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- (71) Applicant: **DOW SILICONES CORPORATION**
[US/US]; 2200 West Salzburg Road, Midland, Michigan
48686-0994 (US).
- (72) Inventors: **CASEY, James A.**; 2651 Salzburg Road, Mid-
land, Michigan 48640 (US). **SERRANO, Charles K.**; 713
Crescent Drive, Midland, Michigan 48640 (US). **WITK-
ER, David**; 2651 Salzburg Road, Midland, Michigan 48640
(US).

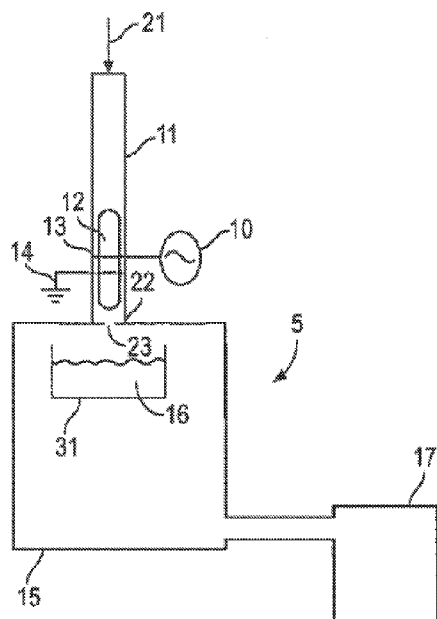
(74) Agent: **MORK, Steven**; The Dow Chemical Company,
P.O. Box 1967, Intellectual Property, Midland, Michigan
48641-1967 (US).

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CENCE WAVELENGTH CHARACTERISTICS OF SILICON NANOPARTICLES

FIG. 1



(57) Abstract: A method of controlling the absorbance and/or luminescence of silicon nanoparticles, the method comprising: synthesizing silicon nanoparticles in a plasma reactor at a first pressure and capturing the synthesized silicon nanoparticles in a capture fluid, where the capture fluid comprises an absorption-modifying functional group.

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SILICON NANOPARTICLES AND THE METHODS FOR CONTROLLING ABSORBANCE
AND/OR LUMINESCENCE WAVELENGTH CHARACTERISTICS OF SILICON
NANOPARTICLES

5 CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] None

FIELD OF THE INVENTION

[0002] The present invention relates, generally, to a method of controlling the absorbance and/or
10 luminescence wavelength of silicon nanoparticles comprising synthesizing silicon nanoparticles and
capturing the synthesized silicon nanoparticles in a capture fluid comprising an absorption-
modifying functional group.

BACKGROUND OF THE INVENTION

15 [0003] The advent of nanotechnology is resulting in a paradigm shift in many technological arts
because the properties of many materials change at nanoscale dimensions. For example, decreasing
the dimensions of some structures to nanoscales can increase the ratio of surface area to volume,
thus causing changes in the electrical, magnetic, reactive, chemical, structural, and thermal
properties of the material. Nanomaterials are already being found in commercial applications and
20 will likely be present in a wide variety of technologies including computers, photovoltaics,
optoelectronics, medicine/pharmaceuticals, structural materials, military applications, and many
others within the next few decades.

[0004] Initial research efforts focused on porous silicon, but much interest and effort has now
shifted from porous silicon to silicon nanoparticles. An important characteristic of small (less than
25 10 nanometers (nm) in average size) silicon nanoparticles is that these particles are
photoluminescent in visible light when stimulated by lower wavelength sources (UV). This is
thought to be caused by a quantum confinement effect that occurs when the diameter of the
nanoparticle is smaller than the exciton radius, which results in bandgap bending (i.e., increasing of
the gap). Researchers have shown how the bandgap energy (in electron volts) of a nanoparticle
30 changes as a function of the diameter of the nanoparticle.

[0005] Although silicon is an indirect bandgap semiconductor in bulk, silicon nanoparticles with
diameters less than 10 nm emulate a direct bandgap material, which is made possible by interface
trapping of excitons. Direct bandgap materials can be used in optoelectronics applications and so
silicon nanoparticles may possibly be the dominant material in future optoelectronic applications.
35 Another interesting property of nanomaterials is the lowering of the melting point following the

surface-phonon instability theory. Researchers have shown that the melting point of a nanomaterial formed of nanoparticles changes as a function of the diameter of the nanoparticle.

[0006] Industry, universities, and laboratories have devoted substantial effort to the development of manufacturing methods and apparatuses that can be used to produce nanoparticles. Some of those techniques include microreactor plasma, aerosol thermal decomposition of silane, ultrasonication of etched silicon, and laser ablation of silicon. Plasma discharge provides another opportunity to produce nanoparticles at high temperatures from atmospheric plasmas or at approximately room temperature with low pressure plasmas. High temperature plasmas also have been investigated.

[0007] Low pressure plasma has been investigated as a method to produce silicon nanoparticles since the 1990's. Nanocrystalline silicon particles have been produced using an ultra-high vacuum (UHV) and very high frequency (VHF, ~144 MHz) capacitively coupled plasma. This approach uses a VHF plasma cell attached to a UHV chamber and decomposes silane with the plasma. A carrier gas of hydrogen or argon is pulsed into the plasma cell to push the nanoparticles, formed in the plasma, through an orifice into the UHV reactor where the particles are deposited. The high frequency allows efficient coupling from the rf power to the discharge producing a high ion density and ion energy plasma. Other researchers have employed an inductively coupled plasma (ICP) reactor to make a 13.56 MHz rf plasma that has high ion energy and density.

[0008] The ICP reactor does not effectively produce nanoparticles and was replaced by a capacitively coupled discharge. The capacitively coupled system with a ring electrode was able to create a plasma instability that produces a constricted plasma that has an ion density and energy that is much higher than the surrounding glow discharge. This instability rotates around the discharge tube reducing the residence time of the particles in the high energy region. The capacitively coupled system produces smaller nanoparticles when the residence time is shorter because the residence time is approximately the time in which the conditions for nucleation of nanoparticles are favorable.

Consequently, reducing the residence time reduces the amount of time available for the particles to nucleate from dissociated precursor(s) molecular fragments and affords a measure of control over the particle size distribution. This method produced nanocrystalline and luminescent silicon particles. However, the radiofrequency power in the capacitively coupled system is not sufficiently coupled to the discharge. Consequently, relatively high input power (~200 W) is needed to deliver even modest power into the plasma (~5 W) because much of the input radiofrequency power is reflected back to the power supply. This greatly reduces the lifetime of the power supply and reduces the cost effectiveness of this technique for production of silicon nanoparticles.

[0009] Low pressure high frequency pulsed plasma reactors and direct fluid capture of the nanoparticles formed in the reactor also have been investigated. This method entails using pressure gradients to shoot the nanoparticles at supersonic speeds into a capture fluid to minimize particle size growth.

[0010] Potential applications for the nanoparticles may require different absorbance and luminescence wavelength properties of the nanoparticles. For example, absorbance in the ultraviolet range would be more important than absorbance in a different range in sun protection applications. Although much work has been focused on reactors and methods for producing nanoparticles effectively and efficiently, little work has been done to control the absorptive and luminescent properties of the nanoparticles produced. Therefore, there exists a need for methods of controlling the properties (i.e., absorbance and luminescence) of nanoparticles produced.

BRIEF SUMMARY OF THE INVENTION

[0011] The present invention is directed to method of controlling the absorbance and/or luminescence wavelength of silicon nanoparticles, the method comprising: synthesizing silicon nanoparticles in a plasma reactor at a first pressure and capturing the synthesized silicon nanoparticles in a capture fluid, where the capture fluid comprises an absorption-modifying functional group.

[0012] The present invention is further directed to silicon nanoparticles formed by the method of the invention.

[0013] The method of the invention allows for the production of silicon nanoparticles with varying luminescence and absorbance wavelength properties.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The following detailed description of the present invention can be best understood when read in conjunction with the following drawings, where like structure is indicated with like reference numerals and in which:

[0015] FIG. 1 schematically illustrates one exemplary embodiment of a low pressure pulsed plasma reactor which can be used to prepare photoluminescent nanoparticles in accordance with embodiments of the present disclosure.

[0016] FIG 2 is a normalized photoluminescent emission spectra for the different silicon nanoparticles captured in different terminal PDMS capture fluids. The top plot are the particle dispersions measured on the day they were synthesized, while the bottom plot are the sample dispersions after temperature and humidity aged.

[0017] FIG 3 is the absorbance spectra of the various silicon nanoparticles dispersed in terminal PDMS capture fluids. The top plot are the samples on Day 0 (day they are synthesized). The bottom plot are the spectra after they were aged in the temperature/humidity ovens.

