



(51) International Patent Classification:
C01G 23/00 (2006.01) C01G 27/00 (2006.01)
C01G 25/00 (2006.01)

(21) International Application Number:
PCT/US2009/052565

(22) International Filing Date:
3 August 2009 (03.08.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/085,582 1 August 2008 (01.08.2008) US

(71) Applicant (for all designated States except US): **THE REGENTS OF THE UNIVERSITY OF COLORADO** [US/US]; 1800 Grant Street, 8th Floor, Denver, CO 80203 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **STOLDT, Conrad, R.** [US/US]; 4101 Yates Street, Denver, CO 80212 (US). **HAAG, Michael, A.** [US/US]; 1571 Bradley Drive, Boulder, CO 80305 (US).

(74) Agent: **BRAIRTON, Scott, A.**; Holland & Hart, LLP, P.O. Box 8749, Denver, CO 80201 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: METHODS FOR THE PREPARATION OF GERMANIUM AND SILICON NANOCRYSTALS

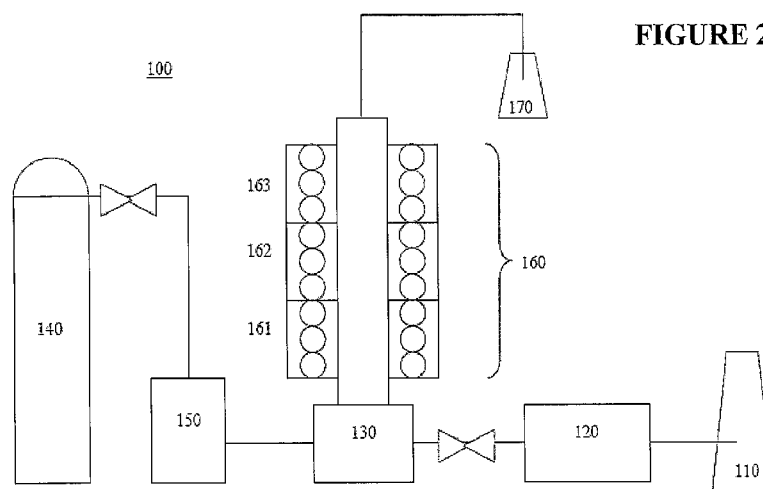


FIGURE 2

(57) Abstract: Methods for preparing Group IV nanocrystals. The method may generally include the use of an ultrasonic aerosol pyrolysis process (DAP). A precursor solution including a Group IV organic compound and a non-aqueous solvent may be nebulized to form aerosol droplets. Each aerosol droplet may include a plurality of liquid precursor molecules suspended in the non-aqueous solvent. The aerosol droplets may then be exposed to a series of carefully selected temperatures to initiate the formation of nanocrystals in which three temperatures exposures may be used.

METHODS FOR THE PREPARATION OF GERMANIUM AND SILICON NANOCRYSTALS

CROSS REFERENCE TO RELATED PATENT APPLICATIONS

5 This application claims priority to U.S. Provisional Application No. 61/085,582, filed August 1, 2008, the entirety of which is hereby incorporated by reference.

BACKGROUND

10 The unique properties of nanocrystals promise to have a revolutionary impact on multiple industries, including opto-electronics, semi-conductors, batteries, solar, and bio-imaging. In particular, the Group IV semiconductor nanocrystals (Si and Ge) are of special interest due to the prevalent use of Si- and Ge-based materials in multiple industries. Fulfilling the promise of wide industrial use of Group IV semiconductor nanocrystals requires a method capable of satisfying demands relating to both nanocrystal characteristics and nanocrystal production. With respect to
15 nanocrystal characteristics, desirable attributes include the ability to uniformly produce chemically pure, non-agglomerated and crystalline nanocrystals at a specified size and surface chemistry. With respect to nanocrystal production, desirable attributes include the ability to operate an inexpensive, single step, continuous process that yields a high throughput, is scalable and produces non-toxic byproducts.

