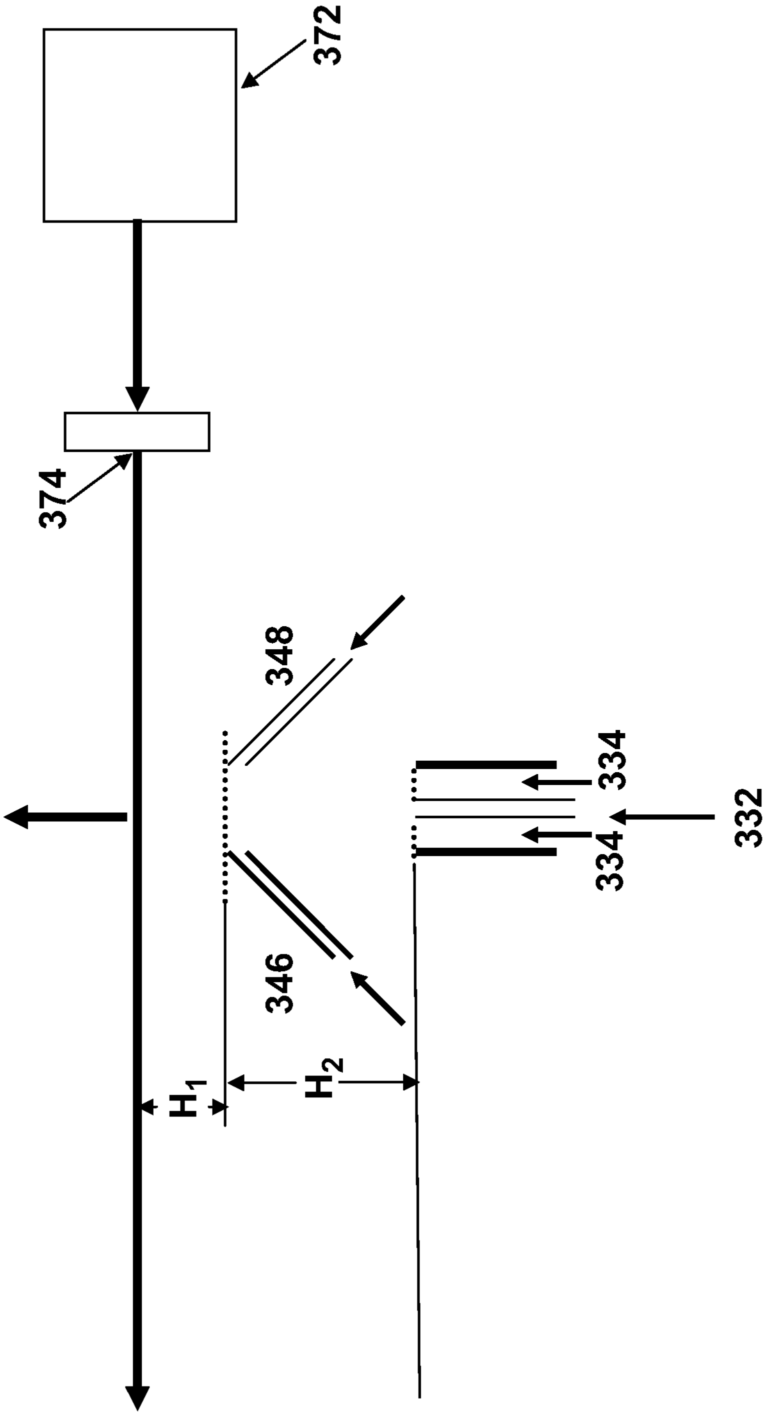
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