DETAILED DESCRIPTION OF THE INVENTION

[0018] A method of controlling the absorbance and/or luminescent wavelength of silicon nanoparticles, the method comprising: synthesizing silicon nanoparticles in a plasma reactor at a

first pressure and capturing the synthesized silicon nanoparticles in a capture fluid, where the capture fluid comprises an absorption-modifying functional group.

[0019] The silicon nanoparticles are synthesized in a plasma reactor at a first pressure.

5 [0020] The silicon nanoparticles have an average diameter ranging from about 2.2 to about 4.7 nm.

[0021] The silicon nanoparticles generally have a photoluminescent intensity that increases upon exposure to oxygen. The silicon nanoparticles typically have a photoluminescent intensity of at least 1×10^6 counts per second at an excitation wavelength of about 365 nm. The silicon nanoparticles typically have a quantum efficiency of at least 4% at an excitation wavelength of about 395 nm. The
10 silicon nanoparticles can comprise a silicon alloy.

[0022] Referring initially to FIG. 1, photoluminescent silicon nanoparticles are prepared by providing at least a first reactant gas mixture to a plasma reactor system 5. The reactant gas mixture typically comprises a first reactive precursor gas and an inert gas. Preferably, the first reactive precursor gas comprises from about 0.1% to about 50% of the total volume of the reactant gas
15 mixture. However, it is also contemplated that the first reactive precursor gas may comprise other volume percentages such as from about 1% to about 50% of the total volume of the reactant gas mixture.

[0023] Preferably, the first reactive precursor gas contains silicon. Generally, the first reactive precursor gas is selected from silanes, disilanes, halogen-substituted silanes, halogen-substituted
20 disilanes, (C₁₋₄)alkyl silanes, (C₁₋₄)alkyldisilanes, and mixtures thereof. The reactant gas mixture can comprise silane which comprises from about 0.1 to about 2% of the total reactant gas mixture. However, the reactant gas mixture may also comprise other percentages of silane. Alternatively, the first reactive precursor gas may also comprise, but is not limited to, SiCl₄, HSiCl₃, and H₂SiCl₂.

[0024] The reactant gas mixture may also optionally comprise an inert gas. Preferably, the inert
25 gas comprises argon. Alternatively, it is also contemplated that the inert gas may comprise xenon, neon, or a mixture of inert gases. When present in the reactant gas mixture, the inert gas may comprise from about 1% to about 99% of the total volume of the reactant gas mixture. However, other volume percentages of inert gas are also contemplated.

[0025] The reactant gas mixture can comprise a second precursor gas which itself can comprise
30 from about 0.1 to about 49.9 volume % of the reactant gas mixture. The second precursor gas comprises BCl₃, B₂H₆, PH₃, GeH₄, or GeCl₄. Alternatively, the second precursor gas may comprise other gases that contain carbon, germanium, boron, phosphorus, or nitrogen. Preferably, the combination of the first reactive precursor gas and the second precursor gas together make up from about 0.1 to about 50% of the total volume of the reactant gas mixture.

35 [0026] The reactant gas mixture can comprise hydrogen gas. Preferably, hydrogen gas is 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.

[0027] Referring again to FIG. 1, the plasma reactor system 5 comprises a plasma generating chamber 11 having a reactant gas inlet 21 and an outlet 22 having an aperture or orifice 23 therein.

5 A particle collection chamber 15 is in communication with the plasma generating chamber 11. The particle collection chamber 15 contains a capture fluid 16 in a container 31. Container 31 may be adapted to be agitated (by means not shown). For example, container 31 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.

10 [0028] The plasma reactor system 5 also includes a vacuum source 17 in communication with the particle collection chamber 15 and plasma generating chamber 11.

[0029] The plasma generating chamber 11 comprises an electrode configuration 13 that is attached to a variable frequency rf amplifier 10. The plasma generating chamber 11 also comprises a second electrode configuration 14. The second electrode configuration 14 is either ground, DC biased, or
15 operated in a push-pull manner relative to the electrode 13. The electrodes 13, 14 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 12. The first reactive precursor gas (or gases) is then dissociated in the plasma to provide charge silicon atoms which nucleate to form silicon nanoparticles having an average silicon core diameter in a range of one to 10 nm, and preferably
20 from between 2.2 to 4.7 nm. However, other discharge tube configurations are contemplated, and may be used in carrying out the method disclosed herein.

[0030] The silicon nanoparticles are collected in particle collection chamber 15 in the capture fluid. To control the diameter of the nanoparticles which are formed, the distance between the aperture 23 in the outlet 22 of plasma generating chamber 11 and the surface of the capture fluid
25 ranges between about 5 to about 50 aperture diameters. We have 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
30 generating chamber and the collection chamber, we have found that based on the operating condition described herein, an acceptable collection distance is from about 1 to about 20 cm, and preferably from about 5 to about 10 cm. Stated another way, an acceptable collection distance is from about 5 to about 50 aperture diameters.

[0031] The plasma generating chamber 11 also comprises a power supply. The power is supplied
35 via a variable frequency radio frequency power amplifier 10 that is triggered by an arbitrary function generator to establish high frequency pulsed plasma in area 12. 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.

[0032] The plasma generating chamber 11 may also comprise a dielectric discharge tube.

- 5 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.

- [0033] The vacuum source 17 typically comprises a vacuum pump. The vacuum source 17 may comprise a mechanical, turbo molecular, or cryogenic pump. However, other vacuum sources are
10 also contemplated.

- [0034] The electrodes 13, 14 for a plasma source inside the plasma generating chamber 11 typically comprise a flow-through showerhead design in which a VHF radio frequency biased upstream porous electrode plate 13 is separated from a downstream porous electrode plate 14, with the pores of the plates aligned with one another. The pores may be circular, rectangular, or any other
15 desirable shape. Alternatively, the plasma generating chamber 11 may enclose an electrode 13 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 11.

- [0035] The VHF radio frequency power source usually operates in a frequency range of 30 about 500 MHz. The pointed tip 13 can be positioned at a variable distance from a VHF radio frequency
20 powered ring 14 operated in a push-pull mode (180° out of phase). The electrodes 13, 14 can include an inductive coil coupled to the VHF radio frequency power source so that radio frequency power is delivered to the reactant gas mixture by an electric field formed by the inductive coil. Portions of the plasma generating chamber 11 can be evacuated to a vacuum level ranging between 0.133
milliPascal to 67 MegaPascal (1×10^{-7} to 500 Torr). However, other electrode coupling
25 configurations are also contemplated for use with the method disclosed herein.

- [0036] In the illustrated embodiment, the plasma in area 12 is initiated with a high frequency plasma via a rf power amplifier such as, for example, an AR Worldwide Model KAA2O4O, 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 (e.g., a Tektronix
30 AFG3252 function generator) that is capable of producing up to 200 watts of power from 0.15 to 150 MHz. The arbitrary function typically 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 reactant gas mixture typically increases as the frequency of the rf power increases. The ability to drive the power at a higher frequency may allow more efficient
35 coupling between the power supply and discharge. The increased coupling may be manifested as a decrease in the voltage standing wave ratio (VSWR).

$$(1) \quad VSWR = (1+p)/(1-p),$$

where p is the reflection coefficient,

5

$$(2) \quad p = (Z_p - Z_c)/(Z_c + Z_p)$$

with Z_p and Z_c representing the impedance of the plasma and coil, respectively. At frequencies below 30 MHz, only 2-15% of the power is delivered to the discharge. This has the effect of producing high reflected power in the rf circuit that leads to increased heating and limited lifetime of the power supply. In contrast, higher frequencies allow more power to be delivered to the discharge, thereby reducing the amount of reflected power in the rf circuit.

[0037] The power and frequency of the plasma system can be preselected to create an optimal operating space for the formation of photoluminescent silicon 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 silicon-containing reactive precursor gas and nucleate the nanoparticles. Appropriate control of both the power and frequency prevents the silicon nanoparticles from growing too large.

[0038] Referring again to FIG. 1, one exemplary embodiment of a low pressure high frequency pulsed plasma reactor **5** is schematically illustrated. In the illustrated embodiment, a reactant gas mixture is introduced to a plasma generating chamber **11**. The plasma reactor **5** may be operated in the frequency range of from 30 MHz to 150 MHz, at pressures from 13 Pascal to 1.33 MegaPascal (100 mTorr to 10 Torr) in the plasma generating chamber **11**, and with a power of from about 1 W to about 200 W. However, other powers, pressures, and frequencies of the plasma reactor **5** are also contemplated.

