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(54) **Title:** METHOD OF RECOVERING NANOPARTICLES FROM A SILICONE MATERIAL

(57) **Abstract:** A method of recovering nanoparticles from a silicone material comprises providing a nanoparticle composition comprising a silicone material and nanoparticles. The method also comprises depolymerizing the silicone material of the nanoparticle composition to form volatile silicon compounds. Finally, the method comprises substantially separating the volatile silicon compounds and the nanoparticles to recover the nanoparticles.



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METHOD OF RECOVERING NANOPARTICLES FROM A SILICONE MATERIAL

FIELD OF THE INVENTION

[0001] The present invention generally relates to a method of recovering nanoparticles and, more specifically, to a method of recovering nanoparticles from a silicone material.

DESCRIPTION OF THE RELATED ART

[0002] Nanoparticles are known in the art and can be prepared via various processes. For example, nanoparticles are often defined as particles having at least one dimension of less than 100 nanometers and are produced either from a bulk material, which is initially larger than a nanoparticle, or from particles smaller than the nanoparticles, such as ions and/or atoms. Nanoparticles are particularly unique in that they may have significantly different properties than the bulk material or the smaller particles from which the nanoparticles are derived. For example, a bulk material that acts as an insulator or semiconductor can be, when in nanoparticle form, electrically conductive.

[0003] Nanoparticles may also be produced via a plasma process. For example, nanoparticles may be produced in a plasma reactor from a precursor gas. In certain plasma processes, the nanoparticles produced in the plasma reactor are captured or collected in a fluid, such as a silicone fluid. It is generally difficult to recover or isolate the nanoparticles from the silicone fluid. Further, even if the silicone fluid including the nanoparticles is utilized in certain applications, the nanoparticles generally may have a long useful life in which they exhibit desirable physical properties, yet nanoparticles are often discarded after their initial use. This is undesirable because the production of nanoparticles can be time consuming and expensive.

SUMMARY OF THE INVENTION AND ADVANTAGES

[0004] The present invention provides a method of recovering nanoparticles from a silicone material. The method comprises providing a nanoparticle composition comprising a silicone material and nanoparticles. The method also comprises depolymerizing the silicone material of the nanoparticle composition to form volatile silicon compounds. Finally, the method comprises substantially separating the volatile silicon compounds and the nanoparticles to recover the nanoparticles.

[0005] The method of the present invention allows for the recovery of nanoparticles from a silicone material, which allows for the recycling or reuse of the silicone material and/or the nanoparticles. The method provides significant benefits and extends the useful life of both the silicone material and the nanoparticles.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] Other advantages and aspects of this invention may be described in the following detailed description when considered in connection with the accompanying drawings wherein:

[0007] Figure 1 illustrates one embodiment of a low pressure high frequency pulsed plasma reactor for producing nanoparticles;

[0008] Figure 2 illustrates another embodiment of a low pressure high frequency pulsed plasma reactor for producing nanoparticles;

[0009] Figure 3 illustrates an embodiment of a system including a low pressure pulsed plasma reactor to produce nanoparticles and a diffusion pump to collect the nanoparticles; and

[0010] Figure 4 illustrates a schematic view of one embodiment of a diffusion pump for collecting nanoparticles produced via a reactor.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The present invention provides a method of recovering nanoparticles from a silicone material. The method of the instant invention allows for recycling the silicone material and/or the nanoparticles. This extends the useful life of both the silicone material and the nanoparticles, and recycling the silicone material and/or the nanoparticles may be less expensive and time consuming than discarding the silicone material and the nanoparticles and reproducing the same.

[0012] The method comprises providing a nanoparticle composition comprising a silicone material and nanoparticles. The silicone material of the nanoparticle composition and the nanoparticles are each described in greater detail below, respectively.

[0013] The nanoparticle composition may be provided in any manner. For example, the nanoparticle composition may be purchased or prepared. When the nanoparticle composition is prepared, the nanoparticles and the silicone material may be purchased and combined to form the nanoparticle composition, or the nanoparticles and/or the silicone material may be prepared prior to forming the nanoparticle composition.

[0014] The silicone material may be any silicone material. By silicone material, it is meant that the silicone material includes at least one siloxane bond, i.e., an Si-O-Si bond. For example, the silicone material may comprise a solid silicone, a liquid silicone, a dispersion of a silicone, a mixture of a silicone with an organic and/or inorganic compound, or a combination thereof. More specifically, the silicone material may comprise a silicone liquid, a silicone fluid, a silicone gum, a silicone gel, a silicone solid, a silicone resin, a cured silicone polymer, an uncured silicone gum, a silicone emulsion, a silicone sealant, a silicone rubber, a silicone oil, a silicone grease, a silicone tubing, liquid silicone rubber, a silicone elastomer, a silicone band, a silicone tubing, a filled silicone polymer, a fiber reinforced silicone polymer, a silicone sheet, a silicone mat, a silicone varnish, a silicone glove, or combinations thereof. The silicone material may be crosslinked or not crosslinked and may be cured or uncured.

[0015] The silicone material may comprise any combination of siloxane units, i.e., the silicone material comprise any combination of $R_3SiO_{1/2}$ units, i.e., M units, $R_2SiO_{2/2}$ units, i.e., D units, $RSiO_{3/2}$ units, i.e., T units, and $SiO_{4/2}$ units, i.e., Q units, where R is typically a substituted or unsubstituted hydrocarbyl group, as defined below. For example, when the silicone material comprises a rubber, elastomer, or gel, the silicone material comprises or is formed from at least one polymer including repeating D units, i.e., a linear or partly branched polymer. Alternatively, when the silicone material is resinous, the silicone material generally includes a silicone resin having T and/or Q units.

[0016] In embodiments in which the silicone material is resinous, the silicone material may comprise a DT resin, an MT resin, an MDT resin, a DTQ resin, an MTQ resin, an MDTQ resin, a DQ resin, an MQ resin, a DTQ resin, an MTQ resin, or an MDQ resin. Combinations of different resins may be present in the silicone material. Moreover, the silicone material may comprise a resin in combination with a polymer.

[0017] When the silicone material is cured or cross-linked, the silicon material may be formed from a variety of reaction mechanisms. For example, the silicone material may be formed from a hydrosilylation-curable silicone composition, a radiation-curable silicone composition, a peroxide-curable silicone composition, or a condensation-curable silicone composition.

[0018] In various embodiments, the silicone material comprises a silicone fluid or polymer. The silicone fluid or polymer may be linear, branched, partly branched, or cyclic. Further, the silicone polymer may be crosslinked to form the silicone material.

[0019] Specific examples of the silicone material include polydimethylsiloxane (PDMS), phenylmethyl siloxane, methylhydrogensiloxane, diphenylsiloxane, vinylmethylsiloxane, fluoroalkylsiloxane, methylsilsesquioxane, phenylsilsesquioxane, and copolymers or combinations thereof

[0020] In embodiments where the silicone material comprises the silicone polymer or fluid, the silicone polymer comprises repeating $R_2SiO_{2/2}$ units, where R is an independently selected substituted or unsubstituted hydrocarbyl group. For example, R may be aliphatic, aromatic, cyclic, alicyclic, etc. Further, R may include ethylenic unsaturation. By “substituted,” it is meant that one or more hydrogen atoms of the hydrocarbon may be replaced with atoms other than hydrogen (e.g. a halogen atom, such as chlorine, fluorine, bromine, etc.), or a carbon atom within the chain of R may be replaced with an atom other than carbon, i.e., R may include one or more heteroatoms within the chain, such as oxygen, sulfur, nitrogen, etc. R typically has from 1 to 10 carbon atoms, alternatively from 1 to 6 carbon atoms. Substituted or unsubstituted hydrocarbyl groups containing at least 3 carbon atoms can have a branched or unbranched structure. Examples of hydrocarbyl groups represented by R include, but are not limited to, alkyl, such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 1-ethylpropyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, hexyl, heptyl, octyl, nonyl, and decyl; alkenyl, such as vinyl; cycloalkyl, such as cyclopentyl, cyclohexyl, and methylcyclohexyl; aryl, such as phenyl and naphthyl; alkaryl, such as tolyl and xylyl; and aralkyl, such as benzyl and phenethyl. Examples of halogen-substituted hydrocarbyl groups represented by R include, but are not limited to, 3,3,3-trifluoropropyl, 3-chloropropyl, chlorophenyl, dichlorophenyl, 2,2,2-trifluoroethyl, 2,2,3,3-tetrafluoropropyl, and 2,2,3,3,4,4,5,5-octafluoropentyl.

[0021] In addition to groups represented by R, the silicone polymer may include additional substituents or functional groups at any terminal or pendent position. For example, the silicone polymer may include silicon-bonded hydroxyl groups, hydrogen atoms, amine groups, silazane groups, (meth)acrylate groups, epoxy groups, etc. Such groups or atoms may be present in the repeating D units (described below) or in

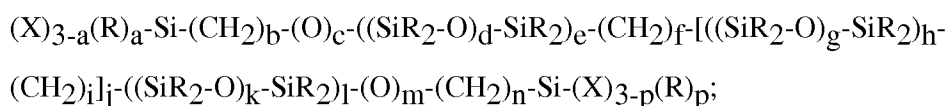
terminal M units (which generally have the formula $R_3SiO_{1/3}$, unless one or more of R is replaced by one of these additional substituents or functional groups). Most typically, if present, such groups are terminal in the silicone polymer.

[0022] Because the silicone polymer comprises repeating $R_2SiO_{2/2}$ units, the silicone polymer has a linear portion. However, the silicone polymer may optionally be branched, partially branched, and/or may include a resinous portion having a three-dimensional networked structure. In such embodiments, the silicone polymer further comprises includes $RSiO_{3/2}$ units and/or $SiO_{4/2}$ units. Branching of the silicone polymer itself, or the resinous portion of the silicone polymer, if present, is attributable to the presence of T and/or Q units.

[0023] The silicone polymer may consist of siloxane bonds (Si-O-Si) within the backbone of the silicone polymer. Alternatively, the silicone polymer may include siloxane bonds separated by one or more bivalent groups, e.g. a CH_2 linking group, where CH_2 may be repeated up to, for example, 10 times. The presence of absence of such bivalent groups is generally attributable to the reaction mechanism by which the silicone polymer is formed, with silicone polymers consisting of siloxane bonds being formed from condensation and silicone polymers including one or more bivalent groups being formed from hydrosilylation.

[0024] The silicone polymer may optionally have functional groups, such as silicon-bonded alkenyl groups, silicon-bonded hydroxyl groups, silicon-bonded alkoxy groups, etc. In various embodiments including such functional groups, the functional groups may be terminal, pendent, or both. Typically, the functional groups are terminal. For example, the silicone polymer may be dimethylvinyl endblocked, divinylmethyl endblocked, dimethylhydroxyl endblocked, dihydroxymethyl endblocked, etc. In certain embodiments, the silicone polymer includes a terminal group selected from a hydrolysable group, an alkenyl group, of combinations thereof. Generally, physical properties of the layers formed from the compositions are improved when the silicone polymer includes such a terminal group.

[0025] In various embodiments in which the silicone material comprises the silicone polymer, the silicone polymer has the following general formula (A):

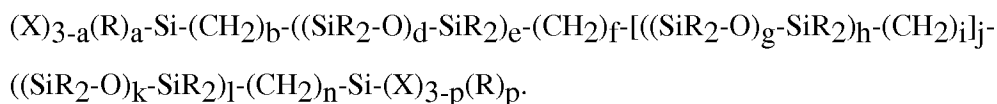


wherein X is an independently selected hydrolysable group; R is defined above; a and p are each integers independently selected from 0 to 3; b, f, i, and n are each integers independently selected from 0 to 10; c and m are each independently 0 or 1; d, g, and k are each integers independently selected from 0 or from 1 to 200 with the proviso that d, g, and k are not simultaneously 0; e, h, and l are each integers independently selected from 0 and 1 with the proviso that e, h, and l are not simultaneously 0; and j is an integer selected from 0 to 5; provided that when subscript d is 0, subscript e is also 0; when subscript d is greater than 0, subscript e is 1; when subscript g is 0, subscripts h, i, and j are also 0; when subscript g is greater than 1, subscript h is 1 and subscript j is at least 1; when subscript k is 0, subscript l is also 0; and when subscript k is greater than 0, subscript l is 1.

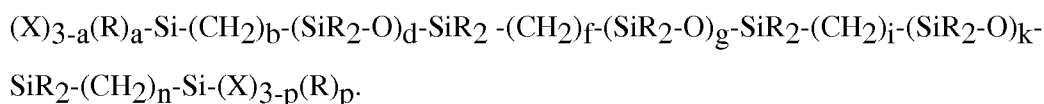
[0026] The hydrolysable groups represented by X in general formula (A) may be selected from known hydrolysable groups, e.g. silanol groups, silicon-bonded hydrogen groups, silicon-bonded alkoxy groups, silicon-bonded halogen atoms, silazane groups, etc.