20 Although the potential of wide industrial impact of Group IV semiconductor nanocrystals is well appreciated, progress has been highly limited because no method has yet been perfected

that achieves most or all the above the stated goals. Methods such as evaporation and laser ablation, co-sputtering on a silicate matrix, UV or IR laser photolysis, microwave discharge, arrested precipitation in solutions, synthesis in structured media (templating), sonochemical methods, and radiolytic methods have all failed to meet demands related to nanocrystal size, uniformity or quality. These methods may also prove to be complex (*i.e.*, require multiple steps in non-atmospheric conditions) while producing only a minimal quantity of nanocrystals. More sophisticated methods that provide more precise control of nanocrystal size, such as gas-phase pyrolysis, chemical anhydrous reduction (liquid), electro-chemical etching, anhydrous solvo-thermal (liquid), supercritical fluid (high pressure, thermal), and non-thermal plasma, have overcome some of the aforementioned problems (*e.g.*, nanocrystal size control and improved process control), but still fail to overcome many of the other shortcomings associated with Group IV nanocrystal production.

One example of a process for manufacturing group IV nanoparticles is described in U.S. Patent No. 7,446,335 to Kortshagen et al. The Kortshagen reference discloses a method wherein gaseous precursor material is injected into a reactor and exposed to non-thermal RF plasma. A vacuum may be created in the reactor and the plasma may provide temperatures in excess of 1,000 °C. Exposure of the precursor gas to the plasma results in the dissociation of the precursor molecules, which may then nucleate and grow into nanoparticles.

However, the method disclosed in the Kortshagen method suffers from several shortcomings. Firstly, the requirement of a vacuum environment and high temperatures generally adds complexity and cost to the overall production of Group IV nanoparticles. Further, as indicated at col. 19, lines 60 and 61 and Figures 5 and 6 of Kortshagen, the nanoparticles

produced by the disclosed method suffer from moderate agglomeration and poor mono-dispersity. Finally, the gaseous precursor material used in the Kortshagen method may ultimately provide only limited opportunities for the dissociated precursor material to nucleate and grow into nanoparticles. This may be due primarily to the amount of space provided between dissociated precursor material when present in a low pressure gas plasma.

Another example of a process for manufacturing Group IV nanoparticle thin films is described in International Publication No. WO 2009/025481 to Hwang et al. The Hwang application discloses a method wherein a Si or Ge-containing reaction gas is injected into a reaction chamber and heated to dissociate the reaction gas and begin the formation of a nanoparticle thin film on a substrate. The introduction of a second reaction gas is required to prevent the formation of amorphous material on the substrate. The temperature required to heat the reaction gas and begin the dissociation may be in excess of 1000°C and the process may also require the creation of a vacuum in the reaction chamber.

As can be seen from the above-description, the method disclosed in the Hwang application requires a relatively complicated process that must be performed under extreme conditions. The use of a second reaction gas to prevent the formation of amorphous material complicates the method in necessitating the control and monitoring of an additional stream of material being injected into the reaction chamber. Furthermore, because the second reaction gas may be HCl, the method may involve the use of potentially hazardous and corrosive materials. Regarding the operating conditions of the process, the requirement for creating a vacuum in the reaction chamber adds complexity and expense to the method. Similarly, requiring heating in excess of 1,000°C requires high energy input that raises the overall cost of the process. Finally,

as in the Kortshagen reference described above, the use of gaseous reaction material may limit nucleation and growth opportunities

SUMMARY

5 Disclosed are embodiments of a method for producing Group IV nanocrystals and Group IV nanocrystals formed therefrom. The method may overcome many of the shortcomings identified with previously known methods for preparing Group IV nanocrystals, including process simplification, increased yield, and better quality nanocrystals.

10 In some embodiments, the method may include contacting a Group IV organic compound with a non-aqueous solvent to form a precursor solution. The method may also include nebulizing the precursor solution to form one or more aerosol droplets. The method may also include exposing the one or more aerosol droplets to a first temperature greater than 550°C to form Group IV nanoparticles. The method may also include cooling the nanoparticles at a temperature below the first temperature to form nanocrystals.