[0039] The pulsed plasma system illustrated in FIG. 1 may be used to produce photoluminescent silicon nanoparticles. Pulsing the plasma enables an operator to directly manage the residence time for particle nucleation, and thereby control the particle size distribution and agglomeration kinetics in the plasma. The pulsing function of the system allows for controlled tuning of the particle residence 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).

[0040] 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. However, it is also contemplated that the VHF radiofrequency may be pulsed at other frequencies.

[0041] 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 is ignited to synthesize the Si 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.

[0042] Generally, the 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 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. The mean particle diameter of nanoparticles can be controlled by controlling the plasma residence time and a high ion energy/density region of a VHF radio frequency low pressure glow discharge can be controlled relative to at least one precursor gas molecular residence time through the discharge.

[0043] The size distribution of the nanoparticles can also be controlled by controlling the plasma residence time, a high ion energy/density region of the VHF radio frequency low pressure glow discharge relative to said at least one precursor gas molecular residence time through the discharge. Typically, the lower the plasma residence time of a VHF radio frequency low pressure glow discharge relative to the gas molecular residence time, the smaller the mean nanoparticle diameter at constant operating conditions. The operating conditions may be defined by the discharge drive frequency, drive amplitude, discharge tube pressure, chamber pressure, plasma power density, precursor mass flow rates, and collection distance from plasma source electrodes. However, other operating conditions are also contemplated. For example, as the plasma residence time of a VHF radio frequency low pressure glow discharge relative to the gas molecular residence time increases, the mean nanoparticle diameter follows an exponential growth model of $y = y_0 - \exp(-t_r/C)$, where y is the mean nanoparticle diameter, y_0 is the offset, t_r is the plasma residence time, and C is a constant. The particle size distribution may also increase as the plasma residence time increases under otherwise constant operating conditions.

[0044] The mean particle diameter of the nucleated nanoparticles (as well as the nanoparticle size distribution) can be controlled by controlling a mass flow rate of at least one precursor gas in a VHF

radio frequency low pressure glow discharge. For example, as the mass flow rate of precursor gas (or gases) increases in the VHF radio frequency low pressure plasma discharge, the synthesized mean nanoparticle diameter may decrease following an exponential decay model of the form $y=y_0+\exp(-\text{MFR}/C')$, where y is the mean nanoparticle diameter, y_0 is the offset, MFR is the precursor mass flow rate, and C' is a constant, for constant operating conditions. Typical operating conditions may include 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. The synthesized mean core nanoparticle particle size distribution may also decrease as an exponential decay model of the form $y=y_0+\exp(-\text{MFR}/K)$, where y is the mean nanoparticle diameter, y_0 is the offset, MFR is the precursor mass flow rate, and K is a constant, for constant operating conditions.

[0045] As described previously, the nucleated nanoparticles formed in the plasma generating chamber 11 are transferred to a particle collection chamber 15 containing the capture fluid 16. Preferably, the charged nanoparticles may be evacuated from chamber 11 to the particle collection chamber 15 by cycling the plasma to a low ion energy state, or by turning the plasma off. Upon transfer to the particle collection chamber 15, the nucleated nanoparticles are absorbed into the capture fluid.

[0046] The nucleated nanoparticles can be transferred from the plasma generating chamber 11 to particle collection chamber 15 containing capture fluid via an aperture or orifice 23 which creates a pressure differential. It is contemplated that the pressure differential between the plasma generating chamber 11 and the particle collection chamber 15 can be controlled through a variety of means. In one configuration, the discharge tube inside diameter of the plasma generating chamber 11 is much less than the inside diameter of the particle collection chamber 15, 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 15 that forces the plasma to reside partially inside the orifice, based on the Debye length of the plasma and the size of the chamber 15. 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 23.

[0047] It is contemplated that the capture fluid may be used as a material handling and storage medium. The capture fluid is typically selected to allow nanoparticles to disperse into the fluid as they are collected and to prevent particle-particle interactions, thus forming a dispersion or suspension of nanoparticles in the capture fluid. Notably, capture fluid can usually be reused multiple times to capture nanoparticles. Generally, to reuse a capture fluid, it is common to isolate nanoparticles from the capture fluid (though not a necessary step) by, for example, filtration, and then using the capture fluid to collect more nanoparticles.

[0048] The capture fluid is selected to have the desired properties for silicon nanoparticle capture, storage, and its effect on absorption properties of the silicon nanoparticles. The vapor pressure of the capture fluid is desirably lower than the operating pressure in the plasma reactor. Preferably, the operating pressure in the reactor and collection chamber 15 range from 0.133 Pascal to 0.667 Pascal (1 to 5 millitorr). Other operating pressures are also contemplated.

[0049] The capture fluid comprises an absorbance and/or luminescence modifying group. The capture fluid may be a single material, where that single material is substituted with the absorbance and/or luminescence modifying group, or a mixture of two or more materials, where one or more of the materials of the mixture comprises the absorbance and/or luminescence modifying group. The capture fluid can contain or be a fluid that is substituted with the absorbance and/or luminescence modifying group. Fluids that may be all or part of the capture fluid comprising an absorbance and/or luminescence modifying group include, but are not limited to, substituted silicone fluids, substituted halocarbons, where the halo is chloro or fluoro, and substituted hydrocarbons, where the substitute groups modify the absorbance and/or luminescence of the silicon nanoparticles. For example,

substituted silicone fluids such as substituted polydimethylsiloxane, mixed substituted phenylmethyl-dimethyl cyclosiloxane, substituted tetramethyltetraphenyltrisiloxane, substituted pentaphenyltrimethyltrisiloxane, substituted hydrocarbon, and substituted halocarbon are all suitable for use as capture fluid comprising an absorbance and/or luminescence modifying group, where the substitution of the fluid is with an absorbance and/or luminescence modifying group.

[0050] As used herein, “absorbance and/or luminescence modifying group” means a group that will change the absorbance wavelength, emission wavelength, or both absorbance and luminescence wavelengths of the nanoparticles captured in the capture fluid comprising the absorbance modifying group compared to nanoparticles captured in the same fluid but not comprising an absorbance and/or luminescence modifying group, alternatively a group that will shift the absorbance and/or luminescence of the nanoparticles captured in the capture fluid substituted with the absorbance and/or luminescence modifying group compared to the nanoparticles captured in the non-substituted capture fluid at least 10 nm, alternatively at least 20 nm, alternatively from 10 to 200 nm, alternatively from 10 to 150, alternatively from 10 to 100 nm. As used herein, “non-substituted capture fluid,” means a single fluid material that is the same as a single capture fluid comprising an absorbance and/or luminescence modifying group except that a hydrogen atom, a C₁₋₆ hydrocarbyl group, or a halo group is present in place of the absorbance and/or luminescence modifying group.

For example, PDMS terminated with trimethylsilyl versus dimethyl(hydroxy)silyl, where the hydroxy is the absorbance and/or luminescence modifying group, are examples of capture fluids with and without an absorbance and/or luminescence modifying group. Absorbance and/or luminescence is observed within 24 hours of synthesis of the nanoparticles and after passivation of the nanoparticles for 6 days. The absorbance and/or luminescence modifying group will cause a shift

in absorbance and/or luminescence either within 24 hours, after passivation for 6 days, or both within 24 hours or after passivation for 6 days.

[0051] The method of the invention can result in a shift in the wavelength of peak photoluminescence intensity of the nanoparticles, alternatively a shift of photoluminescence peak intensity of the nanoparticles of at least 25, alternatively at least 50, alternatively from 25 to 150 nanometers, measured at an excitation wavelength of about 365 nanometers. As used herein the shift in peak photoluminescence intensity is in comparison to the silicon nanoparticles produced not by the method of the invention but produced by the same method except using the corresponding non-substituted capture fluid.

[0052] The method of the invention can result in a peak photoluminescence of the nanoparticles that is at least 5, alternatively at least 10, alternatively from 5 to 30 absorption units (au) different than nanoparticles produced not by the method of the invention but produced by the same method except using the corresponding non-substituted capture fluid

[0053] The absorbance and/or luminescence modifying group can be an unsaturated hydrocarbyl having from 2 to 12 carbon atoms, borate, boronic acid, amide, azide, azo, amino, carbodiimide, imine, isocyanate, nitrile, nitro, alcohol, aldehyde, carboxylic acid, epoxy, ester, ether, hydroxyl, keto, peroxy, phosphate, phosphine, phosphine oxide, phosphinite, phosphite, phosphonate, phosphonite, disulfide, thioether, thiol, or halo, or silanol, alternatively hydroxyl, amine or vinyl.