[0027] In general formula (A) above, subscripts d, g, and k represent the repeating $R_2SiO_2/2$ units of the silicone polymer.

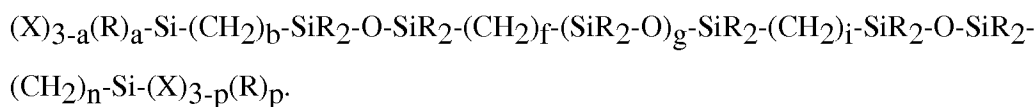
[0028] In various embodiments, subscripts c and m are 0 and subscripts b, d, e, f, g, h, i, j, k, l, and n are each integers of 1 or more. When subscript j is 1, the resulting silicone polymer includes three segments of repeating siloxane bonds each separated by a bivalent linking group, which such bivalent linking groups being represented by subscripts b, f, i, and n, respectively. In these embodiments, the silicone polymer is typically formed from hydrosilylation and may be represented by the following general formula:



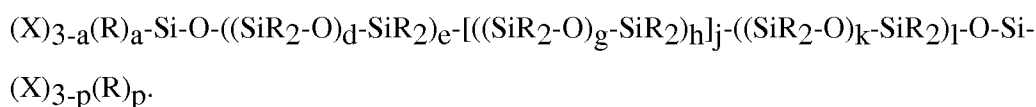
Typically, when subscripts d, g, and k are 1 or more, subscript j is 1 (and as defined above, because subscripts d is greater than 0, subscript e is 1, and because subscript g is greater than 0, subscript h is 1. In these embodiments, the silicone polymer has the following general formula:



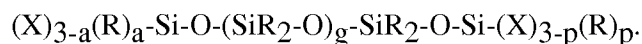
Most typically, subscripts d and k are each 1 and subscript g is an integer greater than 1 such that the block represented by subscript g provides the repeating $R_2SiO_{2/2}$ units in the silicone polymer. In these embodiments, the silicone polymer has the following general formula:



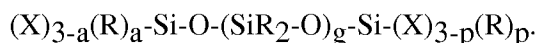
[0029] In other embodiments, subscripts c and m are 1 and subscripts b, f, i, and n are each 0. In these embodiments, the silicone polymer is typically formed from condensation and may be represented by the following general formula:



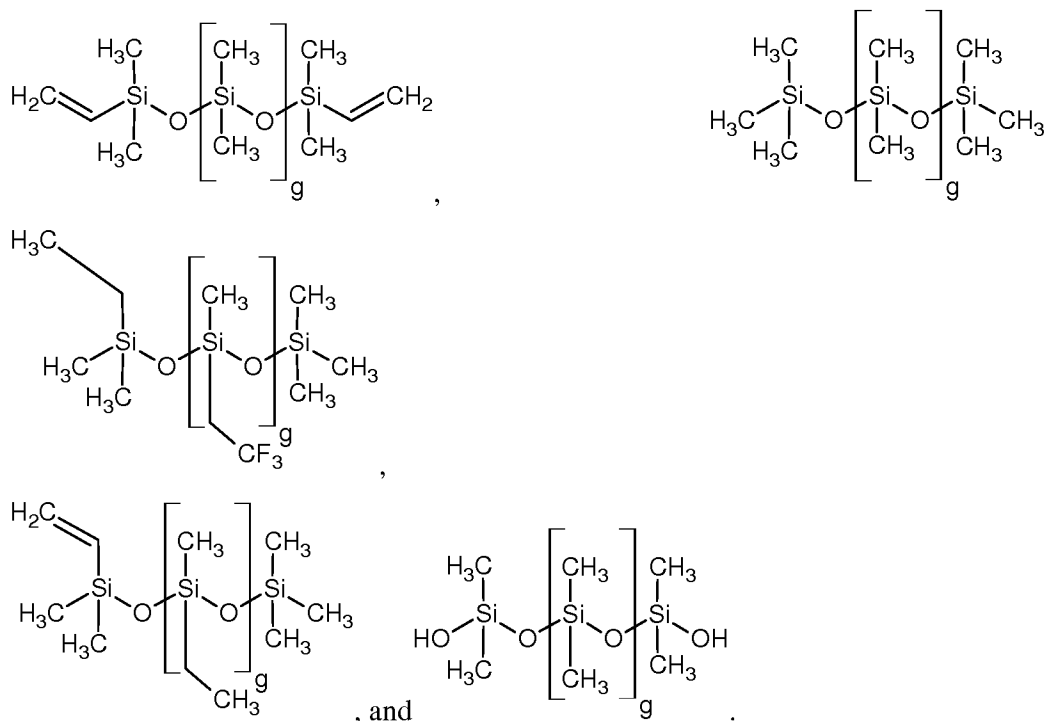
Because R is independently selected and may vary in different $R_2SiO_{2/2}$ units, the general formula above may be rewritten to exclude any of the blocks represented by subscripts e, h, j, and l, so long as not all of these subscripts are simultaneously 0. For example, the general formula above may be rewritten while only including the $R_2SiO_{2/2}$ units within the block represented by subscript d, subscript h, subscript j, and/or subscript l, as each of these formulas would be duplicative with one another, save for potential differences in molecular weight in embodiments in which the silicone polymer includes greater than 200 repeating $R_2SiO_{2/2}$ units. As but one example, the general formula introduced above is rewritten below where subscripts d, e, k, and l are 0, subscript g is an integer greater than 1, and subscripts h and j are 1:



Further, because R is independently selected, the general formula introduced immediately above may be further condensed as follows:



Subscripts a and p may each independently be from 0 to 3 such that the silicone polymer of these embodiments need not have any silicon-bonded hydrolysable groups. Specific species of the silicone polymer within the general formula immediately above are set forth below for illustrative purposes only:



In each of these examples, subscript g represents the repeating $R_2SiO_{2/2}$ units, and g is selected based on the desired molecular weight and viscosity of the silicone polymer.

[0030] A single species of the silicone polymer may be utilized or various combinations of different species of the silicone polymer may be utilized in concert with one another in the silicone material. For example, two different types of silicone polymers may be utilized in combination with one another, or a silicone polymer may be utilized in combination with a silicone resin, e.g. an MQ resin.

[0031] In one specific embodiment, the nanoparticle composition may be that of U.S. Ser. No. 61/823,500, which is incorporated by reference herein in its entirety.

[0032] As introduced above, the nanoparticle composition further comprises nanoparticles. The nanoparticles may be formed from any method and may comprise any type of material contingent on the application or end use in which the nanoparticle composition is utilized. In certain embodiments, the silicone material of the nanoparticle composition is a liquid such that the nanoparticle composition is a suspension of the nanoparticles in the silicone material. Generally, the nanoparticles have at least one dimension less than 100, alternatively less than 75, alternatively less than 50, nanometers, as described in greater detail below. Alternatively, the

nanoparticles have an average largest dimension of less than 100, alternatively less than 75, alternatively less than 50, nanometers.

[0033] In certain embodiments, the nanoparticles of the nanoparticle composition are produced via a plasma process. As readily understood in the art, the process by which nanoparticles are produced generally impacts the physical properties of the nanoparticles. Specific plasma processes and corresponding plasma reactors or systems suitable for producing the nanoparticles of the nanoparticle composition are described below.

[0034] In various embodiments, the nanoparticles of the nanoparticle composition are produced via an RF plasma-based process. In these embodiments, a constricted RF plasma may be utilized to produce the nanoparticles. More specifically, these processes utilize an RF plasma operated in a constricted mode to produce nanoparticles from a precursor gas.

[0035] In these embodiments, the process of producing the nanoparticles may be carried out by introducing a precursor gas and, optionally, a buffer gas into a plasma chamber and generating an RF capacitive plasma in the chamber. The RF plasma may be created under pressure and RF power conditions that promote the formation of a plasma instability (i.e., a spatially and temporally strongly non-uniform plasma) which causes a constricted plasma to form in the chamber. The constricted plasma, sometimes also referred to as contracted plasma, leads to the formation of a high-plasma density filament, sometimes also referred to as a plasma channel. The plasma channel is characterized by a strongly enhanced plasma density, ionization rate, and gas temperature as compared to the surrounding plasma. It can be either stationary or non-stationary. Periodic rotations of the filament in the discharge tube may be observed, e.g. the filament may randomly change its direction of rotation, trajectory and frequency of rotation. The filament may appear longitudinally non-uniform, or striated. In other cases, the filament may be longitudinally uniform.

[0036] An inert buffer or carrier gas, such as neon, argon, krypton or xenon, may desirably be included with the precursor gas. The inclusion of such gases in the constricted plasma-based methods is particularly desirable because these gases promote the formation of the thermal instability to achieve the thermal constriction. In the RF plasmas, dissociated precursor gas species (i.e., the dissociation products

resulting from the dissociation of the precursor molecules) nucleate and grow into nanoparticles.

[0037] It is believed that the formation of a constricted RF plasma promotes crystalline nanoparticle formation because the constricted plasma results in the formation of a high current density current channel (i.e., filament) in which the local degree of ionization, plasma density and gas temperature are much higher than those of ordinary diffuse plasmas which tend to produce amorphous nanoparticles. For example, in some instances gas temperatures of at least about 1000 K with plasma densities of up to about 10^{13} cm^{-3} may be achieved in the constricted plasma. Additional effects could lead to further heating of the nanoparticles to temperatures even higher than the gas temperature. These include recombination of plasma electrons and ions at the nanoparticle surface, hydrogen recombination at the particle surface and the condensation heat release related to nanoparticle surface growth. In some instances the nanoparticles may be heated to temperatures several hundred degrees Kelvin above the gas temperature. The plasma may be continuous, rather than a pulsed plasma.

[0038] Thus, some embodiments of the present processes use an RF plasma constriction to provide high gas temperatures using relatively low plasma frequencies.

[0039] Conditions that promote the formation of a constricted plasma may be achieved by using sufficiently high RF powers and gas pressures when generating the RF plasma. Any RF power and gas pressures that result in the formation of a constricted RF plasma capable of promoting nanoparticle formation from dissociated precursor gas species may be employed. Appropriate RF power and gas pressure levels may vary somewhat depending upon the plasma reactor geometry. However, in one illustrative embodiment of the processes provided herein, the RF power used to ignite the RF plasma is at least about 100 Watts and the total pressure in the plasma chamber in the presence of the plasma (i.e., the total plasma pressure) is at least about 1 Torr. This includes embodiments where the RF power is at least about 110 Watts and further includes embodiments where the RF power is at least about 120 Watts. This also includes embodiments where the total pressure in the plasma chamber in the presence of the plasma is at least about 5 Torr and further includes embodiments where the total pressure in the plasma chamber in the presence of the plasma is at least about 10 Torr (e.g. from about 10 to 15 Torr).

[0040] Conditions that promote the formation of a non-constricted RF plasmas may be similar to those described above for the production of constricted plasmas. However, nanoparticles are generally formed in the non-constricted plasmas at lower pressures, higher precursor gas flow rates, and lower buffer gas flow rates. For example, in some embodiments, the nanoparticles are produced in an RF plasma at a total pressure less than about 5 Torr and, desirably, less than about 3 Torr. This includes embodiments where the total pressure in the plasma reactor in the presence of the plasma is about 1 to 3 Torr. Typical flow rates for the precursor gas in these embodiments may be at least 5 sccm, including embodiments where the flow rate for the precursor gas is at least about 10 sccm. Typical flow rates for buffer gases in these embodiments may be about 1 to 50 sccm.

[0041] The frequency of the RF voltage used to ignite the radiofrequency plasmas may vary within the RF range. In certain embodiments, a frequency of 13.56 MHz is employed, which is the major frequency used in the RF plasma processing industry. However, the frequency may desirably be lower than the microwave frequency range, i.e., lower than about 1 GHz. This includes embodiments where the frequency will desirably be lower than the very high frequency (VHF) range (e.g. lower than about 30 MHz). For example, the present methods may generate radiofrequency plasmas using radiofrequencies of 25 MHz or less.

[0042] Additional aspects relating to this particular embodiment in which the nanoparticles are produced via this plasma process are described in U.S. Pat. No. 7,446,335 and U.S. Pat. No. 8,016,944, which are each incorporated by reference herein in their respective entireties.

[0043] In other embodiments, the nanoparticles of the silicone composition are prepared in a low pressure plasma reactor, such as a low pressure high frequency pulsed plasma reactor.