15 In some embodiments, a plurality of simultaneously formed nanocrystals is disclosed. The nanocrystals may be Group IV nanocrystals. The plurality of nanocrystals may have a mean diameter in the range of from 2 nm to 50 nm and a standard deviation of no more than 15% of the mean diameter. In some embodiments, a Group IV nanocrystal is disclosed. The Group IV nanocrystal may be formed by contacting a Group IV organic compound with a non-aqueous
20 solvent to form a precursor solution. The precursor may then be nebulized to form one or more aerosol droplets. The one or more aerosol droplets may then be exposed to a first temperature

greater than 550°C to form Group IV nanoparticles. The nanoparticles may then be cooled at a temperature below the first temperature to form nanocrystals.

BRIEF DESCRIPTION OF THE DRAWINGS

5 The preferred and other embodiments are disclosed in association with the accompanying drawings in which:

Figure 1 is a flow diagram summarizing a method for forming Group IV nanocrystals as described herein;

10 Figure 2 is a schematic diagram of a system for system forming Group IV nanocrystals as described herein;

Figs. 3A-E show representative TEM images of Ge nanocrystals with mean diameters (A) 3.1 ± 0.4 nm; (B) 4.0 ± 0.6 nm; (C) 7.0 ± 1.6 nm; (D) 9.7 ± 2.0 nm; (E) 11.1 ± 3.6 nm synthesized at 700°C from 25, 35, 45, 55 and 65 μ L of tetrapropylgermane (TPG) per 100 mL of toluene, respectively;

15 Fig. 4A shows high resolution TEM images of Ge nanocrystals with about 13 nm and 10 nm diameter synthesized from 55 and 65 μ L of TPG per 100 mL of toluene, respectively;

Fig. 4B shows a powder X-ray diffraction spectrum of a representative Ge nanocrystal. The diffraction peaks correspond to a diamond cubic Ge crystal structure;

Fig. 5 is a TEM image of Si nanocrystals produced by an embodiment of the method described herein and discussed in greater detail Example 1.

Fig. 6 is a TEM image of Si nanocrystals produced by an embodiment of the method described herein and discussed in greater detail Example 1.

5

DETAILED DESCRIPTION

Group IV nanocrystals may be formed by a method generally utilizing ultrasonic aerosol pyrolysis (UAP). In the UAP process, submicron materials may be produced by ultrasonic nebulization of a precursor solution, followed by thermal decomposition of the precursor solution to initiate nucleation and growth of nanoparticles within the aerosol droplets. The UAP process may also include controlled cooling of the nanoparticles to form freestanding nanocrystals. The UAP process may be used to form Si nanocrystals or Ge nanocrystals.

Figure 1 illustrates a flow chart for a process of manufacturing Group IV nanocrystals. The method includes contacting a Group IV organic compound with a non-aqueous solvent at 10 to form a precursor solution. The method also includes nebulizing the precursor solution at 20 to form one or more aerosol droplets. The method also includes sequentially exposing the one or more aerosol droplets to at least one heating temperature and at least one cooling temperature at 30.

As noted above, the method may begin with the formation of a precursor solution at 10 by contacting a Group IV compound with solvent. The Group IV compound may be any

compound that includes one or more Group IV atoms. The Group IV compound may provide the building blocks for the nanocrystals. During the thermal decomposition of the precursor solution, the Group IV atoms may be isolated from the rest of the compound, so that the Group IV atoms may nucleate and grow into nanoparticles. In some embodiments, the Group IV
5 compound is the only reaction material present in the precursor solution.

In some embodiments, the Group IV compound may be an organic compound. Any suitable Group IV organic compound may be used. Exemplary Group IV organic compounds for use in the formation of Si nanocrystals include, but are not limited to, diethylsilane, tetraethylsilane, tetrapropylsilane, trisilane, phenylsilane, diphenylsilane, and triphenylsilane.
10 Any Si organometallic compounds may also be used. One or more Si organic compounds may be used together as part of the precursor solution. Exemplary Group IV organic compounds for use in formation of Ge nanocrystals include, but are not limited to, tetrapropylgermane, tetraethylgermane, diphenylgermane, and tetramethylgermane. Any Ge organometallic compounds may also be used. One or more Ge organic compounds may be used together as part
15 of the precursor solution. Any SiGe alloys may also be used, and any mixtures of any of the above compounds may be used.