[0054] Unsaturated hydrocarbyl groups that may be the absorbance and/or luminescence modifying group comprise 2 to 12 carbon atoms, alternatively 2 to 6 carbon atoms, alternatively 2 to 4 carbon atoms. Examples of unsaturated hydrocarbyl groups include, but are not limited to alkenyl, such as ethenyl, propenyl, isopropenyl, butenyl, isobutenyl, *t*-butenyl, pentenyl, octenyl, and docecenyl, and alkynyl, such as ethynyl, propynyl, butynyl, pentyne, octynyl, and dodecynyl.

[0055] Amide groups that may be the absorbance and/or luminescence modifying group are according to the formula $R-C(O)NR^1R^2$, where each R, R^1 , and R^2 is independently hydrocarbyl having from 1 to 10, alternatively from 1 to 6, alternatively from 1 to 3 carbon atoms, or R^5 , where R^5 is a bond or a hydrocarbylene linking group having from 1 to 10, alternatively from 1 to 6, alternatively from 1 to 4 carbon atoms, linking the absorbance and/or luminescence modifying group to the remain atoms of a material of the capture fluid, forming the capture fluid, and where one of R, R^1 , or R^2 is R^5 .

[0056] Acyclic hydrocarbyl groups represented by R, R^1 , or R^2 and containing at least 3 carbon atoms can have a branched or unbranched structure. Examples of hydrocarbyl groups represented by R, R^1 , and R^2 include, but are not limited to, alkyl, such as methyl, ethyl, propyl, 1-methylethyl, butyl, pentyl, hexyl, octyl, nonyl, and decyl, and their isomers; cycloalkyl, such as cyclopentyl, cyclohexyl, methylcyclohexyl; aryl, such as phenyl, and naphthyl; alkaryl such as methylphenyl,

- where the methyl can be in ortho, meta, or para position, tolyl and xylyl; aralkyl, such as benzyl and phenethyl; alkenyl, such as vinyl, allyl, and propenyl, butenyl, hexenyl, and actenyl; arylalkenyl, such as styryl and cinnamyl; and alkynyl, such as ethynyl and propynyl. Hydrocarbyl groups represented by R , R^1 , and R^2 can include, but are not limited to, methyl, ethyl, propyl, or butyl, alternatively methyl, ethyl, propyl, or *t*-butyl, alternatively methyl, ethyl, isopropyl, or *t*-butyl.
- Hydrocarbylene groups represented by R^5 include, but are not limited to, methylene, ethane-1,2-diyl, propane-1,3-diyl, butane-1,4-diyl and 1,3-phenylene.
- [0057] Azide groups that may be the absorbance and/or luminescence modifying group are according to the formula $R^5-N=N^+=N^-$, where R^5 is as described above.
- 10 [0058] Azo groups that may be the absorbance and/or luminescence modifying group are according to the formula $R-N=N-R$, where each R is independently as defined above and only one R group is R^5 , where R^5 is as described above.
- [0059] Amino groups that may be the absorbance and/or luminescence modifying group are according to the formula R^5NRR^6 , wherein R^6 is H or R , and R and R^5 are as described above.
- 15 [0060] Cabodiimide groups that may be the absorbance and/or luminescence modifying group are according to the formula $RN=C=NR^1$, wherein R and R^1 are as defined above, and where one of R and R^1 is R^5 , where R^5 is as described above.
- [0061] Imine groups that may be the absorbance and/or luminescence modifying group are according to the formula $RR^1C=NR^4$, where each R and R^1 is independently as described above, $R^4 = R^2$, R^5 , hydroxyl or NH_2 , and where one of R , R^1 or R^4 is R^5 , where R^5 is as described
- 20 above.
- [0062] Isocyanate groups that may be the absorbance and/or luminescence modifying group are according to the formula $R^5N=C=O$, where R^5 is as described above.
- [0063] Nitrile groups that may be the absorbance and/or luminescence modifying group are
- 25 according to the formula $R^5-C\equiv N$, where R^5 is as described above.
- [0064] Nitro groups that may be the absorbance and/or luminescence modifying group are according to the formula R^5NO_2 , where R^5 is as described above.
- [0065] Alcohol groups that may be the absorbance and/or luminescence modifying group are according to the formula R^5OH , where R^5 is as described above.
- 30 [0066] Aldehyde groups that may be the absorbance and/or luminescence modifying group are according to the formula R^5CHO , where R^5 is as described above.
- [0067] Carboxylic acid groups that may be the absorbance and/or luminescence modifying group are according to the formula R^5CO_2H , where R^5 is as described above.

[0068] Epoxy groups that may be the absorbance and/or luminescence modifying group is a hydrocarbyl group substituted with epoxy (-HC(O)CH-), where the hydrocarbyl group may be cyclic, branched or linear and has from 2 to 12, alternatively 2 to 6, carbon atoms.

[0069] Ester groups that may be the absorbance and/or luminescence modifying group are according to the formula RCO_2R , where each R independently is as defined above and where one of R is R^5 , where R^5 is as described above.

[0070] Ether groups that may be the absorbance and/or luminescence modifying group are according to the formula R^5OR , where R and R^5 is as described above.

[0071] Hydroxyl groups may be bonded to a carbon or silicon atom. When bonded to a silicon atom, the group is a silanol group. The alcohol may be bonded in the capture fluid through R^5 , where R^5 is as described above.

[0072] Keto groups that may be the absorbance and/or luminescence modifying group are according to the formula $\text{R}^5\text{C}(=\text{O})\text{R}$, where R and R^5 is as described above.

[0073] Peroxy groups that may be the absorbance and/or luminescence modifying group are according to the formula R^5OOR , where R and R^5 is as described above.

[0074] Phosphate may be bonded in the capture fluid through R^5 , where R^5 is as described above.

[0075] Phosphine groups that may be the absorbance and/or luminescence modifying group are according to the formula R^5PR^6_2 , where each R^6 and R^5 are independently as described above.

[0076] Phosphine oxide groups that may be the absorbance and/or luminescence modifying group are according to the formula $\text{R}^5\text{P}(=\text{O})\text{R}^6_2$, where each R^6 and R^5 are independently as described above, alternatively R^6 is alkyl or aryl.

[0077] Phosphinite groups that may be the absorbance and/or luminescence modifying group are according to the formula $\text{R}^5\text{P}(\text{OR})\text{R}$, where each R independently and R^5 is as described above.

[0078] Phosphite groups, phosphite anions or phosphite ester, and phosphonate groups that may be the absorbance and/or luminescence modifying group are linked in the capture fluid by P-O- R^5 bond, where R^5 is as described above and P may be further bonded to additional atoms of the absorption modifying groups such as O or, where R is as defined above.

[0079] Phosphonite groups that may be the absorbance and/or luminescence modifying group are according to the formula $\text{R}^6\text{P}(\text{OR}^6)_2$, where each R^6 independently is as described above, and one of R^6 is R^5 , where R^5 is as described above.

[0080] Disulfide groups that may be the absorbance and/or luminescence modifying group are according to the formula R^5SSR , where R and R^5 are as described above.