[0044] In these embodiments, pulsing the plasma enables an operator to directly set the residence time for particle nucleation and thereby control the particle size distribution and agglomeration kinetics in the plasma. For example, the operating parameters of the pulsed reactor may be adjusted to form crystalline nanoparticles or amorphous nanoparticles. Semiconductor containing precursors enter into the dielectric discharge tube where the capacitively coupled plasma, or inductively coupled plasma, is operated. Nanoparticles start to nucleate as the precursor

molecules are dissociated in the plasma. When the plasma is off, or in a low ion energy state, during the pulsing cycle, the charged nanoparticles can be evacuated to the reactor chamber where they may be deposited on a substrate or subjected to further processing.

[0045] The power may be supplied via a variable frequency radio frequency power amplifier that is triggered by an arbitrary function generator to establish the high frequency pulsed plasma. In one embodiment, the radiofrequency power is capacitively coupled into the plasma using a ring electrode, parallel plates, or an anode/cathode setup in the gas. Alternatively, the radiofrequency power may be inductively coupled mode into the plasma using an RF coil setup around the discharge tube. The precursor gases can be controlled via mass flow controllers or calibrated rotometers. The pressure differential from the discharge tube to the reactor chamber can be controlled through a changeable grounded or biased orifice. Depending on the orifice size and pressures, the nanoparticle distributions into the reactor chamber may change, thus providing another process parameter that can be used to adjust the properties of the resulting nanoparticles.

[0046] In one embodiment, the plasma reactor may be operated in the frequency from 10 MHz to 500 MHz at pressures from 100 mTorr to 10 Torr in the discharge tube and powers from 5 watts to 100 watts.

[0047] Referring now to Figure 1, one exemplary embodiment of a low pressure high frequency pulsed plasma reactor is shown. In the illustrated embodiment, precursor gas (or gases) may be introduced to a vacuum evacuated dielectric discharge tube 11. The discharge tube 11 includes an electrode configuration 13 that is attached to a variable frequency RF amplifier 10. The other portion of the electrode 14 is either grounded, DC biased, or operated in a push-pull manner relative to electrode 13. The electrodes 13, 14 are used to couple the very high frequency (VHF) power into the precursor gas (or gases) to ignite and sustain a glow discharge or plasma 12. The precursor gas (or gases) may then be disassociated in the plasma and nucleate to form nanoparticles.

[0048] In one embodiment, the electrodes 13, 14 for a plasma source inside the dielectric tube 11 that is a flow-through showerhead design in which a VHF radio frequency biased upstream porous electrode plate 13 is separated from a down stream porous electrode plate 14, with the pores of the plates aligned with one another. The

pores could be circular, rectangular, or any other desirable shape. Alternatively, the dielectric tube 11 may enclose an electrode 13 that is coupled to the VHF radio frequency power source 10 and has a pointed tip that has a variable distance between the tip and a grounded ring 14 inside the dielectric tube 11. In this case, the VHF radio frequency power source 10 operates in a frequency range of about 10 to 500 MHz. In another alternative embodiment, the pointed tip 13 can be positioned at a variable distance between the tip and a VHF radio frequency powered ring 14 operated in a push-pull mode (180° out of phase). In yet another alternative embodiment, the electrodes 13, 14 include an inductive coil coupled to the VHF radio frequency power source so that radio frequency power is delivered to the precursor gas (or gases) by an electric field formed by the inductive coil. Portions of the dielectric tube 11 can be evacuated to a vacuum level between 1×10^{-7} to 500 Torr.

[0049] The nucleated nanoparticles may pass into a larger vacuum evacuated reactor 15, where collection on a solid substrate 16 (including a chuck) or into an appropriate liquid substrate/solution can occur. For example, the nanoparticles may be collected in a silicone material to form the nanoparticle composition. Alternatively, the nanoparticles may be collected in a capture fluid and subsequently introduced to the curable silicone composition to form the silicone composition. The solid substrate 16 can be electrically grounded, biased, temperature controlled, rotating, positioned relative the electrodes producing the nanoparticles, or on a roll-to-roll system. If deposition onto substrates is not the choice, then the particles are evacuated into a suitable pump for transition to atmospheric pressure. The nanoparticles can then be sent to an atmospheric classification system, such as a differential mobility analyzer, and collected for further functionalization or other processing.

[0050] In the illustrated embodiment, the plasma is initiated with a high frequency plasma via an RF power amplifier such as an AR Worldwide Model KAA2040 or an Electronics and Innovation 3200L. The amplifier can be driven (or pulsed) by an arbitrary function generator (e.g., a Tektronix AFG3252 function generator) that is capable of producing up to 200 watts of power from 0.15 to 150 MHz. In various embodiments, the arbitrary function may be able to drive the power amplifier with pulse trains, amplitude modulation, frequency modulation, or different waveforms. The power coupling between the amplifier and the precursor gas typically increases as the

frequency of the RF power increases. The ability to drive the power at a higher frequency may therefore allow more efficient coupling between the power supply and discharge.

[0051] If desired, nanoparticles having varying agglomeration lengths can be produced by nucleating the nanoparticles from at least one precursor gas in a VHF radio frequency low pressure plasma discharge and collecting the nucleated nanoparticles by controlling the mean free path of the nanoparticles as an aerosol, thus allowing particle - particle interactions prior to collection. The nucleated nanoparticles may be collected on a solid substrate within a vacuum environment where the collection distance is greater than the mean free path of the particles controlled via the pressure. The agglomeration lengths of the nanoparticles can thereby be controlled. Alternatively, the nucleated nanoparticles may be collected in a liquid substrate within a vacuum environment where the collection distance is greater than the mean free path of the particles controlled via the pressure thus controlling the agglomeration lengths of the nanoparticles. The further away the substrate is from the nucleation region (plasma discharge), the longer the agglomerations are at a constant pressure. The synthesized nanoparticles may be evacuated out of the low pressure environment into an atmospheric environment as an aerosol so that the agglomeration length is at least partially controlled by the concentration of the aerosol.

[0052] In certain embodiments, nanoparticles can be produced by synthesizing crystalline or amorphous core nanoparticles using VHF radio frequency low pressure plasma that is discharged in a low pressure environment by pulsing the discharge to control the plasma residence time. For example, the amorphous core nanoparticles can be synthesized at increased plasma residence time relative to the precursor gas molecular residence time through a VHF radio frequency low pressure plasma discharge. Alternatively, crystalline core nanoparticles can be synthesized at lower plasma residence times at the same operating conditions of discharge drive frequency, drive amplitude, discharge tube pressure, chamber pressure, plasma power density, gas molecule residence time through the plasma, and collection distance from plasma source electrodes.

[0053] Additional aspects relating to this particular embodiment in which the nanoparticles are produced via this plasma process are described in International

(PCT) Publication No. WO 2010/027959 (PCT/US2009/055587), which is incorporate by reference herein in its entirety.

[0054] Referring to Figure 2, an alternative embodiment of a plasma reactor system is shown at 20. In this embodiment, the plasma reactor system 20 comprises a plasma generating chamber 22 having a reactant gas inlet 29 and an outlet 30 having an aperture or orifice 31 therein. A particle collection chamber 26 is in communication with the plasma generating chamber 22. The particle collection chamber 26 contains a capture fluid 27 in a container 32. The container 32 may be adapted to be agitated (by means not shown). For example, the container 32 may be positioned on a rotatable support (not shown) or may include a stirring mechanism. Preferably the capture fluid is a liquid at the temperatures of operation of the system. The plasma reactor system 5 also includes a vacuum source 28 in communication with the particle collection chamber 26 and plasma generating chamber 22.

[0055] The plasma generating chamber 22 comprises an electrode configuration 24 that is attached to a variable frequency RF amplifier 21. The plasma generating chamber 22 also comprises a second electrode configuration 25. The second electrode configuration 25 is either ground, DC biased, or operated in a push-pull manner relative to the electrode configuration 24. The electrodes 24, 25 are used to couple the very high frequency (VHF) power to the reactant gas mixture to ignite and sustain a glow discharge of plasma within the area identified as 23. The first reactive precursor gas (or gases) is then dissociated in the plasma to provide charged atoms which nucleate to form nanoparticles. However, other discharge tube configurations are contemplated, and may be used in carrying out the method disclosed herein.

[0056] In the embodiment of Figure 2, the nanoparticles are collected in the particle collection chamber 26 in the capture fluid. To control the diameter of the nanoparticles which are formed, the distance between the aperture 31 in the outlet 22 of plasma generating chamber 22 and the surface of the capture fluid ranges between about 5 to about 50 aperture diameters. It has been found that positioning the surface of the capture fluid too close to the outlet of the plasma generating chamber may result in undesirable interactions of plasma with the capture fluid. Conversely, positioning the surface of the capture fluid too far from the aperture reduces particle collection efficiency. As collection distance is a function of the aperture diameter of the outlet and the pressure drop between the plasma generating chamber and the

collection chamber, based on the operating condition described herein, an acceptable collection distance is from about 1 to about 20, alternatively from about 5 to about 10, cm. Said differently, an acceptable collection distance is from about 5 to about 50 aperture diameters.

[0057] The plasma generating chamber 22 also comprises a power supply. The power is supplied via a variable frequency radio frequency power amplifier 21 that is triggered by an arbitrary function generator to establish high frequency pulsed plasma in area 23. Preferably, the radiofrequency power is capacitively coupled into the plasma using a ring electrode, parallel plates, or an anode/cathode setup in the gas. Alternatively, the radiofrequency power may be inductively coupled mode into the plasma using an RF coil setup around the discharge tube.

[0058] The plasma generating chamber 11 may also comprise a dielectric discharge tube. Preferably, a reactant gas mixture enters the dielectric discharge tube where the plasma is generated. Nanoparticles which form from the reactant gas mixture start to nucleate as the first reactive precursor gas molecules are dissociated in the plasma.

[0059] The vacuum source 28 may comprise a vacuum pump. Alternatively, the vacuum source 28 may comprise a mechanical, turbo molecular, or cryogenic pump.

[0060] In one embodiment, the electrodes 24, 25 for a plasma source inside the plasma generating chamber 22 comprise a flow-through showerhead design in which a VHF radio frequency biased upstream porous electrode plate 24 is separated from a down stream porous electrode plate 25, with the pores of the plates aligned with one another. The pores may be circular, rectangular, or any other desirable shape. Alternatively, the plasma generating chamber 22 may enclose an electrode 24 that is coupled to the VHF radio frequency power source and has a pointed tip that has a variable distance between the tip and a grounded ring inside the chamber 22.

[0061] In one embodiment, the VHF radio frequency power source may be operated in a manner substantially similar to that described above with respect to the embodiment of Figure 1. The plasma in area 23 may be initiated with a high frequency plasma via an RF power amplifier such as an AR Worldwide Model KAA2040, or an Electronics and Innovation Model 3200L, or an EM Power RF Systems, Inc. Model BBS2E3KUT. The amplifier can be driven (or pulsed) by an arbitrary function generator, as described above relative to the embodiment of Figure 1.

[0062] In one embodiment, the power and frequency of the plasma system is preselected to create an optimal operating space for the formation of the nanoparticles. Preferably, tuning both the power and frequency creates an appropriate ion and electron energy distribution in the discharge to help dissociate the molecules of the reactive precursor gas and nucleate the nanoparticles.

[0063] The plasma reactor system 20 illustrated in Figure 2 may be pulsed to enable an operator to directly manage the resident time for particle nucleation, and thereby control the particle size distribution and agglomeration kinetics in the plasma. The pulsing function of the system 20 allows for controlled tuning of the particle resident time in the plasma, which affects the size of the nanoparticles. By decreasing the "on" time of the plasma, the nucleating particles have less time to agglomerate, and therefore the size of the nanoparticles may be reduced on average (i.e., the nanoparticle distribution may be shifted to smaller diameter particle sizes).

[0064] Advantageously, the operation of the plasma reactor system 20 at higher frequency ranges and pulsing the plasma provides the same conditions as in conventional constricted/filament discharge techniques that use a plasma instability to produce the high ion energies/densities, but with the additional advantage that users can control operating conditions to select and produce nanoparticles having various sizes, which impacts their characteristic physical properties, e.g. photoluminescence..

[0065] For a pulse injection, the synthesis of the nanoparticles can be done with a pulsed energy source, such as a pulsed very high frequency RF plasma, a high frequency RF plasma, or a pulsed laser for pyrolysis. Preferably, the VHF radiofrequency is pulsed at a frequency ranging from about 1 to about 50 kHz.