The precursor solution may also include a solvent. Any suitable solvent may be used with the Group IV compound to form the precursor solution. In some embodiments, the solvent may be n-alkanes, n-alcohols, n-carboxylic acids, or any combination thereof. Exemplary
20 solvent include, but are not limited to, toluene, pentane, hexane, heptane, octane, decane, tridecane, methanol, ethanol, octanol, heptanol, acetone, or any combination thereof. These

solvents may possess the desired surface tension and viscosity for a solvent component of the precursor solution. In some embodiments, the solvent may be a non-aqueous solvent. For example, the solvent may be in a gaseous state.

The precursor solution may generally be formed by contacting the Group IV compound with the solvent. Any suitable manner for contacting the Group IV compound and the solvent to form the precursor solution may be used, including any mixing process. In some embodiments, the Group IV compound may be in an organic liquid or solid state while the non-aqueous solvent may be in a gaseous state.

The concentration of the Group IV compound and the solvent in the precursor solution may be any suitable concentration for growth of nanocrystals. In some embodiments, 10 microliters to 15 milliliters of Group IV compound per 100 milliliters of solvent may be used. More preferably, 25 microliters to 200 microliters per 100 milliliters of solvent may be used.

Upon formation of the precursor solution, the precursor solution may undergo nebulization at 20 to form aerosol droplets. Any method for nebulizing the precursor solution may be used. In some embodiments, an ultrasonic transducer may be used to nebulize the precursor solution. Any commercially available transducer may be used. The aerosol droplets formed via nebulization may generally have the form of one or more liquid phase precursor molecules suspended in a discrete quantity of non-aqueous solvent. The precursor solution may be delivered to the ultrasonic transducer in any suitable manner. In some embodiments, the precursor solution may be introduced into an ultrasonic transducer via a syringe pump.

In some embodiments, the nebulization of the precursor solution may be carried out so as to form aerosol droplets having a diameter of less than 10 microns, such as in the range of from 0.1 microns to 10 microns. When an ultrasonic transducer is utilized for nebulization, the frequency of the ultrasonic transducer may be adjusted to alter the size of the aerosol droplets. In order to achieve sub-10 micron aerosol droplets, a frequency range of from 1.65 MHz to 2.2 MHz may be used.

In some embodiments, the operating conditions of the nebulization process may also be altered to affect the density of the aerosol produced (*i.e.*, number of aerosol droplets per a given volume). The density of the aerosol may be achieved by varying the amplitude of the ultrasonic transducer between 1 and 200 microns.

The use of a non-aqueous solvent, the concentration of the precursor solution, and the frequency and the amplitude of the ultrasonic transducer are all important factors that may impact the size of the nanocrystals produced by the method.

The non-aqueous solvent may affect the size of the nanocrystals formed due to the smaller aerosol droplets that may be formed during nebulization when a non-aqueous solvent is used in the precursor solution, as opposed to an inherently larger aerosol droplet size generated from an aqueous solvent. The smaller aerosol droplets may provide a higher density of precursor molecules per aerosol droplet, which in turn may increase the probability of reaction (*i.e.*, nucleation and growth) between Group IV atoms. An increased number of reactions may produce larger nanocrystals. Altering the frequency of the ultrasonic transducer (which may affect the size of the aerosol droplets) may impact nanocrystal size for the same reason.

The concentration of the precursor solution also affects the size of the nanocrystals due to an increased likelihood of reaction between Group IV atoms. The higher concentrations of Group IV compound in the precursor solution may increase the probability that reactions will occur between Group IV atoms and may also result in a higher overall number of reactions.

5 Accordingly, higher Group IV precursor molecule concentrations may result in larger nanocrystals.

Once the precursor solution has been nebulized, the aerosol droplets may be exposed to two or more temperatures at 30 in order to initiate thermal decomposition of the Group IV compounds and then crystallize any nanoparticles formed as a result of isolated Group IV atoms
10 nucleating and growing. Generally, the aerosol droplets may be exposed to one or more temperatures at or above a critical temperature at which thermal decomposition of the Group IV compounds will take place, followed by exposing the material to one or more temperatures lower than at least one of the critical temperatures to promote crystallization. In some embodiments, this general method is carried out using three different temperatures. The first temperature may
15 be used for thermal decomposition of the Group IV compounds and the nucleation and growth of Group IV atoms, while the second two temperatures may be used to crystallize nanoparticles formed at the first temperature. The terms "first," "second," and "third" indicate order relative to one another and do not preclude exposure of the aerosol droplets to additional temperatures at any other point in the method, including prior to exposure to the first temperature.