- [0081] Thioether groups that may be the absorbance and/or luminescence modifying group are according to the formula R^5SR , where R and R^5 are as described above.
- [0082] Thiol groups that may be the absorbance and/or luminescence modifying group are according to the formula R^5SH , where R^5 is as described above.
- 5 [0083] Halo groups that may be the absorbance and/or luminescence modifying group are according to the formula R^5X , where R^5 is as described above and X is halo, alternatively Br or Cl, alternatively Cl.
- [0084] Silanol groups that may be the absorbance and/or luminescence modifying group are according to the formula $R^5Si(OH)R_2$, where each R independently and R^5 is as described above.
- 10 [0085] Boron groups (borate or boronic acid) that may be the absorbance and/or luminescence modifying group are according to the formula $R^5_aB(OR^5)_{1-a}(OR)_2$, where a is 0 or 1, and R and R^5 are as described above.
- [0086] The capture fluid may comprise one or more absorbance and/or luminescence modifying groups. The capture fluid can comprise more than one absorbance and/or luminescence modifying group. The absorbance and/or luminescence modifying group may be terminal or pendant, alternatively terminal, alternatively pendant.
- 15 [0087] The capture fluid can be made by methods known in the art. For example, absorbance and/or luminescence modifying group terminated polydimethyl siloxanes can be made by the hydrosilylation reaction between a Si-H terminated polydimethylsiloxane and an unsaturated
- 20 hydrocarbyl group comprising the absorbance and/or luminescence modifying group. For example, Si-H terminated polydimethyl siloxane may be reacted with compounds according to the formula R^7X , where R^7 is allyl and X is the absorbance and/or luminescence modifying group in the presence of a platinum hydrosilylation catalyst. Polydimethylsiloxanes having pendant absorbance and/or luminescence modifying groups can be made similarly by the reaction of trimethylsilyl-
- 25 terminated polydimethyl(methylhydrogen)siloxanes with the compound R^7X defined above. Groups represented by X include, but are not limited to, (C_{2-10}) alkene, (C_{2-10}) alkyne, borate, boronic acid, amide, azide, azo, amino, carbodiimide, imine, isocyanate, nitrile, nitro, alcohol, aldehyde, carboxylic acid, epoxy, ester, ether, hydroxyl, keto, peroxy, phosphate, phosphine, phosphine oxide, phosphinite, phosphite, phosphonate, phosphonite,
- 30 disulfide, thioether, thiol, or halo, or silanol, alternatively hydroxyl, amine or vinyl.
- [0088] Other methods of manufacturing are also contemplated including, but not limited to, the reaction of pendant or terminal amino groups of the polydimethylsiloxane with a reactive group such as epoxide, carboxylic acid, or primary halide of a compound comprising the absorbance and/or luminescence modifying group; or the reaction of pendant or terminal epoxy or carboxylic acid
- 35 groups of a polydimethylsiloxane with a reactive group such as an amine compound comprising the

absorbance and/or luminescence modifying group; or where the reaction of the pendant or terminal group of a polydimethylsiloxane with a compound comprising a reactive group as described above produces the absorbance and/or luminescence modifying group as in the case of a pendant or terminal amine of a polydimethylsiloxane reacting with a carboxylic acid group of a compound to produce an amide. One skilled in the art would know how to make the capture fluid of the invention.

[0089] Examples of the capture fluids include, but are not limited to, silanol-terminated polydimethylsiloxane, polydimethyl(methylhydroxy)siloxane, aminopropyl-terminated polydimethylsiloxane, polydimethyl(methylaminopropyl)siloxane, vinyl-terminated polydimethylsiloxane, polydimethyl(methylvinyl)siloxane, hydrocarbon fluid with hydroxyl, amino, or vinyl groups, and fluoro- or chlorocarbons substituted with hydroxyl, vinyl or amino groups.

[0090] The hydrocarbon fluids comprising an absorbance and/or luminescence modifying group are branched and linear hydrocarbons having from 20 to 40 carbon atoms with the absorbance and/or luminescence modifying group linked in any position.

[0091] The capture fluid can comprise a mixture of an unsubstituted fluid and a material substituted with the absorbance and/or luminescence modifying group. For example, the absorbance and/or luminescence modifying group may be on a solid particle or a separate liquid dispersed and/or forming a soluble mixture with the capture fluid. The capture fluid substituted with an absorbance and/or luminescence modifying group can form a mixture with an unsubstituted capture fluid. For example, the capture fluid may be a mixture of polydimethylsiloxane and a polydimethylsiloxane substituted with the absorbance and/or luminescence modifying group, such as an amino, allyl, or hydroxy group, where the substitution is in a terminal or pendant position on the polydimethylsiloxane.

[0092] The capture fluid has a viscosity sufficient to capture the silicon nanoparticles and to be agitated to keep the particle from agglomerating, alternatively a viscosity from 1 to 500, alternatively from 10 to 100 milliPascals*seconds (centipoise). One skilled in the art would know how to measure the viscosity of a fluid. Measure viscosity using at 25 °C using a Brookfield LV Series Viscometer, spindle 12, at 12 rpm.

[0093] The capture liquid is desirably agitated during the direct capture of the nanoparticles.

Contemplated forms of agitation that are acceptable include stirring, rotation, inversion, and other suitable means. If higher absorption rates of the nanoparticles into the capture liquid are desired, more intense forms of agitation are contemplated. For example, one method of such intense agitation contemplated for use includes ultrasonication.

[0094] Turning back to Figure 1, upon the dissociation of the first reactive precursor gas in the plasma generation chamber 11, silicon 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 particles interact within the gas phase, agglomerations of numerous individual small particles will form and be captured in the capture fluid. If too much interaction takes place within the gas phase, the particles may sinter together and form particles larger than 10 nm in diameter. The collection distance is defined as the distance from the outlet of the plasma generating chamber to the surface of the capture fluid. The collection distance typically ranges from about 5 to about 50 aperture diameters.

[0095] Stated another way, the collection distance ranges from about 1 to about 20 cm. The collection distance may more usually range from between about 6 to about 12 cm, and preferably from about 5 to about 10 cm. However, other collection distances are also contemplated.

[0096] The nanoparticles can comprise silicon alloys. Silicon alloys that may be formed include, but are not limited to, silicon carbide, silicon germanium, silicon boron, silicon phosphorus, 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.

[0097] The silicon nanoparticles can undergo an additional doping step. Preferably, the silicon nanoparticles undergo gas phase doping in the plasma, where a second precursor gas is dissociated and is incorporated in the silicon nanoparticles as they are nucleated. Alternatively, the silicon nanoparticles may undergo doping in the gas phase downstream of the production of the nanoparticles, but before the silicon nanoparticles are captured in the liquid. Furthermore, doped silicon nanoparticles may also be produced in the capture fluid where the dopant is preloaded into the capture 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, for example, BCl_3 , B_2H_6 , PH_3 , GeH_4 , or GeCl_4 .

[0098] The direct liquid capture of the nanoparticles in fluid provides unique properties of the composition. Silicon nanoparticles that are directly captured in a capture fluid show visible photoluminescence when removed from the system and 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. The photoluminescent silicon nanoparticles which are directly captured typically have a photoluminescent intensity of at least 1×10^6 at an excitation wavelength of about 365 nm. The photoluminescent silicon nanoparticles which are directly captured can have a quantum efficiency of at least 4% at an excitation wavelength of about 395 nm as measured on an Ocean Optics spectrophotometer with an integrating sphere with an absorption of >10% of the incident photons.

- [0099] Furthermore, both the photoluminescent intensity and luminescent quantum efficiency of the direct capture composition continue to increase over time when the nanoparticle containing capture fluid is exposed to air. The maximum emission wavelength of the nanoparticles directly captured in a fluid generally shift to shorter wavelengths over time when exposed to oxygen.
- 5 Preferably, the luminescent quantum efficiency of the directly captured silicon nanoparticle composition is 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 silicon nanoparticles in the fluid. However, other increases in the
- 10 photoluminescent intensity are also contemplated. The wavelength emitted from the direct capture composition also experiences a blue shift of the emission spectrum. The maximum emission wavelength generally shifts about 100 nm, based on about a 1 nm decrease in silicon core size, depending on the time exposed to oxygen. However, other maximum emission wavelength shifts are also contemplated.
- 15 [0100] Still further, the capture fluid of the invention comprising an absorbance and/or luminescence modifying group alter the absorbance and photoluminescence of the silicon nanoparticles when first made and when aged while exposed to oxygen.
- [0101] The silicon nanoparticles in the capture fluid can be passivated by exposing the liquid to an oxygen containing environment. Alternatively, or additionally, passivation of the silicon
- 20 nanoparticle can occur by forming a nitride surface layer on the silicon core nanoparticles by bubbling a nitrogen-containing gas such as ammonia gas into the capture fluid.
- [0102] Also provided is a composition comprising photoluminescent silicon nanoparticles in a capture fluid wherein the silicon nanoparticles have a luminescent quantum efficiency that increases upon exposure to oxygen. The silicon nanoparticles can have a maximum emission wavelength that
- 25 shifts to shorter wavelengths upon exposure to oxygen.

EXAMPLES

- [0103] The following examples are presented to better illustrate the method of the present invention, but are not to be considered as limiting the invention, which is delineated in the appended
- 30 claims. Unless otherwise noted, all parts and percentages reported in the examples are by weight; the temperature is at 20 °C; and the pressure is 1 atmosphere. The following table describes the abbreviations used in the examples:

Table 1. List of abbreviations used in the examples.