[0066] Another method to transfer the nanoparticles to the capture fluid is to pulse the input of the reactant gas mixture while the plasma is ignited. For example, one could ignite the plasma in which a first reactive precursor gas is present to synthesize the nanoparticles, with at least one other gas present to sustain the discharge, such as an inert gas. The nanoparticle synthesis is stopped when the flow of first reactive precursor gas is stopped with a mass flow controller. The synthesis of the nanoparticles continues when the flow of the first reactive precursor gas is started again. This produces a pulsed stream of nanoparticles. This technique can be used to increase the concentration of nanoparticles in the capture fluid if the flux of

nanoparticles impinging on the capture fluid is greater than the absorption rate of the nanoparticles into the capture fluid.

[0067] In another embodiment, the nucleated nanoparticles are transferred from the plasma generating chamber 22 to particle collection chamber 26 containing capture fluid via the aperture or orifice 31 which creates a pressure differential. It is contemplated that the pressure differential between the plasma generating chamber 22 and the particle collection chamber 26 can be controlled through a variety of ways. In one configuration, the discharge tube inside diameter of the plasma generating chamber 22 is much less than the inside diameter of the particle collection chamber 26, thus creating a pressure drop. In another configuration, a grounded physical aperture or orifice may be placed between the discharge tube and the collection chamber 26 that forces the plasma to reside partially inside the orifice, based on the Debye length of the plasma and the size of the chamber 22. Another configuration comprises using a varying electrostatic orifice in which a positive concentric charge is developed that forces the negatively charged plasma through the aperture 31.

[0068] It is contemplated that the capture fluid may be used as a material handling and storage medium. In one embodiment, the capture fluid is selected to allow nanoparticles to be absorbed and disperse into the fluid as they are collected, thus forming a dispersion or suspension of nanoparticles in the capture fluid. Nanoparticles will be adsorbed into the fluid if they are miscible with the fluid. For example, the capture fluid may comprise a silicone material such that the nanoparticles may be collected in the silicone material to form the nanoparticle composition. Alternatively, the nanoparticles may be collected in a capture fluid and subsequently introduced to a silicone material to form the nanoparticle composition.

[0069] The capture fluid is selected to have the desired properties for nanoparticle capture and storage. In a specific embodiment, the vapor pressure of the capture fluid is lower than the operating pressure in the plasma reactor. Preferably, the operating pressure in the reactor and collection chamber 26 range from about 1 to about 5 mTorr. Other operating pressures are also contemplated. The capture fluid may comprise a silicone fluid such as polydimethylsiloxane, phenylmethyl-dimethyl cyclosiloxane, tetramethyltetraphenyltrisiloxane, and/or pentaphenyltrimethyltrisiloxane. These silicone fluids may constitute the silicone material of the nanoparticle composition, in which case the nanoparticle composition

may be prepared upon collecting or capturing the nanoparticles in the silicone fluid. Typically, however, the capture fluid comprises a silicone fluid such that the nanoparticle composition is formed once the nanoparticles are captured or collected in the capture fluid. In these embodiments, the nanoparticle composition is typically a suspension of nanoparticles in the silicone material, which is a liquid.

[0070] The capture fluid may be agitated during the direct capture of the nanoparticles, e.g. by stirring, rotation, inversion, and other suitable methods of providing agitation. If higher absorption rates of the nanoparticles into the capture liquid are desired, more intense forms of agitation are contemplated, e.g. ultrasonication.

[0071] As first introduced above, in the embodiment of Figure 2, upon the dissociation of the first reactive precursor gas in the plasma generation chamber 22, nanoparticles form and are entrained in the gas phase. The distance between the nanoparticle synthesis location and the surface of capture fluid must be short enough so that no unwanted functionalization occurs while the nanoparticles are entrained. If the nanoparticles interact within the gas phase, agglomerations of numerous individual small nanoparticles will form and be captured in the capture fluid. If too much interaction takes place within the gas phase, the nanoparticles may sinter together and form nanoparticles having larger average diameters. The collection distance is defined as the distance from the outlet of the plasma generating chamber to the surface of the capture fluid.

[0072] Additional aspects relating to this particular embodiment in which the nanoparticles are produced via this plasma process are described in International (PCT) Publication No. WO 2011/109299 (PCT/US2011/026491), which is incorporated by reference herein in its entirety.

[0073] Referring to Figure 3, an alternative embodiment of a plasma reactor system is shown at 50. In this embodiment, the nanoparticles of the silicone composition are prepared in a system having a reactor for producing a nanoparticle aerosol (e.g., nanoparticles in a gas) and a diffusion pump in fluid communication with the reactor for collecting the nanoparticles of the aerosol. For example, nanoparticles of various size distributions and properties can be prepared by introducing a nanoparticle aerosol produced in a reactor (e.g. a low-pressure plasma reactor) into a diffusion pump in fluid communication with the reactor, capturing the nanoparticles of the aerosol in a

condensate from a diffusion pump oil, liquid, or fluid (e.g. silicone fluid), and collecting the captured nanoparticles in a reservoir.

[0074] Example reactors are described in WO 2010/027959 and WO 2011/109229, each of which is described above and incorporated by reference in its entirety herein. Such reactors can be, but are not limited to, low pressure high frequency pulsed plasma reactors. For example, Figure 3 illustrates the plasma reactor of the embodiment of Figure 2, but includes the diffusion pump in fluid communication with the reactor. To this end, description relative to this particular plasma reactor is not repeated herein with respect to the embodiment of Figure 3.

[0075] In the embodiment of Figure 3, the plasma reactor system 50 includes a diffusion pump 120. As such, the nanoparticles can be collected by the diffusion pump 120. A particle collection chamber 26 may be in fluid communication with the plasma generating chamber 22. The diffusion pump 120 may be in fluid communication with the particle collection chamber 26 and the plasma generating chamber 22. In other forms of the present disclosure, the system 50 may not include the particle collection chamber 26. For example, the outlet 30 may be coupled to an inlet 103 of the diffusion pump 120, or the diffusion pump 120 may be in substantially direct fluid communication with the plasma generating chamber 22.

[0076] Figure 4 is a cross-sectional schematic of an example diffusion pump 120 suitable for the system 50 of the embodiment of Figure 3. The diffusion pump 120 can include a chamber 101 having an inlet 103 and an outlet 105. The inlet 103 may have a diameter of about 2 to about 55 inches, and the outlet may have a diameter of about 0.5 to about 8 inches. The inlet 103 of the chamber 101 is in fluid communication with the outlet 30 of the reactor 20. The diffusion pump 120 may have, for example, a pumping speed of about 65 to about 65,000 liters/second or greater than about 65,000 liters/second.

[0077] The diffusion pump 120 includes a reservoir 107 in fluid communication with the chamber 101. The reservoir 107 supports or contains a diffusion pump fluid. The reservoir may have a volume of about 30 cc to about 15 liters. The volume of diffusion pump fluid in the diffusion pump may be about 30 cc to about 15 liters.

[0078] The diffusion pump 120 can further include a heater 109 for vaporizing the diffusion pump fluid in the reservoir 107 to a vapor. The heater 109 heats up the diffusion pump fluid and vaporizes the diffusion pump fluid to form a vapor (e.g.,

liquid to gas phase transformation). For example, the diffusion pump fluid may be heated to about 100 to about 400 °C or about 180 to about 250 °C.

[0079] A jet assembly 111 can be in fluid communication with the reservoir 107 comprising a nozzle 113 for discharging the vaporized diffusion pump fluid into the chamber 101. The vaporized diffusion pump fluid flows and rises up through the jet assembly 111 and emitted out the nozzles 113. The flow of the vaporized diffusion pump fluid is illustrated in Figure 4 with arrows. The vaporized diffusion pump fluid condenses and flows back to the reservoir 107. For example, the nozzle 113 can discharge the vaporized diffusion pump fluid against a wall of the chamber 101. The walls of the chamber 101 may be cooled with a cooling system 113 such as a water cooled system. The cooled walls of the chamber 101 can cause the vaporized diffusion pump fluid to condense. The condensed diffusion pump fluid can then flow along and down the walls of the chamber 101 and back to the reservoir 107. The diffusion pump fluid can be continuously cycled through diffusion pump 120. The flow of the diffusion pump fluid causes gas that enters the inlet 103 to diffuse from the inlet 103 to the outlet 105 of the chamber 101. A vacuum source 33 may be in fluid communication with the outlet 105 of the chamber 101 to assist removal of the gas from the outlet 105.

[0080] As the gas flows through the chamber 101, nanoparticles in the gas can be absorbed by the diffusion pump fluid, thereby collecting the nanoparticles from the gas. For example, a surface of the nanoparticles may be wetted by the vaporized and/or condensed diffusion pump fluid. Furthermore, the agitating of cycled diffusion pump fluid may further improve absorption rate of the nanoparticles compared to a static fluid. The pressure within the chamber 101 may be less than about 1 mTorr.

[0081] The diffusion pump fluid with the nanoparticles can then be removed from the diffusion pump 120. For example, the diffusion pump fluid with the nanoparticles may be continuously removed and replaced with diffusion pump fluid that substantially does not have nanoparticles.

[0082] Advantageously, the diffusion pump 120 can be used not only for collecting nanoparticles but also evacuating the reactor 20 (and collection chamber 26). For example, the operating pressure in the reactor 20 can be a low pressure, e.g. less than atmospheric pressure, less than 760 Torr, or between about 1 and about 760 Torr. The

collection chamber 26 can, for example, range from about 1 to about 5 mTorr. Other operating pressures are also contemplated.

[0083] The diffusion pump fluid can be selected to have the desired properties for nanoparticle capture and storage. The diffusion pump fluid may be the same as the capture fluid described above relative to the embodiment of Figure 2. Similarly, the diffusion pump fluid may comprise a silicone material, e.g. any of the silicone fluids described above, such that the nanoparticle composition is formed once the nanoparticles are captured in the diffusion pump fluid. Alternatively, the nanoparticles may be separated or isolated from the diffusion pump fluid and combined with the silicone material to form the nanoparticle composition. For example, the diffusion pump fluid may be centrifuged and/or decanted to concentrate or isolate the nanoparticles therein. Other diffusion pump fluids and oils may include hydrocarbons, phenyl ethers, fluorinated polyphenyl ethers, and ionic fluids. The fluid may have a viscosity of from 0.001 to 1, from 0.005 to 0.5, or from 0.01 to 0.1, Pa·s at 23 ± 3 °C. Furthermore, the fluid may have a vapor pressure of less than about 1×10^{-4} Torr. Typically, the diffusion pump fluid comprises a silicone diffusion pump fluid such that the nanoparticle composition is formed once the nanoparticles are captured or collected in the silicone diffusion pump fluid (once condensed). In these embodiments, the nanoparticle composition is typically a suspension of nanoparticles in the silicone material, which is a liquid.

[0084] The system 50 may also include a vacuum pump or vacuum source 33 in fluid communication with the outlet 105 of the diffusion pump 120. The vacuum source 33 can be selected in order for the diffusion pump 120 to operate properly. In one form of the present disclosure, the vacuum source 33 comprises a vacuum pump (e.g., auxiliary pump). The vacuum source 33 may comprise a mechanical, turbo molecular, or cryogenic pump. However, other vacuum sources are also contemplated.

[0085] One method of producing nanoparticles with the system 50 of Figure 3 can include forming a nanoparticle aerosol in the reactor 20. The nanoparticle aerosol can comprise nanoparticles in a gas, and the method further includes introducing the nanoparticle aerosol into the diffusion pump 120 from the reactor 5. The method also may include heating the diffusion pump fluid in a reservoir 107 to form a vapor, sending the vapor through a jet assembly 111, emitting the vapor through a nozzle 113 into a chamber 101 of the diffusion pump 120, condensing the vapor to form a

condensate, and flowing the condensate back to the reservoir 107. Furthermore, the method can further include capturing the nanoparticles of the aerosol in the condensate and collecting the captured nanoparticles in the reservoir 107. The method can further include removing the gas from the diffusion pump with a vacuum pump.

[0086] Additional aspects relating to this particular embodiment in which the nanoparticles are produced via this plasma process are described in U.S. Appln. Ser. No. 61/655,635, which is incorporated by reference herein in its entirety.

[0087] Regardless of the particular plasma system and process utilized to produce the nanoparticles of the silicone composition, the plasma system generally relies on a precursor gas, as introduced above in the various embodiments. The precursor gas may alternatively be referred to as a reactant gas mixture or a gas mixture. The precursor gas is generally selected based on a desired composition of the nanoparticles, as described in greater detail below with reference to the nanoparticles. For example, when the nanoparticles comprise silicon nanoparticles, the precursor gas may contain silicon, and when the nanoparticles comprise germanium, the precursor gas may contain germanium. Furthermore, the precursor gas may be selected from silanes, disilanes, halogen-substituted silanes, halogen-substituted disilanes, C₁-C₄ alkyl silanes, C₁-C₄ alkyl disilanes, and mixtures thereof. In one form of the present disclosure, precursor gas may comprise silane which comprises from about 0.1 to about 2% of the total gas mixture. However, the gas mixture may also comprise other percentages of silane and/or additional or alternative precursor gases, as described below with reference to the nanoparticles formed therefrom.