20 Each aerosol droplet exposed to the two or more temperatures may be considered as its own reactor in which each of the nanocrystal formation steps take place. In other words, each

nanoparticle formed may be a product of the dissociated Group IV atoms within a single aerosol droplet reacting with one another. After thermal decomposition of the Group IV compound to isolate the Group IV atoms, the Group IV atoms do not leave the aerosol droplet in which they were formed. Rather, they begin to interact with only the atoms in the same aerosol droplet to ultimately form a nanocrystal.

Exposure to the various temperatures may be carried out in any suitable manner. Exemplary heating mechanisms may include, but are not limited to, ovens, lasers, and microwaves. In some embodiments, the exposure to the various temperatures is carried out by transporting the aerosol droplets through a multi-temperature furnace. In some embodiments, the multi-temperature furnace may be a vertically oriented tube furnace, although horizontally oriented tube furnaces may also be suitable for the method. When a vertically oriented tube furnace is utilized, the aerosol droplets may travel through the vertically oriented tube furnace in a top down manner (*i.e.*, aerosol droplets introduced into the tube furnace at the top end and travel down the length of the tube furnace) or a bottom up manner (*i.e.*, aerosol droplets introduced into the tube furnace at the bottom end and travel up the length of the tube furnace). The dimensions and material of the tube furnace are not limited. In some embodiments, the tube furnace may have a diameter ranging from 1/4 inch to 6 inches, such as 1 inch, and may be made of quartz. The tube furnace may provide one or more temperature zones along the length of the furnace. Heat may be provided to the furnace in any suitable fashion.

The aerosol droplets may be transported to and through a multi-temperature furnace with the aid of a carrier gas. In some embodiments, the carrier gas may be an inert gas. The specific

type of inert carrier gas used may depend on the Group IV element present in the Group IV compound. For example, Group IV compounds containing Si may use a mixture of hydrogen and argon, hydrogen, helium or a combination thereof. In some embodiments, the hydrogen may comprise from 1 to 10% of the carrier gas. Group IV compounds containing Ge may use argon, 5 hydrogen, helium or a combination thereof. A mass flow controller may be used to provide the carrier gas to the aerosol droplets in a controlled amount. The flow of the aerosol droplets to and through the multi-temperature furnace may be a laminar flow, such as having a Reynolds number less than 20. Laminar flow may ensure that the aerosol droplets do not mix with one another.

In some embodiments, the tube furnace may include at least two temperature zones along 10 the length of the tube furnace for carrying out the decomposition, nucleation, growth and crystallization of the materials injected therein. A first zone exposes the material to a temperature above the critical temperature at which thermal decomposition of the Group IV compounds takes place. In some embodiments, this may include exposing the material to a temperature greater than 550°C or 650°C. A second zone may expose the material to a 15 temperature below the critical temperature used in the first zone. The second zone may promote crystallization of any Group IV nanoparticles formed in the first zone.

In some embodiments, the tube furnace may include three temperature zones along the length of the tube furnace for carrying out the decomposition, nucleation, growth and crystallization of the materials injected therein. The first zone may provide the highest 20 temperature, followed by an intermediate temperature in the second zone and a lowest temperature in the third zone. The first zone with the highest temperature may provide the

conditions necessary to decompose the Group IV compound and allow for Group IV atoms to nucleate and grow into nanoparticles. The second and third zones may provide the conditions necessary to crystallize the nanoparticles.