Abbreviation	Word	Abbreviation	Word
g	gram	mL	milliliters
Me	methyl	cm	Centimeter
wt	weight	au	Absorbance units
%	percent	MHz	Megahertz
mol	mole	cSt.	Centistokes
hr	hour	PDMS	Polydimethylsiloxane
°C	degrees Celsius		

- [0104] Basic Plasma Nanoparticle Synthesis Procedure: The silicon nanoparticles were synthesized from a very high frequency low pressure plasma system. Ultra-high purity precursor gases (Ar, H₂, and SiH₄) were metered into a quartz tube via mass flow controllers at a specific ratio and pressure. Typical pressures of the quartz discharge tube were 133 Pascal to 667 Pascal (1 – 5 Torr). The gases were then dissociated via a very high frequency plasma discharge (100 – 150 MHz). The frequency was chosen to maximize the plasma coupling while minimizing the drive amplitude of the function generator that provides the sinusoidal signal to the Class A radio frequency amplifier.
- [0105] The precursors gases were dissociated in the very high frequency plasma discharge via numerous reactions that follow Maxwell-Boltzmann statistics (due to the non-equilibrium nature of a plasma discharge). Silicon atoms coalesced, nucleated, and grew to form silicon nanocrystals in the plasma. The power of the plasma discharge controlled the temperature of the individual particles, allowing crystallinity control of the particles. Higher power yielded crystalline particles, while low power produced amorphous particles. The concentration of silicon atoms and the residence time of the atoms within the plasma controlled the size of the nanoparticles. Once the nanoparticles exited the plasma, via an orifice located at the bottom of the quartz plasma chamber, they no longer grew. The particles exited the plasma with SiH_x (x<4), radicals (dangling bonds), and/or halogen species (if present in the discharge tube) on the surface. The particles were evacuated through the orifice by a large pressure drop into the deposition chamber. The pressure of the deposition chamber was less than 1.33 milliPascal (< 1x10⁻⁵ Torr) (produced by a high vacuum pump, i.e., turbo-molecular, cryogenic, or diffusion pump). This large pressure drop created a supersonic jet of particles streaming out of the plasma chamber. The supersonic jet minimized any gas phase particle to particle interactions, thus keeping the particles monodispersed in the gas stream.

[0106] An agitated fluid (capture fluid), that is a low viscosity liquid (viscosity less than 0.2 Pascal seconds) at a pressure of less than 1.33 milliPascal ($< 1 \times 10^{-5}$ Torr), was placed in a cup and is used to capture the particles at a low pressure. The location of the surface of the capture fluid was located within the distance of orifice in which the particles stay dispersed in the supersonic jet. The low viscosity of the capture fluid allowed the particles to be injected into the fluid without forming a film on the fluid's surface. Agitation of the fluid was used to refresh the surface of the capture fluid and force the captured particle away from the centerline of the orifice.

[0107] Once the silicon nanoparticle were captured in the capture fluid, the fluid and particle dispersion were removed from the vacuum chamber and the photoluminescence spectra measured.

This measurement was performed on a Horiba FL3 spectrofluorometer with a 450 watt Xenon source. The excitation monochromator was set to 365 nm with a slit width of 2 nm. A 400 nm edge filter was placed in the beam path leading to the emission monochromator, downstream of the sample. The sample (silicon nanoparticles dispersed in the capture fluid), was placed in a 1 cm path length cuvette (either quartz or methacrylate). [0108] The emission spectra was measured at a right angle relative to the excitation beam (or at a 22.5° angle – front facing, if the sample is not transparent enough to allow a right angle measurement). The emission monochromator has a 2 nm slit width and the measurements were performed with an integration time of 0.1s per wavelength and measured every 1 nm. The spectra is corrected for the quantum yield of the emission detector. The emission data is then fitted to a distribution (typically a Gaussian distribution for the silicon nanoparticles) with an adjusted $R^2 > 0.98$. From this fit, the emission maximum wavelength, emission full width at half maximum (FWHM), and emission intensity were obtained. The emission spectra was then transformed to a diameter spectra via an equation that was fitted to the data produced by the silicon quantum dot model developed by Luo, Stradins, and Zunger,

$$d_p = -1.401 \ln \left[0.195618 \left(\frac{hc}{\lambda} - 1.246 \right) \right]$$

where d_p is the particle diameter, h is Planck's constant, c is the speed of light, and λ is the emission wavelength. This transformed spectra was then fitted to a Gaussian distribution and the mean particle diameter and diameter standard deviation were obtained.

[0109] The silicon nanoparticle and capture fluid dispersions were then placed into a temperature-humidity oven (typically 60°C and 85% relative humidity) for five to six days to passivate the surface of the particles with a diffusion limited oxide (SiO_x , $x < 2$). This passivation blue-shifts the emission spectra and increases the photoluminescent intensity via passivation of the exciton trap states, effectively turning more particles ON.

The absorbance of the silicon nanoparticle/capture fluid dispersion was measured via a Shimadzu UV 1800 uv-vis spectrophotometer. This is a double beam spectrophotometer with a measurement

range of 190 – 1100 nm and a bandwidth of 1 nm. The neat capture fluid and the nanoparticle/capture fluid dispersion were placed into 1 cm path length matched quartz cuvettes. The absorbance spectra of the sample was then measured, subtracting out the spectra of the capture fluid (reference sample).

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EXAMPLES 1-3; COMPARATIVE EXAMPLE 1

[0110] Table 2 show the run conditions used to synthesize the silicon nanoparticles utilized in these examples. The processing conditions for all the runs were similar in order to produce nanoparticles of approximately the same size. The capture fluids used were 10 cSt. PDMS (control sample), and 3:1 mass ratio of various terminal (SiOH, amine, and vinyl terminations) PDMS in 10 cSt. PDMS. The time (30 min.), Argon gas volume % (91.36), H₂ gas volume % (8), SiH₄ gas volume % (0.64), the frequency (129 MHz), and PDMS capture fluid viscosity (10 cSt.) were the same for all examples. For the practical examples, the capture fluid was a blend of PDMS and capture fluid comprising the absorbance and/or luminescence modifying group at a ratio of PDMS (10 cSt.) to capture fluid comprising the absorbance and/or luminescence modifying group of 3:1.

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Table 2: Runs with conditions used in this study. The gas precursors values are the gas volume percentage. The frequency is the radio frequency of the plasma. P_F is the forward power, P_R is the reflected power, P_C is the power coupled, and P_{eff} is the power efficiency.

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Example	Capture Fluid	P_F (W)	P_g (W)	P_c (W)	P_{eff} (%)	Discharge Tube Pressure (Pascal)
Comparative Example 1	PDMS alone	192	68	124	64.58	435
Example 1	SiOH Terminal	189	68	121	64.02	443
Example 2	Amine Terminal	191	68	123	64.40	447
Example 3	Vinyl Terminal	187	67	120	64.17	429

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[0111] Day 0 samples were measured for absorbance and photoluminescence on the day they were synthesized. Aged samples were aged in a temperature humidity oven for the given days. Figure 2 shows the Day 0 and Aged photoluminescence emission spectra of the silicon nanoparticles captured in different terminal PDMS fluids. The emission spectra are normalized to the maximum emission intensity of the silicon nanoparticles deposited in the 10 cSt. PDMS (control sample). As can be seen in Figure 2, the maximum photoluminescence emission intensity and peak wavelength were different from the different samples as they were synthesized (Day 0). The Aged samples

normalized photoluminescence emission spectra (normalized to the peak emission intensity of Day 0 silicon nanoparticle/PDMS control sample) are displayed in the bottom plot of Figure 2. It is obvious that the intensity of all samples have increased with the temperature/humidity aging. The aged samples increased in intensity to various levels relative to the control PDMS sample on the day it was synthesized. The wavelength of the peak emission intensity also varied greatly amongst the samples. All of the samples blue-shifted, but the amount of the shift was related to the terminal species of the capture fluids. The SiOH (Example 1) and amine (Example 2) terminated sample shifted the most after aging. PDMS control is in Figure 2 is Comparative Example 1, and Vinyl terminal is Example 3.

[0112] Table 3 displays the particle size of the silicon nanoparticles dispersed in different terminal PDMS capture fluids on the day they were synthesized and the temperature/humidity aged. The particle size and standard deviation were calculated from the Luo, Stradins, and Zunger based equation above.

[0113] From the particle size data in Table 3, we find that all the particle dispersions reduced in particle size during the aging process due to oxidation of the silicon particle core. However, the amount of core reduction is unexpected in some cases. The silicon nanoparticle PDMS dispersion sample is the control and the particle size reduced 0.99 nm over 6 days of temperature/humidity treatment (-0.165 nm/day diameter decrease). The silicon nanoparticles dispersed in amine terminated PDMS loss 1.04 nm in diameter over the aging period (-0.173 nm/day diameter decrease), again consistent with the PDMS control, though slightly higher. However, the starting particle diameter for the amine terminated PDMS sample is 0.46 nm smaller than the control PDMS dispersion. This is unexpected since the process conditions were approximately equivalent for both synthesis conditions. The SiOH terminated PDMS dispersion had a reduction of 1.25 nm over the aging period (-0.208 nm/day diameter decrease), much greater than the control PDMS dispersion. The vinyl terminated PDMS dispersion showed a much lower particle size as synthesized (Day 0), 0.37 nm less than the control PDMS dispersion, again an unexpected result.