[0088] The precursor gas may be mixed with other gases such as inert gases to form a gas mixture. Examples of inert gases that may be included in the gas mixture include argon, xenon, neon, or a mixture of inert gases. When present in the gas mixture, the inert gas may comprise from about 1% to about 99% of the total volume of the gas mixture. The precursor gas may have from about 0.1% to about 50% of the total volume of the gas mixture. However, it is also contemplated that the precursor gas may comprise other volume percentages such as from about 1% to about 50% of the total volume of the gas mixture.

[0089] In one form of the present disclosure, the reactant gas mixture also comprises a second precursor gas which itself can comprise from about 0.1 to about 49.9 volume % of the reactant gas mixture. The second precursor gas may comprise BCl₃, B₂H₆,

PH₃, GeH₄, or GeCl₄. The second precursor gas may also comprise other gases that contain carbon, germanium, boron, phosphorous, or nitrogen. The combination of the first precursor gas and the second precursor gas together may make up from about 0.1 to about 50% of the total volume of the reactant gas mixture.

[0090] In another form of the present disclosure, the reactant gas mixture further comprises hydrogen gas. Hydrogen gas can be present in an amount of from about 1% to about 10% of the total volume of the reactant gas mixture. However, it is also contemplated that the reactant gas mixture may comprise other percentages of hydrogen gas.

[0091] Nanoparticles for the nanoparticle composition can be prepared by any of the methods described above. Contingent on the precursor gas and molecules utilized in the plasma process, nanoparticles of various composition may be produced. For example, the nanoparticles may be semiconducting nanoparticles comprising at least one element selected from Group IV, Group IV-IV, Group II-IV, and Group III-V. Alternatively, the nanoparticles may be metal nanoparticles comprising at least one element selected from Group IIA, Group IIIA, Group IVA, Group VA, Group IB, Group IIB, Group IVB, Group VB, Group VIB, Group VIIB, and Group VIIIB metals. These Group designations of the periodic table are generally from the CAS or old IUPAC nomenclature, although Group IV elements are referred to as group 14 elements under the modern IUPAC system, as readily understood in the art. Alternatively still, the nanoparticles may be metal alloy nanoparticles, metal oxide nanoparticles, metal nitride nanoparticles, ceramic nanoparticles, etc.

[0092] The processes disclosed herein are particularly well-suited for use in the production of nanoparticles that are single-crystal and comprise Group IV semiconductors, including silicon, germanium and tin, from precursor molecules containing these elements. Silane and germane are examples of precursor molecules that may be used in the production of nanoparticles comprising silicon and germanium, respectively. Organometallic precursor molecules may also be used. These molecules include a Group IV metal and organic groups. Organometallic Group IV precursors include, but are not limited to organosilicon, organogermanium and organotin compounds. Some examples of Group IV precursors include, but are not limited to, alkylgermaniums, alkylsilanes, alkylstannanes, chlorosilanes, chlorogermaniums, chlorostannanes, aromatic silanes, aromatic germaniums and

aromatic stannanes. Other examples of silicon precursors include, but are not limited to, disilane (Si_2H_6), silicon tetrachloride (SiCl_4), trichlorosilane (HSiCl_3) and dichlorosilane (H_2SiCl_2). Still other suitable precursor molecules for use in forming crystalline silicon nanoparticles include alkyl and aromatic silanes, such as dimethylsilane ($\text{H}_3\text{C--SiH}_2\text{--CH}_3$), tetraethyl silane ($(\text{CH}_3\text{CH}_2)_4\text{Si}$) and diphenylsilane ($\text{Ph-SiH}_2\text{-Ph}$). In addition to germane, particular examples of germanium precursor molecules that may be used to form crystalline Ge nanoparticles include, but are not limited to, germanium tetrachloride (GeCl_4), tetraethyl germane ($(\text{CH}_3\text{CH}_2)_4\text{Ge}$) and diphenylgermane ($\text{Ph-GeH}_2\text{-Ph}$).

[0093] In certain embodiments, the nanoparticles comprise at least one of silicon and germanium. Further, the nanoparticles may comprise silicon alloys and/or germanium alloys. Silicon alloys that may be formed include, but are not limited to, silicon carbide, silicon germanium, silicon boron, silicon phosphorous, and silicon nitride. The silicon alloys may be formed by mixing at least one first precursor gas with the second precursor gas or using a precursor gas that contains the different elements. However, other methods of forming alloyed nanoparticles are also contemplated.

[0094] In another form of the present disclosure, the nanoparticles may undergo an additional doping step. For example, the nanoparticles may undergo gas phase doping in the plasma, where a second precursor gas is dissociated and is incorporated in the nanoparticles as they are nucleated. The nanoparticles may also undergo doping in the gas phase downstream of the production of the nanoparticles, but before the nanoparticles are captured in the liquid. Furthermore, doped nanoparticles may also be produced in the diffusion pump fluid where the dopant is preloaded into the diffusion pump fluid and interacts with the nanoparticles after they are captured. Doped nanoparticles can be formed by contact with organosilicon gases or liquids, including, but not limited to trimethylsilane, disilane, and trisilane. Gas phase dopants may include, but are not limited to, BCl_3 , B_2H_6 , PH_3 , GeH_4 , or GeCl_4 .

[0095] The nanoparticles may exhibit a number of unique electronic, magnetic, catalytic, physical, optoelectronic and optical properties due to quantum confinement effects. For example, many semiconductor nanoparticles exhibit photoluminescence effects that are significantly greater than the photoluminescence effects of macroscopic materials having the same composition.

[0096] The nanoparticles may have a largest dimension or average largest dimension less than 50, less than 20, less than 10, or less than 5, nm. Furthermore, the largest dimension or average largest dimension of the nanoparticles may be between 1 and 50, between 2 and 50, between 2 and 20, between 2 and 10, or between about 2.2 and about 4.7, nm. The nanoparticles can be measured by a variety of methods, such as with a transmission electron microscope (TEM). For example, as understood in the art, particle size distributions are often calculated via TEM image analysis of hundreds of different nanoparticles. In various embodiments, the nanoparticles may comprise quantum dots, typically silicon quantum dots. Quantum dots have excitons confined in all three spatial dimensions and may comprise individual crystals, i.e., each quantum dot is a single crystal.

[0097] In various embodiments, the nanoparticles may be photoluminescent when excited by exposure to UV light. Depending on the average diameter of the nanoparticles, they may photoluminesce in any of the wavelengths in the visible spectrum and may visually appear to be red, orange, green, blue, violet, or any other color in the visible spectrum. For example, nanoparticles with an average diameter less than about 5 nm may produce visible photoluminescence, and nanoparticles with an average diameter less than about 10 nm may produce near infrared (IR) luminescence. In one form of the present disclosure, the photoluminescent silicon nanoparticles have a photoluminescent intensity of at least 1×10^6 at an excitation wavelength of about 365 nm. The photoluminescent intensity may be measured with a Fluorolog3 spectrofluorometer (commercially available from Horiba of Edison, NJ) with a 450 W Xe excitation source, excitation monochromator, sample holder, edge band filter (400 nm), emission monochromator, and a silicon detector photomultiplier tube. To measure photoluminescent intensity, the excitation and emission slit width are set to 2 nm and the integration time is set to 0.1s. In these or other embodiments, the photoluminescent silicon nanoparticles may have a quantum efficiency of at least 4% at an excitation wavelength of about 395 nm as measured on an HR400 spectrophotometer (commercially available from Ocean Optics of Dunedin, Florida) via a 1000 micron optical fiber coupled to an integrating sphere and the spectrophotometer with an absorption of >10% of the incident photons. Quantum efficiency was calculated by placing a sample into the integrating sphere and exciting the sample via a 395 nm LED driven by an Ocean Optics LED driver. The system was

calibrated with a known lamp source to measure absolute irradiance from the integrating sphere. The quantum efficiency was then calculated by the ratio of total photons emitted by the nanoparticles to the total photons absorbed by the nanoparticles. Further, in these or other embodiments, the nanoparticles may have a full width at half maximum emission of from 20 to 250 at an excitation wavelength of 270-500 nm.

[0098] Furthermore, both the photoluminescent intensity and luminescent quantum efficiency may continue to increase over time when the nanoparticles (optionally in the capture fluid, diffusion pump fluid, or silicone material) are exposed to air. In another form of the present disclosure, the maximum emission wavelength of the nanoparticles shifts to shorter wavelengths over time when exposed to oxygen. The luminescent quantum efficiency of the nanoparticle composition may be increased by about 200% to about 2500% upon exposure to oxygen. However, other increases in the luminescent quantum efficiency are also contemplated. The photoluminescent intensity may increase from 400 to 4500% depending on the time exposure to oxygen and the concentration of the nanoparticles in the silicone material (or capture fluid if different from the silicone material). However, other increases in the photoluminescent intensity are also contemplated. The wavelength emitted from the direct capture composition also experiences a blue shift of the emission spectrum. In one form of the present disclosure, the maximum emission wavelength shifts about 100 nm, based on about a 1 nm decrease in nanoparticle core size, depending on the time exposed to oxygen. However, other maximum emission wavelength shifts are also contemplated.

[0099] Independent of the particular silicone material nanoparticles utilized in the nanoparticle composition, the method further comprises depolymerizing the silicone material of the nanoparticle composition to form volatile silicon compounds. Depolymerizing the silicone material may comprise any known method to depolymerize a silicone material and may be a continuous, semi-continuous, or batch process.

[00100] In one embodiment, the silicone material is depolymerized in the presence of a dialkyl carbonate. In this embodiment, the silicone material may, alternatively may not, be depolymerized in the presence of a catalyst in addition to the dialkyl carbonate. Specific examples of catalysts suitable for depolymerization

include inorganic salts, metal oxides, metal hydroxides, inorganic bases, and organic Lewis bases, optionally in combination with an alcohol. The catalyst may increase the rate of depolymerization of the silicone material. Various combinations of catalysts may optionally be utilized in depolymerization. For example, two different types of inorganic salts may be utilized in combination with one another, and/or an inorganic salt may be utilized in combination with a metal oxide, etc. The volatile silicon compounds produced via this depolymerization method are typically alkoxysilanes, as described below.

[00101] Dialkyl carbonates are known in the art and generally refer to a carbonate ester (i.e., an organic carbonate). Dialkyl carbonates are commonly esters of carbonic acid. To this end, in certain embodiments, the dialkyl carbonate utilized to depolymerize the silicone material typically has the following general formula: $(R^1O)_2C=O$, where R^1 is an independently selected C_1 - C_{12} alkyl group. In certain embodiments, R^1 is independently selected from methyl, ethyl, and propyl groups. Specific examples of dialkyl carbonates suitable for depolymerizing the silicone material include dimethyl carbonate, diethyl carbonate, and dipropyl carbonate, although the alkyl groups need not be identical in the dialkyl carbonate.

[00102] The dialkyl carbonate may be utilized in varying amounts, although the amount utilized is typically sufficient for depolymerization of the silicone material. In one embodiment, the dialkyl carbonate is utilized in an amount of at least 0.1, alternatively at least 0.2, alternatively at least 0.5, alternatively at least 1, alternatively at least 2, alternatively at least 5, alternatively up to 10, moles of dialkyl carbonate per mole of silicon in the silicone material.

[00103] As introduced above, the silicone may be depolymerized in the presence of a catalyst. Specific examples of inorganic salts suitable for the catalyst include alkali metal salts, such as KF, NaF, NaCl, LiCl, KI, KCl, and CsCl. Specific examples of metal oxides suitable for the catalyst include those comprising alkali metals or alkaline earth metals, such as CaO, Na_2O , K_2O , and MgO. Specific examples of metal hydroxides suitable for the catalyst similarly include those comprising alkali metals or alkaline earth metals, such as KOH, NaOH, CsOH, LiOH, and $Ca(OH)_2$.

[00104] Alternatively or in addition, the catalyst may comprise an organic Lewis base. The organic Lewis base may be selected from known organic Lewis bases.

Organic Lewis bases generally have a lone electron pair that may be donated to a Lewis acid to form a Lewis adduct. The organic Lewis base may be a liquid or a solid at atmospheric pressure. Alternatively, the organic Lewis base may be a homogenous catalyst or a heterogeneous catalyst. A homogenous catalyst is one that is generally co-dissolved in solvent such that the organic Lewis base is in the same phase as the reactants. A heterogeneous catalyst is one that is in a phase different from that of the reactants, e.g. solid vs. gas. The different phase may also be liquid-liquid where the liquids are immiscible with one another. Typically, the organic Lewis base is selected such that it is soluble to miscible with the dialkyl carbonate at atmospheric pressure.

[00105] The organic Lewis base may comprise, for example, nitrogen, phosphorus, sulfur, oxygen, selenium, and/or tellurium. For example, when the organic Lewis base is nitrogen-containing, the organic Lewis base may include a primary amine, a secondary amine, a tertiary amine, a heterocyclic amine, a bicyclic amine, or combinations thereof. Alternatively, when the organic Lewis base is phosphorus-containing, the organic Lewis base may include a primary phosphine, a secondary phosphine, a tertiary phosphine, a phosphazene, a cyclic phosphazene, or combinations thereof.

[00106] In specific embodiments, the organic Lewis base comprises at least one of 1,4-diazabicyclo[2.2.2]octane (DABCO), quinuclidine, N,N-dimethylbenzylamine, and morpholine.

[00107] The organic Lewis base may be utilized in varying amounts, although the amount utilized is typically sufficient for depolymerization of the silicone material. In one embodiment, the organic Lewis base is utilized in a weight ratio of from 1:1,000 to 5:1; alternatively from 1:100 to about 1:1; organic Lewis base to silicone material.

[00108] When depolymerizing the silicone material includes the alcohol, the alcohol is typically an organic compound having a single hydroxy functional group, although the alcohol may have two or more hydroxy functional groups. Typically, the hydroxy functional group is terminal in the alcohol, although the hydroxy functional group may alternatively be pending from the chain of the organic compound. The organic compound may be a C₁-C₁₂ organic compound. Specific examples of alcohols include methanol, ethanol, isopropyl alcohol, butanol, etc.

[00109] If utilized, the alcohol may be utilized in various amounts. In certain embodiments, the alcohol is utilized in a volume ratio of from 1:50 to 5:1,

alternatively from 1:30 to 4:1, alternatively from 1:20 to 3:1, alternatively at least 2:10, 3:10, 4:10, 5:10, 6:10, 7:10, 8:10, 9:10, 1:1, 1.5:1, 2:1, or 2.5:1, of alcohol to dialkyl carbonate.

[00110] If desired, the silicone material may be depolymerized in the presence of an acid catalyst or in the absence of an acid catalyst.

[00111] Depolymerizing the silicone material generally comprises heating a mixture comprising the nanoparticle composition, the dialkyl carbonate, the catalyst, and optionally the alcohol. Heating the mixture may be carried out at pressures above or below atmospheric pressure. In certain embodiments, the mixture is heated to a temperature of less than 275, alternatively less than 225, alternatively less than 175, °C. For example, the mixture may be heated in various embodiments to a temperature of from 75 to 250 °C. However, because the catalyst and alcohol are optional in depolymerization, one of skill in the art can optimize the parameters of the method (e.g. temperature, pressure, and relative amount of dialkyl carbonate) to obviate the need for the catalyst and/or alcohol.

[00112] Depolymerizing the silicone material may optionally be carried out in an inert atmosphere, e.g. an atmosphere comprises nitrogen (N₂) and/or Argon (Ar).

[00113] The period of time during which the silicone material is depolymerized is generally sufficient for substantial depolymerization of the silicone material, as described below. The period of time may be from 5 to 72, alternatively from 6 to 64, hours.

[00114] As first introduced above, in this embodiment, the volatile silicon compounds produced by depolymerizing the silicone material are generally alkoxysilanes and/or alkoxysiloxanes. The alkoxysilanes may be a mixture of different alkoxysilanes or a mixture comprising a plurality of identical alkoxysilanes. The alkoxysilanes generally include from 0 to 3 substituted or unsubstituted hydrocarbyl groups and 1-4 alkoxy groups, provided the alkoxysilanes include but one silicon atom. However, the alkoxysilanes may be monomeric or oligomeric, although the latter are generally alkoxysiloxanes.

[00115] The volatile silicon compounds, i.e., the alkoxysilanes, generally have the following general formula: $(R^2)_W(R^3)_XSi(OR^4)_Y(OR^5)_Z$, where R²-R⁵ are independently selected from R above, i.e., R²-R⁵ are independently selected from

substituted or unsubstituted hydrocarbonyl groups; $y+z \geq 1$; and $w+x+y+z = 4$. Specific examples of R^2 - R^5 include alkyl groups, aryl groups, arylalkyl groups, and alkylaryl groups.

[00116] Generally, the type of alkyl carbonate utilized impacts the resulting alkoxysilane. For example, R^1 of the alkyl carbonate generally is identical to R^4 and/or R^5 of the alkoxysilane.

[00117] Specific examples of alkoxysilanes that may be formed via depolymerization include $\text{Me}_2\text{Si}(\text{OMe})_2$, $\text{PhMeSi}(\text{OMe})_2$, $\text{Me}_2\text{Si}(\text{OEt})_2$, $(\text{MeO})_2\text{SiMe}(\text{CH}_2\text{CH}_2\text{CF}_3)$, $\text{MeSi}(\text{OMe})_3$, $\text{PhSi}(\text{OMe})_3$, $\text{Ph}_2\text{Si}(\text{OMe})_2$, and $\text{Me}_2(\text{OMe})\text{Si-O-SiMe}_2(\text{OMe})$.

[00118] In specific embodiments, the alkoxysilane is obtained in a yield of at least about 40, alternatively at least 50, alternatively at least 75, alternatively at least 90, alternatively at least 95, alternatively at least 98, weight percent relative to the silicone content of the silicone material.

[00119] Additional information relating to this particular depolymerization technique can be found in U.S. Pat. Appln. Ser. No. 61/768,709, which is incorporated by reference herein in its entirety.

[00120] In an alternative embodiment, the silicone material is depolymerized in the presence of a depolymerization catalyst other than the dialkyl carbonate described above. In these embodiments, the volatile silicon compounds typically comprise cyclosiloxane compounds.

[00121] In this alternative embodiment, the depolymerization catalyst may be selected from any depolymerization catalyst suitable for depolymerizing a silicone material. In certain embodiments, the depolymerization catalyst comprises an organic or inorganic base. In other embodiments, the depolymerization catalyst comprises an organic or inorganic acid.

[00122] Specific examples of solid acids that may be utilized as the depolymerization catalyst include aluminosilicates, acid treated aluminosilicates, zeolites, mixed metal oxides, heteropolyacids, sulfated metal oxides, carbon based solid acids, ion exchange resins, sulfonated polymers, high molecular weight carboxylic acids, acidic metal salts, and combinations thereof.

[00123] Alternatively, the depolymerization catalyst may comprise a clay, a mixed metal oxide, a sulfonated metal oxide, or combinations thereof. Alternatively still, the

depolymerization catalyst may comprise kaolin, smectite, illite, chlorites, palygorskite, sepiolite, or combinations thereof. The clay may be acid washed, i.e., the clay may comprise an acid-washed clay. Further examples of the depolymerization catalyst include montmorillonite, saponite, nontronite (ironsmectite), beidellite, bentonite, hectorite, and combinations thereof.

[00124] In various embodiments, depolymerizing the silicone material is carried out in the presence of an organic polymer in addition to the depolymerization catalyst described above. The organic polymer may be a waste product otherwise suitable for recycling. The organic polymer may be a thermoplastic organic polymer, e.g. a polyolefin.

[00125] In specific embodiments, the organic polymer includes at least one of a straight-chain polyolefin or copolymer polyolefin, a branched polyolefin or copolymer polyolefin, a grafted polyolefin or copolymer polyolefin, a borane-grafted polyolefin, a polyolefin with side hydroxyl group, a polyolefin grafted with another polymer, a blend of polyolefin with another polymer, and a polyolefin filled with an inorganic material.

[00126] In specific embodiments, the organic polymer comprises at least one of polyethylene (PE), polypropylene (PP), polymethylpentene (PMP), polybutene-1 (PB-1), polyisobutylene, poly(ethylene-copropylene), poly(propylene-co-1,4-hexadiene), poly(isobutylene-co-isoprene), poly(ethylene-copropylene-co-1,4-hexadiene), PE-g-PVA, PP-g-PMMA, PP-g-PVA, PE-g-PCL, PP-g-PCL, EP-g-PMMA, butyl-g-PMMA, PMMA, PVA, PS, PVC, PVAC, and a polyolefin filled with at least one of mica, calcium carbonate, silica, glass, magnesium oxide, aluminum oxide, and clay. The polyethylene may be, for example, low density polyethylene (LDPE), medium density polyethylene (MDPE), and/or high density polyethylene (HDPE).

[00127] In specific embodiments, the organic polymer is a thermoplastic organic polymer that includes at least one of polyoxymethylene, polyoxymethylene copolymer with oxyethylene and optionally other structural units, polymethylmethacrylate (PMMA), PMMA copolymers, polystyrene, polystyrene copolymers, celluloid, celluloid acetate, cyclic olefin copolymers, ethylene-vinyl acetate (EVA), ethylenevinyl alcohol (EVOH), fluoroplastics, PTFE, acrylonitrile-butadiene-styrene (ABS), polyacrylates, polyamides, polyamide-imide, polyimides, polyetherimide, polysulfones, polyethersulfones, polyketones, polyetheretherketone

(PEEK), polycarbonate, polyesters, polycaprolactone, polybutylene terephthalate, polyethylene terephthalate, polylactic acid, polyphenylene oxide, polyphenylene sulfide, thermoplastic polyurethane, polyvinylacetate (PVA), polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), and styrene-acrylonitrile (SAN) copolymer.

[00128] When depolymerization of the silicone material of the nanoparticle composition is carried out in the presence of the organic polymer, it is contemplated that the nanoparticles may optionally be incorporated directly into the organic polymer during and/or after depolymerization of the silicone material. Incorporation of the nanoparticles into the organic polymer may be carried out before, during, or after any separation of the volatile silicon compounds from the nanoparticle/organic polymer mixture.

[00129] Generally, the nanoparticle composition, the depolymerization catalyst, and optionally the organic polymer are combined to form a mixture. The mixture may comprise the depolymerization catalyst in an amount of from 0.01 to 25, alternatively from 0.01 to 20, alternatively from 0.01 to 15, alternatively from 0.01 to 10, percent by weight based on the total weight of the mixture. In these embodiments, the mixture may comprise the organic polymer, if present, in an amount of from 0.1 to 99 weight percent based on the total weight of the mixture. In certain embodiments, the mixture may comprise the organic polymer, if present, in an amount of at least 90, alternatively at least 95, percent by weight based on the total weight of the mixture. In other embodiments, the mixture comprises the organic polymer, if present, in an amount of from 1 to 25 percent by weight based on the total weight of the mixture.

[00130] The mixture may optionally be subjected to shear to form a homogenous or semi-homogenous mixture. For example, the nanoparticle composition, optionally the organic polymer, and the depolymerization catalyst may be combined and mixed to form the mixture in a high shear mechanical device, an extruder, a twin-screw extruder, etc., optionally with degassing ports.

[00131] While the mixture may be free from solvent, the mixture may also include an organic solvent. Typically, however, the mixture comprises organic solvent in an amount of less than 20, alternatively less than 10, alternatively less than 1, alternatively less than 0.5, alternatively less than 0.1, alternatively less than 0.05, percent by weight based on the total weight of the mixture.

[00132] The silicone material is generally depolymerized in this embodiment by heating the mixture described above. Heating may be carried out for a period of time sufficient to depolymerize the silicone material to form the volatile silicon compounds. In certain embodiments, the mixture is heated for at least 0.1, alternatively at least 1, alternatively at least 5, alternatively at least 10, alternatively at least 30, alternatively at least 60, minutes. Heating may be carried out for much longer than 60 minutes, e.g. for 24 hours.

[00133] The temperature at which the mixture is heated is typically less than 350 °C. When depolymerization is carried out in the presence of the organic polymer, the temperature is typically less than a decomposition temperature of the organic polymer, e.g. at least 5, alternatively at least 10, °C below the decomposition temperature of the organic polymer. To this end, the temperature at which the mixture is heated is contingent on the organic polymer utilized in the mixture. The temperature is typically from 60 to 340 °C. This temperature range is generally utilized even when the mixture does not include the organic polymer.