Table 3: Particle size of the samples in this example.

Sample	Particle Size – Day 0	Particle Size – Aged
PDMS	4.07 ± 0.46 nm	3.08 ± 0.31 nm
SiOH terminal	3.92 ± 0.45 nm	2.67 ± 0.32 nm
Amine terminal	3.61 ± 0.45 nm	2.57 ± 0.29 nm
Vinyl terminal	3.70 ± 0.46 nm	2.93 ± 0.35 nm

[0114] Absorbance Spectra of Examples and Comparative Example: Figure 3 displays the Day 0 and Aged absorbance spectra of the silicon nanoparticle dispersed in the various terminal PDMS capture fluids. The solid curve represents the Comparative Example silicon nanoparticle/PDMS dispersion. The other curves represent the Examples. The aging process decreases the silicon particle's core via oxidizing the outer silicon atoms, thus blue shifting the absorbance spectra, as seen in Figure 3. The silicon nanoparticle/SiOH terminal PDMS dispersion is represented with the dashed curves. The as synthesized (Day 0) dispersion has a similar absorbance to the control PDMS dispersion with a slight increase transmittance rate starting around 475 nm. However, the aging of the dispersion with temperature and humidity conditions greatly alters the shape and absorbance rate of the SiOH terminated PDMS dispersion (Example 1), Aged dashed curve in Figure 3. The silicon nanoparticle/amine terminal PDMS dispersion (Example 2) is plotted as the dotted curve in Figure 3. This dispersion has a much sharper absorbance drop off relative to the PDMS comparative example, even on the day of synthesis (Day 0). When the amine terminated PDMS dispersion is aged, the absorbance has a large blue shift and the slope of the absorbance is much sharper than the other dispersions. The silicon nanoparticle/vinyl terminated PDMS dispersion (Example 3) is represented with the dash-dot curves in Figure 3. The as deposited (Day 0) vinyl terminal dispersion (Example 3) has a large blue-shift and steeper absorbance curve compared to the PDMS comparative dispersion. Aging of the vinyl dispersion has a small absorbance blue-shift relative to the as deposited sample, but not nearly as great as the other dispersion examples. Examining the absorbance blue shift of the silicon nanoparticles dispersed in various terminal PDMS fluids, the absorbance at 2 AU for the Day 0 and Aged sample were evaluated. This analysis yields absorbance blue shifts (@ 2 AU) of: PDMS Comparative Example 1 – 0.644 eV, SiOH terminal Example 1 – 1.516 eV, amine terminal Example 2 – 1.456 eV, and vinyl terminal Example 3 – 0.459 eV. The blue shift of the peak photoluminescent maximum intensity wavelength of the silicon nanoparticle dispersions are: PDMS Comparative Example – 0.289 eV, SiOH terminal Example 1 – 0.452 eV, amine terminal Example 2 – 0.472 eV, and vinyl terminal Example 3 – 0.264 eV. Reviewing the absorbance blue shifts (at 2 AU) to the blue shift of the peak photoluminescent emission intensity wavelength, finds the Example 2 amine terminal dispersion's absorbance is the largest while the Example 1 SiOH terminal dispersion has the largest photoluminescence emission wavelength shift. The Example 3 vinyl terminated dispersion has the smallest blue shift of any of the dispersions when examine via absorbance and photoluminescence. This variation of the blue shift suggest potential HOMO-LUMO tuning of the particles compared to size reduction that is controlling the absorbance and optical properties of the silicon nanoparticle within the dispersions.

That which is claimed is:

1. A method of controlling the absorbance and/or luminescence of silicon nanoparticles, the method comprising: synthesizing silicon nanoparticles in a plasma reactor at a first pressure and capturing the synthesized silicon nanoparticles in a capture fluid, where the capture fluid comprises an absorption-modifying functional group.
2. A method according to claim 1, where the absorption-modifying functional group is unsaturated hydrocarbyl having from 1 to 12 carbon atoms, amide, azide, azo, amino, carbodiimide, imine, isocyanate, nitrile, nitro, alcohol, aldehyde, carboxylic acid, epoxy, ester, ether, hydroxyl, keto, peroxy, phosphate, phosphine, phosphine oxide, phosphinite, phosphite, phosphonate, phosphonite, disulfide, thioether, thiol, or halo, or silanol.
3. A method according to claim 2, wherein the capture fluid is a polyorganosiloxane substituted with the absorption-modifying functional group.
4. A method according to claim 3, wherein the polyorganosiloxane is linear, branched, or cyclic, where at least one terminus of the linear or branched polyorganosiloxane comprises the absorption-modifying functional group, and wherein the ring of the cyclic polyorganosiloxane comprises at least one silicon-bonded absorption-modifying functional group.
5. A method according to claim 4, wherein the organo of the polyorganosiloxane is i) methyl, ii) ethyl, iii) propyl, iv) phenyl, or two or more of i), ii), iii), and iv), and wherein i), ii), iii), and iv) are silicon-bonded.
6. A method according to any one of the preceding claims, wherein the absorption-modifying group is at least one of trimethylsilyl, dimethylethenylsilyl, (C₁₋₅)alcohol, —Si(CH₃)₂OH, or amino group having from 0 to 5 carbon atoms, or one or more of trimethylsilyl, dimethylethenylsilyl, hydroxyl, silanol, and amino group having from 0 to 5 carbon atoms.
7. A method according to claim 6, wherein the silicon capture fluid is trimethylsilyl-terminated polydimethylsiloxane, dimethylethenylsilyl-terminated polydimethylsiloxane, propanol-terminated polydimethylsiloxane, silanol-terminated polydimethylsiloxane, or amino-terminated polydimethylsiloxane.
8. A method according to claim 7, wherein the amino group of the amino-terminated polydimethylsiloxane is —NH₂ or 3-aminopropyl.
9. A method according to any one of the preceding claims, wherein the capture fluid is housed in a vacuum particle collection chamber at a second pressure downstream of the plasma reactor, where the second pressure is lower than the first pressure.