[00134] As introduced above, the volatile silicon compounds produced in this particular embodiment comprise cyclosiloxanes. Cyclosiloxanes are known in the art and comprise repeating D siloxy units. For example, when the volatile silicon compounds comprise cyclosiloxanes, the cyclosiloxanes may have the general formula: $(R^6R^7SiO_2)_{n'}$, wherein R^6 and R^7 are independently selected from R, which is defined above. Subscript n' designates the number of siloxy units in the cyclosiloxane. The cyclosiloxanes produced via depolymerizing the silicone material may comprise a mixture where the cyclosiloxanes may vary in terms of their substitution and/or number of siloxy units. Generally, n' is an integer from 3 to 25, alternatively 3 to 20, alternatively 3 to 12, alternatively 3 to 7. When n' is less than 3, the cyclosiloxane cannot be cyclic in nature.

[00135] Volatile silicon compounds other than and in addition to the cyclosiloxanes may be produced via depolymerizing the silicone material. For example, the volatile silicon compounds may additionally comprise an acyclic siloxane oligomer and/or monomer. Further, the volatile silicon compounds may additionally comprise a linear siloxane oligomer or monomer.

[00136] Additional information relating to this particular depolymerization technique can be found in U.S. Pat. Appln. Ser. No. 61/768,710, which is incorporated by reference herein in its entirety.

[00137] Independent of the technique utilized to depolymerized the silicone material of the nanoparticle composition, the method further comprises the step of substantially separating the nanoparticles from the volatile silicon compounds. When the silicone material is depolymerized as the nanoparticle composition is present in the mixture, the method may comprise the step of substantially separating the nanoparticles from the mixture. This may alternatively be referred to as substantially isolating the nanoparticles. Substantially separating or isolating the nanoparticles allows for their incorporation or use into other compositions or applications, thus increasing a useful life of the nanoparticles.

[00138] “Substantially,” as used herein with reference to the nanoparticles being substantially separated from the volatile silicon compounds, means a reduction of at least 10, alternatively at least 20, alternatively at least 30, alternatively at least 40, alternatively at least 50, alternatively at least 60, alternatively at least 70, alternatively at least 75, alternatively at least 80, alternatively at least 85, alternatively at least 90, percent by weight of the original weight of the nanoparticle composition is removed via substantially separating the nanoparticles and the volatile silicon compounds. For example, assuming a mass of 100 kg of the nanoparticle composition, after depolymerizing the silicone material and substantially separating the nanoparticles and the volatile silicon compounds and other byproducts, including silicon(e) monomers, oligomers, or polymers, the resulting composition has a mass less than 100 kg, e.g. in an amount of only 10 kg, which corresponds to a 90% reduction by mass. This can be easily measured by measuring an initial mass of the nanoparticle composition and a resulting mass of the nanoparticles after substantially separating the nanoparticles and the volatile silicon compounds and any other byproducts. The reduction also is dependent upon the content of the nanoparticles in the nanoparticle composition, which may vary. For example, if the nanoparticle composition comprises nanoparticles in an amount of 50% by weight based on the total weight of the nanoparticle composition, the reduction in mass will generally not exceed 50%.

[00139] The volatile silicon compounds may and the nanoparticles may be substantially separated from known methods. For example, the volatile silicon

compounds and the nanoparticles may be separated via distillation and/or degassing. Distillation temperatures and conditions generally depend on the volatile silicon compounds produced via depolymerization of the silicone material and their boiling points.

[00140] Once the nanoparticles and the volatile silicon compounds are substantially separated, the nanoparticles and/or the volatile silicon compounds may be reused or recycled into other end uses and applications. For example, the nanoparticles may be included in other compositions contingent on the physical properties and utilized in numerous end uses. The volatile silicon compounds may be polymerized to form a silicone.

[00141] It is to be understood that the appended claims are not limited to express and particular compounds, compositions, or methods described in the detailed description, which may vary between particular embodiments which fall within the scope of the appended claims. With respect to any Markush groups relied upon herein for describing particular features or aspects of various embodiments, different, special, and/or unexpected results may be obtained from each member of the respective Markush group independent from all other Markush members. Each member of a Markush group may be relied upon individually and or in combination and provides adequate support for specific embodiments within the scope of the appended claims.

[00142] Further, any ranges and subranges relied upon in describing various embodiments of the present invention independently and collectively fall within the scope of the appended claims, and are understood to describe and contemplate all ranges including whole and/or fractional values therein, even if such values are not expressly written herein. One of skill in the art readily recognizes that the enumerated ranges and subranges sufficiently describe and enable various embodiments of the present invention, and such ranges and subranges may be further delineated into relevant halves, thirds, quarters, fifths, and so on. As just one example, a range “of from 0.1 to 0.9” may be further delineated into a lower third, i.e., from 0.1 to 0.3, a middle third, i.e., from 0.4 to 0.6, and an upper third, i.e., from 0.7 to 0.9, which individually and collectively are within the scope of the appended claims, and may be relied upon individually and/or collectively and provide adequate support for specific embodiments within the scope of the appended claims. In addition, with respect to the language which defines or modifies a range, such as “at least,” “greater than,” “less

than,” “no more than,” and the like, it is to be understood that such language includes subranges and/or an upper or lower limit. As another example, a range of “at least 10” inherently includes a subrange of from at least 10 to 35, a subrange of from at least 10 to 25, a subrange of from 25 to 35, and so on, and each subrange may be relied upon individually and/or collectively and provides adequate support for specific embodiments within the scope of the appended claims. Finally, an individual number within a disclosed range may be relied upon and provides adequate support for specific embodiments within the scope of the appended claims. For example, a range “of from 1 to 9” includes various individual integers, such as 3, as well as individual numbers including a decimal point (or fraction), such as 4.1, which may be relied upon and provide adequate support for specific embodiments within the scope of the appended claims.

[00143] The following examples are intended to illustrate the invention and are not to be viewed in any way as limiting to the scope of the invention.

EXAMPLES

[00144] Example 1:

[00145] A nanoparticle composition is prepared in situ by producing nanoparticles via a plasma process and capturing or collecting the nanoparticles directly in a silicone material. In particular, nanoparticles are prepared via a plasma reactor system from a precursor gas comprising SiH_4 (2% vol. in Ar) at 16 sccm with additional Ar and H_2 in the precursor gas. The precursor gas is delivered to the reactor via mass flow controllers.

[00146] Silicon nanoparticles are produced and captured or collected in the silicone material to produce the nanoparticle composition. The silicone material comprises a polydimethylsiloxane fluid. The nanoparticle composition is removed from the plasma reactor system and aged in a humid oven to increase photoluminescent intensity of the silicon nanoparticles of the nanoparticle composition.

[00147] 5 g of the nanoparticle composition and 0.25 g of a depolymerization catalyst are disposed in a round-bottom flask and sonicated for 5 minutes. The depolymerization catalyst comprises an acidified clay (montmorillonite). The flask is attached to a rotary evaporator and spun at 85 to 90 °C for 2 hours at atmospheric pressure. A vacuum is applied and the temperature is increased to 145 °C such that the contents of the flask are distilled for about 1 hour. The temperature is increased to

about 180 °C over one hour, and the contents of the flask are distilled at this temperature for about 15 additional minutes. Distillation causes substantial separation of volatile silicon compounds formed from the depolymerization of the silicone material, i.e., the polydimethylsiloxane fluid, and the nanoparticles. The contents of the flask are cooled and toluene is disposed in the flask. The contents of the flask are subjected to a sonic bath and filtered via a fine glass filter while rinsing with additional toluene. Toluene is removed by rotary evaporation to isolate the nanoparticles. The isolated nanoparticles have a reduction in mass of about 90% as compared to the original nanoparticle composition, attributable to the depolymerization of the silicone material and the substantial separation of the nanoparticles from the volatile silicon compounds. The isolated nanoparticles demonstrate bright red photoluminescence when irradiated with UV radiation.

[00148] Example 2:

[00149] A nanoparticle composition is prepared in the same manner as the nanoparticle composition of Example 1.

[00150] 5 g of the nanoparticle composition, 8.5 g of dimethyl carbonate, 20 g of methanol, 17 g of mesitylene, and 0.25 g of NaCl are disposed in a 100 mL Parr reactor vessel, which is subsequently sealed. The vessel is set to stir at 600 rpm and purged with N₂ for about 10 minutes, after which the vessel is resealed. The vessel is heated to about 180 °C under stirring for 16 hours to depolymerize the silicone material of the nanoparticle composition to form volatile silicon compounds. Once the vessel is cooled and the pressure is reduced to near atmospheric pressure, a vent valve is opened on the vessel and a vacuum is applied. The vessel is slowly heated to 80 °C and distillates comprising the volatile silicon compounds are collected in a flask under a dry-ice cold trap. After distilling, the contents of the vessel are measured, and it is determined that about 50% by weight of the liquid phase, i.e., the silicone material, was depolymerized and removed via distillation. Said differently, the nanoparticles were substantially separated from the volatile silicon compounds formed from the depolymerization of the silicone material, i.e., the polydimethylsiloxane fluid.

[00151] The invention has been described in an illustrative manner, and it is to be understood that the terminology which has been used is intended to be in the nature of words of description rather than of limitation. Obviously, many modifications and

variations of the present invention are possible in light of the above teachings. The invention may be practiced otherwise than as specifically described.

CLAIMS

1. A method of recovering nanoparticles from a silicone material, said method comprising:

providing a nanoparticle composition comprising a silicone material and nanoparticles;

depolymerizing the silicone material of the nanoparticle composition to form volatile silicon compounds; and

substantially separating the volatile silicon compounds and the nanoparticles to recover the nanoparticles.

2. The method according to claim 1 wherein the silicone material is selected from a silicone fluid, a silicone gel, a silicone resin, and a silicone elastomer.

3. The method according to any one of claims 1 and 2 wherein the silicone material is a silicone fluid.

4. The method according to any one preceding claim wherein the nanoparticles of the nanoparticle composition are produced via a plasma process.

5. The method according any one preceding claim wherein the nanoparticle composition is produced by forming a nanoparticle aerosol in a low pressure reactor, wherein the nanoparticle aerosol comprises nanoparticles in a gas, and collecting the nanoparticles of the nanoparticle aerosol in a silicone fluid to produce the nanoparticle composition.

6. The method according to claim 5 wherein the nanoparticle composition is produced by a method comprising:

applying a preselected VHF radio frequency having a continuous frequency ranging from about 10 to about 500 MHz and a coupled power ranging from about 5 to about 1000 W to a reactant gas mixture in a plasma reactor having a reactant gas inlet and an outlet having an aperture therein, to generate a plasma for a time sufficient to form the nanoparticle aerosol, with the reactant gas mixture comprising from about 0.1 to about 50% by volume of a first precursor gas, and at least one inert gas; and

collecting the nanoparticles of the nanoparticle aerosol in a silicone fluid to produce the nanoparticle composition.

7. The method according to claim 5 wherein the nanoparticle composition

is produced by a method comprising:

- forming the nanoparticle aerosol in the reactor;
- introducing the nanoparticle aerosol into a diffusion pump from the reactor;
- heating a silicone diffusion pump fluid in a reservoir to form a vapor and sending the vapor through a jet assembly;
- emitting the vapor through a nozzle into a chamber of the diffusion pump and condensing the vapor to form a condensate;
- flowing the condensate back to the reservoir;
- capturing the nanoparticles of the aerosol in the condensate; and
- collecting the captured nanoparticles in the reservoir to produce the nanoparticle composition.

8. The method according to any one preceding claim wherein depolymerizing the silicone material comprises heating the silicone material in the presence of acidified clay.

9. The method according to any one preceding claim wherein depolymerizing the silicone material comprises heating the silicone material in the presence of a dialkyl carbonate.

10. The method according to any one preceding claim wherein substantially separating the volatile silicon compounds and the nanoparticles comprises distilling the volatile silicon compounds and the nanoparticles.

11. The method according to any one preceding claim wherein the nanoparticles of the nanoparticle composition are photoluminescent.

12. The method according to claim 11 wherein the nanoparticles have a mean diameter of less than 5 nm.

13. The method according to any one of claims 11 and 12 wherein the nanoparticle composition has a photoluminescent intensity of at least 1×10^6 at an excitation wavelength of about 365 nm.

14. The method according to any one of claims 11-13 wherein the nanoparticle composition has a quantum efficiency of at least 4% at an excitation wavelength of about 365 nm.

15. The method according to any one of claims 11-14 wherein nanoparticle composition has a full width at half maximum emission of from 20 to 250 at an excitation wavelength of 270-500 nm.