FIG. 1

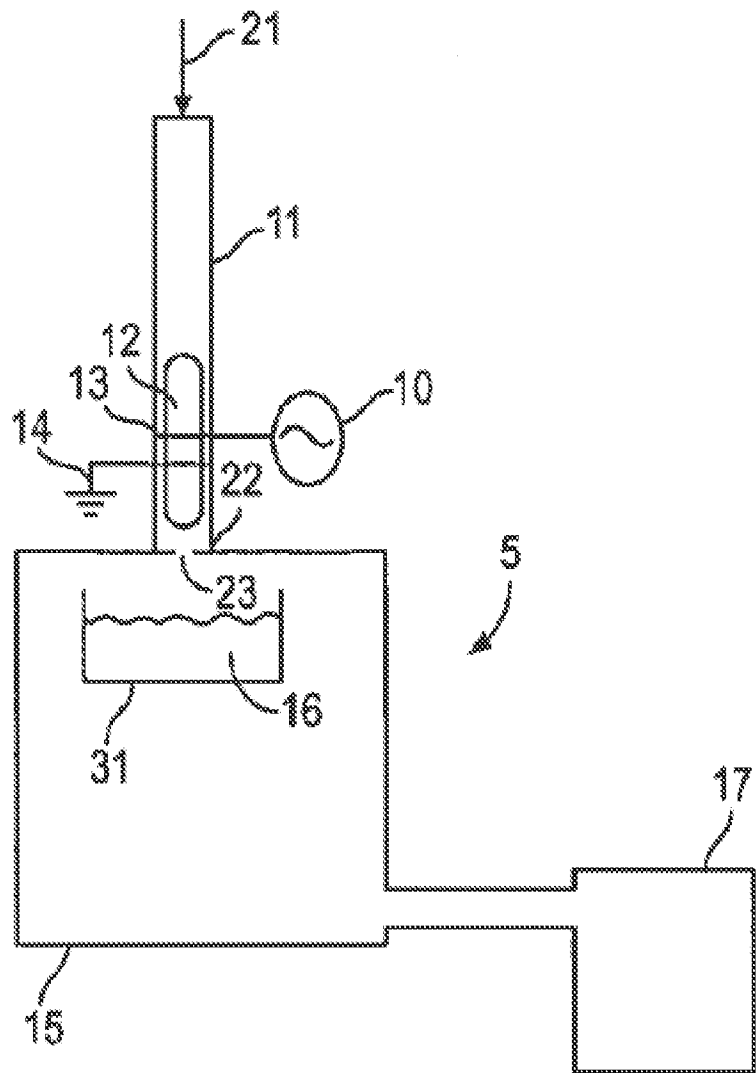


FIG. 2

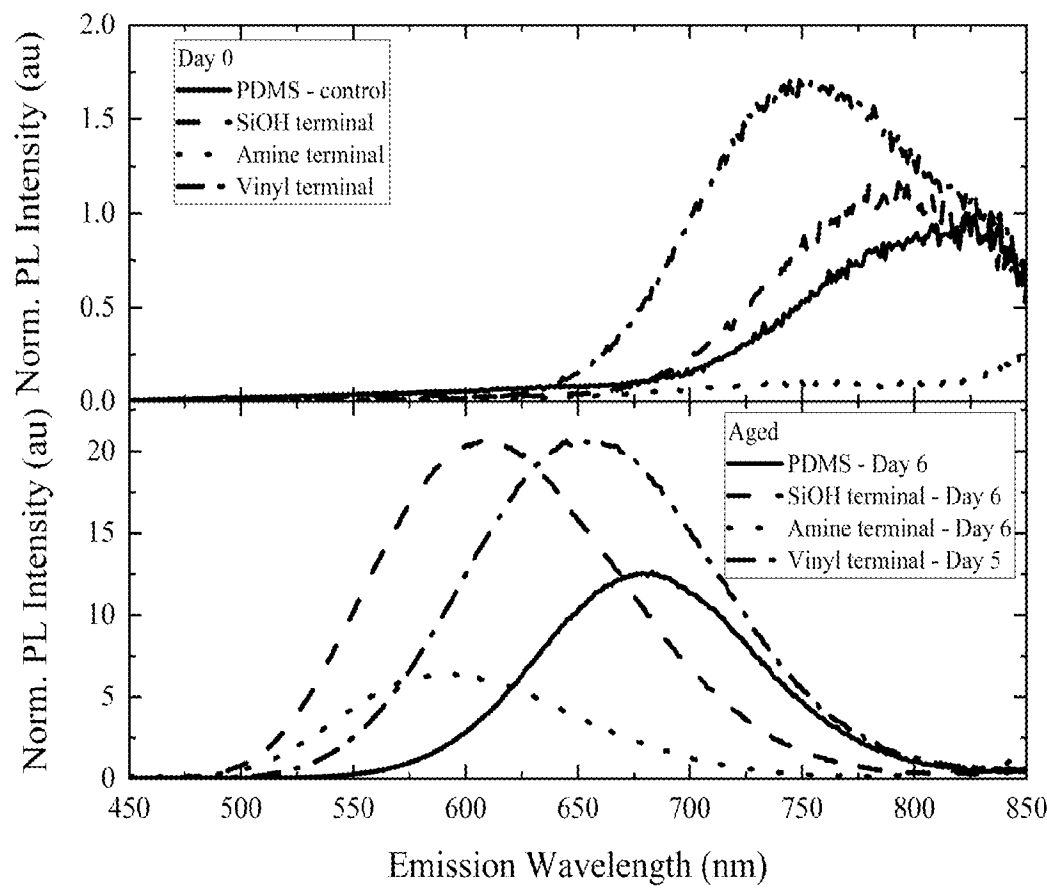
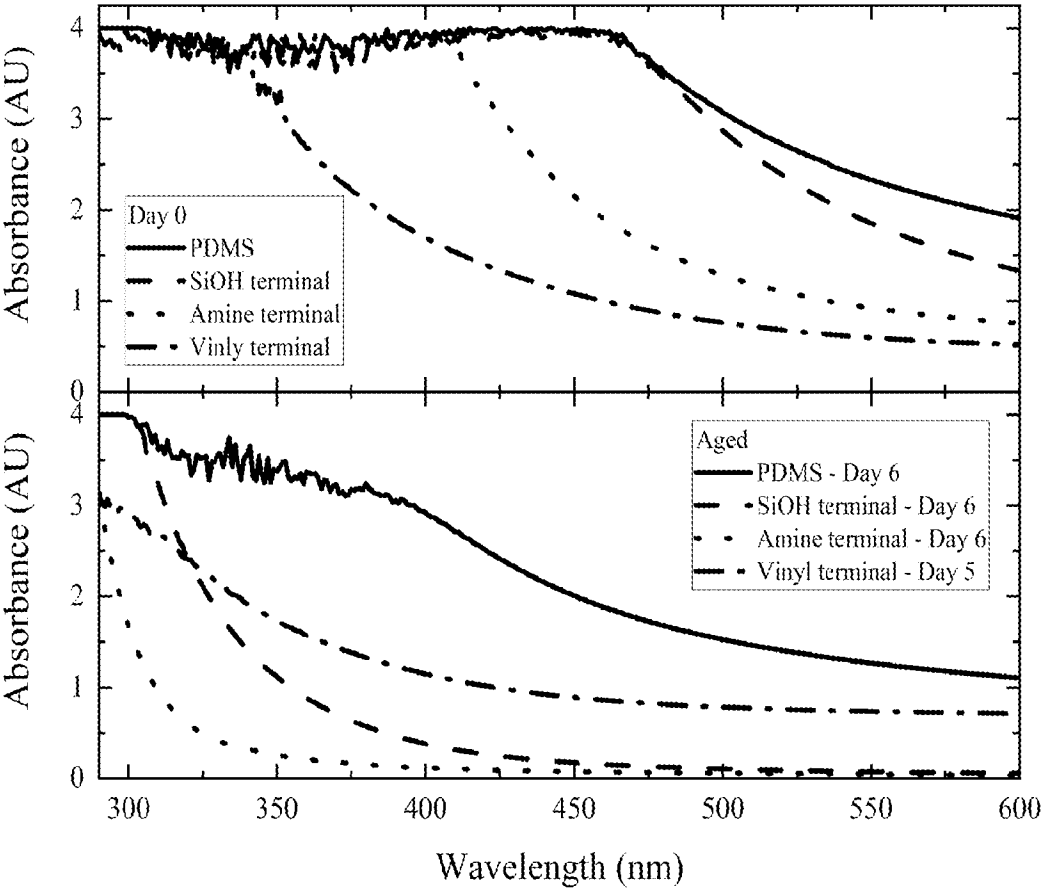


FIG. 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/013960

A. CLASSIFICATION OF SUBJECT MATTER

INV. C01B33/027 C09K11/00
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)

C01B H05B C09K

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2020/205722 A1 (DOW SILICONES CORP [US]) 8 October 2020 (2020-10-08) paragraphs [0006], [0014] - [0016], [0019], [0027] - [0029], [0046] - [0048], [0064] - [0065], [0074], [0085] - [0088], [0124] - [0130]; examples 1,3 -----	1 - 9
X	WO 2014/194181 A1 (DOW CORNING [US]) 4 December 2014 (2014-12-04) paragraphs [0004], [0023] - [0028], [0068] - [0069], [0087] - [0088]; examples 1-6 -----	1 - 9
A	WO 2020/205872 A1 (DOW SILICONES CORP [US]) 8 October 2020 (2020-10-08) paragraphs [0005] - [0007], [0037] - [0049], [0059] - [0061], [0074] - [0076] ----- - / - -	1 - 9



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search

3 June 2024

Date of mailing of the international search report

25/06/2024

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Lecerf, Nicolas

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/013960

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2020/205850 A1 (DOW SILICONES CORP [US]) 8 October 2020 (2020-10-08) paragraphs [0005] - [0007], [0026] - [0029], [0048] - [0049], [0054] - [0061], [0068] - [0076] -----	1 - 9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2024/013960

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2020205722 A1	08-10-2020	CN 113613769 A EP 3946708 A1 JP 2022525518 A KR 20210137572 A US 2022176333 A1 WO 2020205722 A1	05-11-2021 09-02-2022 17-05-2022 17-11-2021 09-06-2022 08-10-2020
WO 2014194181 A1	04-12-2014	TW 201501785 A WO 2014194181 A1	16-01-2015 04-12-2014
WO 2020205872 A1	08-10-2020	CN 113631513 A EP 3947279 A1 JP 2022525892 A KR 20210144832 A US 2022185681 A1 WO 2020205872 A1	09-11-2021 09-02-2022 20-05-2022 30-11-2021 16-06-2022 08-10-2020
WO 2020205850 A1	08-10-2020	NONE	