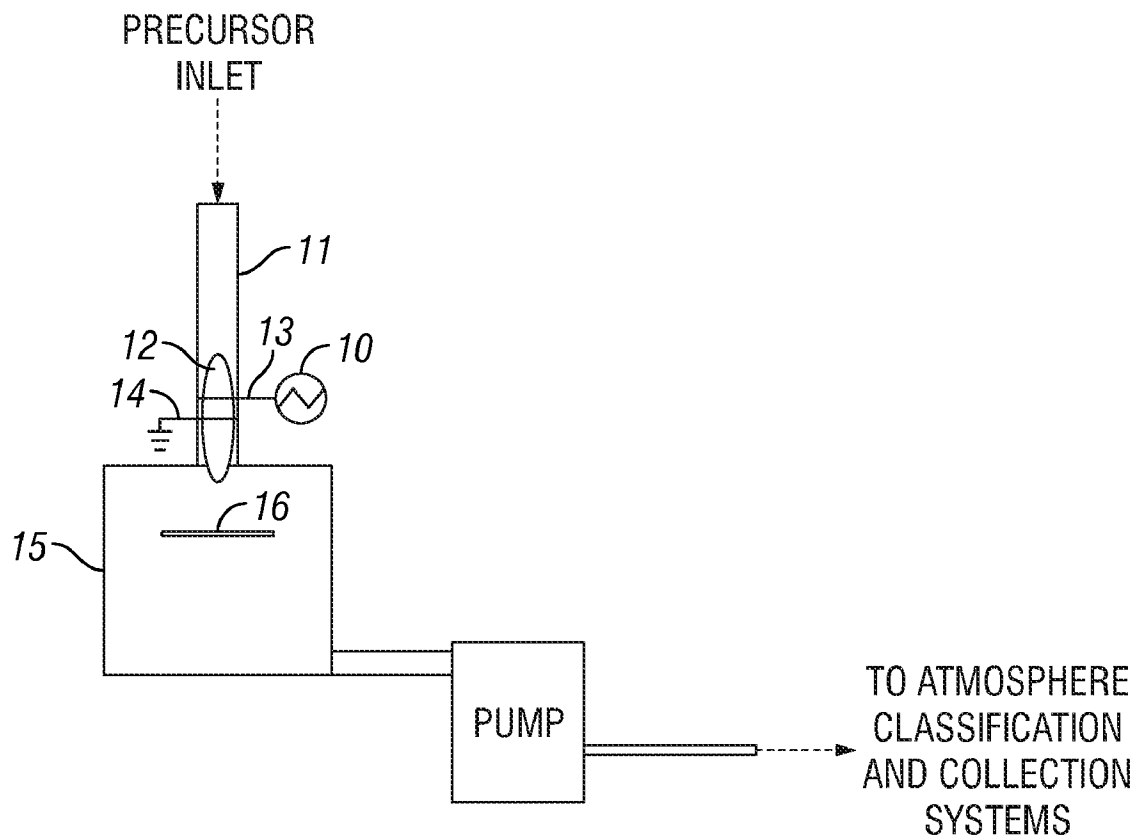


Figure 1

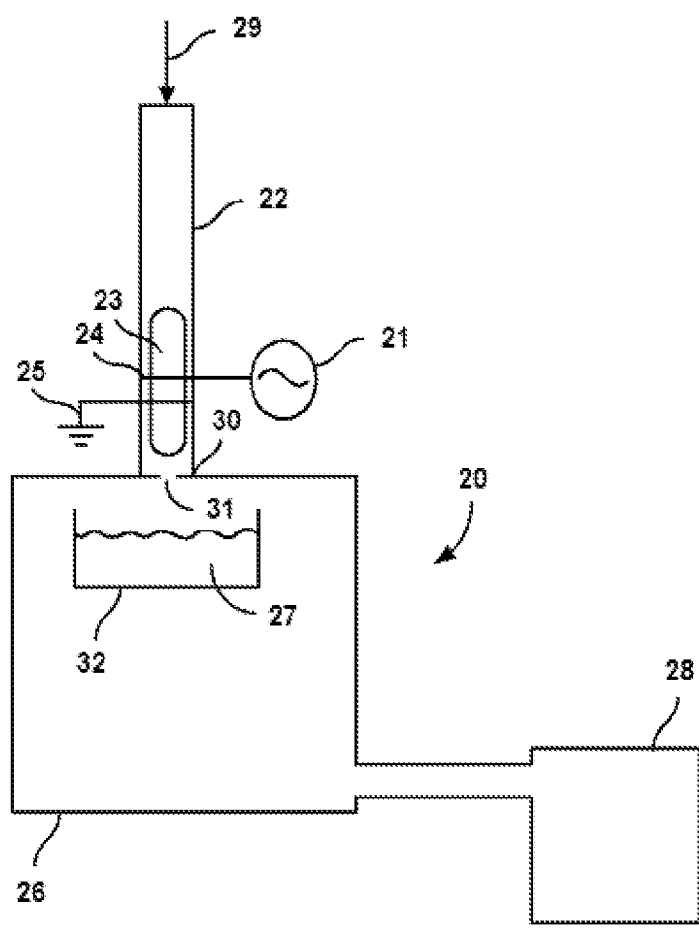


Figure 2

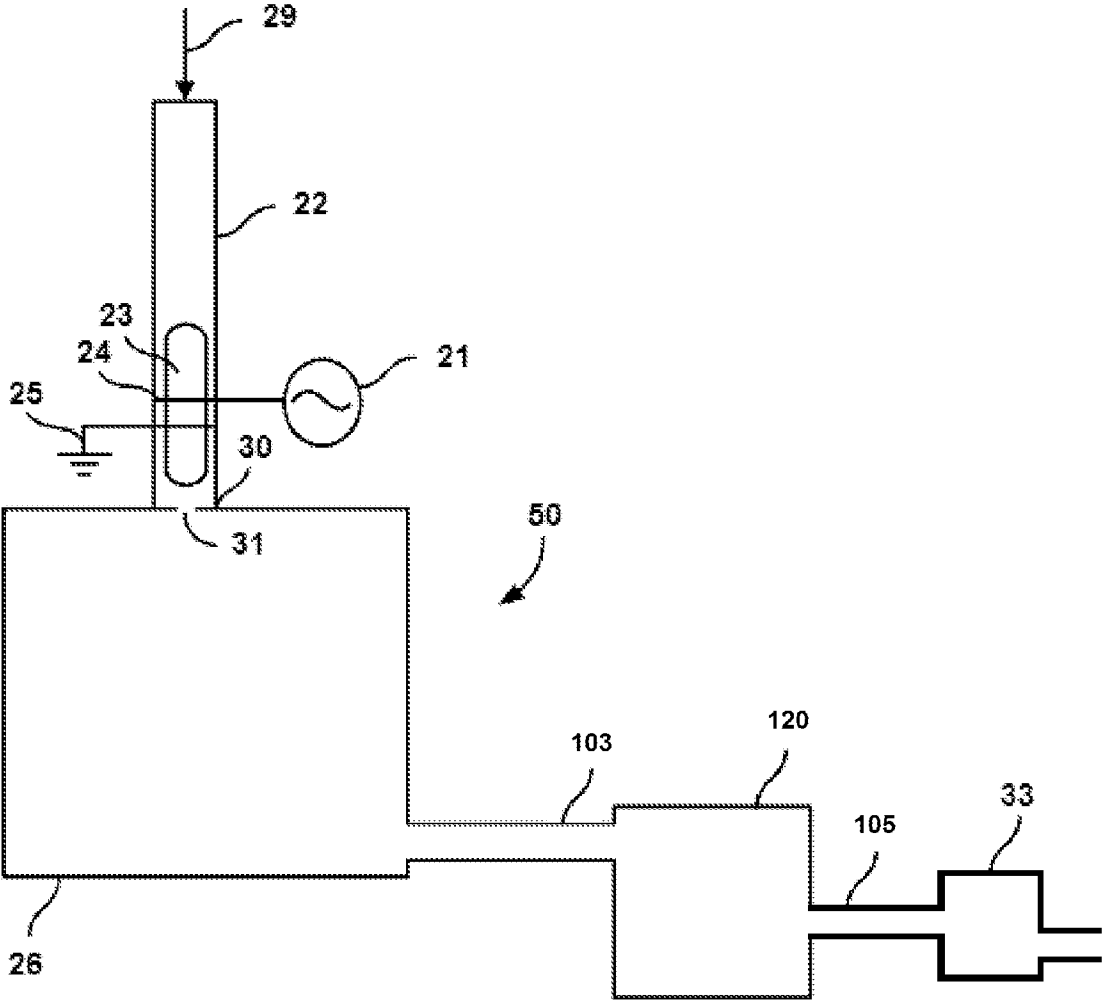


Figure 3

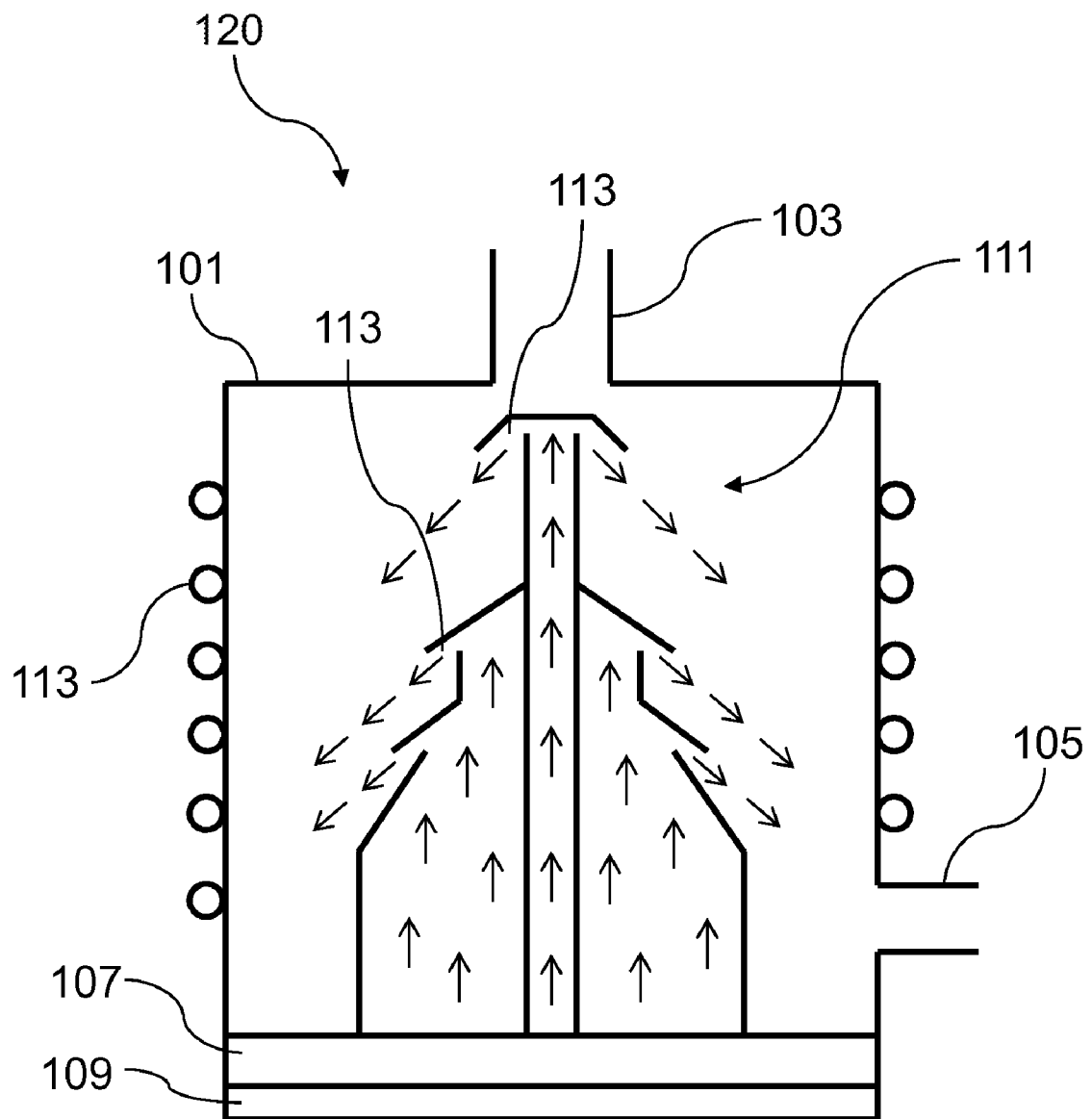


Figure 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/038128

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J11/00 C08J11/12
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08J

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 783 609 A (CHO TSURAHIDE [JP] ET AL) 21 July 1998 (1998-07-21) claims 1,19 column 12, line 13 - line 48 -----	1-15
A	JP 2003 342372 A (KANSAI ELECTRIC POWER CO; OKU AKIRA) 3 December 2003 (2003-12-03) abstract -----	1



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

23 September 2014

Date of mailing of the international search report

01/10/2014

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/038128

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