In some embodiments, the first temperature to which the aerosol droplets are exposed may be greater than 550°C. In some embodiment, the first temperature is in the range of from 550°C to 900°C. This range of temperature provides for the thermal decomposition of the Group IV compounds. Temperatures in this range are required in order to overcome the highly covalent nature of the Group IV materials. For aerosol droplets including Si compounds, the first temperature may preferably be in the range of from 750°C to 900°C, more preferably 800°C to 850°C, most preferably 815°C to 835°C. For aerosol droplets including Ge compounds, the first temperature may preferably be in the range of from 650°C to 800°C, more preferably 700°C to 750°C, most preferably 715°C to 735°C. Upon being exposed to the first temperature for a suitable period of time, the aerosol droplets include nanoparticles instead of Group IV compounds.

In some embodiments, the second temperature to which the nanoparticles are exposed may be in the range of from 550°C to 700°C, more preferably 600°C to 650°C, most preferably 615°C to 635°C. These ranges of temperatures provide for the crystallization of the nanoparticles formed during exposure of the aerosol droplets to the first temperature. The Group IV atoms that have joined together to form the nanoparticles are capable of ordering themselves in a crystalline form at these temperatures.

In some embodiments, the third temperature to which the nanoparticles are exposed may be in the range of from 230°C to 400°C. This range of temperature provides for the further crystallization of the nanoparticles. For Si nanoparticles, the third temperature may preferably be in the range of from 250°C to 400°C, more preferably 300°C to 350°C, most preferably 315°C to 335°C. For Ge nanoparticles, the third temperature may preferably be in the range of from 230°C to 380°C, more preferably 280°C to 330°C, most preferably 295°C to 315°C.

As stated previously, the use of the terms “first,” “second,” and “third” in the preceding paragraphs indicate order relative to one another and do not preclude additional zones or temperatures at any other point during the method, including prior to the “first zone” or “first temperature”.

These temperatures ranges are an important component of the method and are believed to be primarily responsible for the creation of uniformly high quality nanocrystals at a relatively high production rate. Variations outside of any one of the ranges may result in any of a number of undesirable outcomes, including decreased production rates, amorphous materials, nanocrystals with poor surface conditions, and agglomerated nanocrystals.

Furthermore, the temperature ranges used in the various zones have been shown to provide significant improvements over previously known methods. Example 1 below describes the specific improvements achieved using the temperatures provided above as compared to previously known methods. As shown in Example 1, the temperature ranges used in the various zones have resulted in volumetric output an order of magnitude greater than output achieved by previously know methods for producing Group IV nanocrystals. Furthermore, the uniformity in

size of nanocrystals produced as a result of the temperature ranges is significantly improved over previously known methods as evidenced by the significantly lower standard deviation from the mean nanocrystal diameter achieved by the above-described method as compared to the standard deviation calculated when using previously know methods for producing Group IV nanocrystals.

5 The time during which the aerosol droplets are exposed to the various temperatures is also an important factor to ensure proper decomposition, nucleation, growth and crystallization. For example, if the aerosol droplets are not exposed to the first temperature for a sufficient period of time, insufficient decomposition, nucleation and growth will occur. Conversely, if the aerosol droplets are exposed to the first temperature for too long a period of time, laminar flow is
10 destroyed and mixing between aerosol droplets may occur. With respect to the second and third temperatures, if the nanoparticles are exposed to the cooling temperatures for too short a period of time, amorphous material may be produced by quenching. Ultimately, the nanoparticles need to be exposed to the cooling temperatures for a long enough period of time as is needed to enable ordering of the Group IV structure and the formation of crystalline bonds between the Group IV
15 atoms. In some embodiments, the time period in each zone may range from 0.6 to 1 seconds, more preferably from 0.69 to 0.85 seconds , and most preferably from 0.73 to 0.81 seconds. Generally speaking, if the nanoparticles are kept in flight for too long a period of time, agglomeration and sedimentation out of the flow may result

 The amount of time during which the aerosol droplets are exposed to the various
20 temperatures may be controlled by varying the carrier gas flow rate and pressure. In some embodiments, the carrier gas flow may be about 1 standard liter/minute and the pressure may be

from 1 atm to 2 atm. The carrier gas flow rates and pressures may be adjusted when tube furnaces of varying dimensions (e.g., length and diameter) are used. The carrier gas flow may also be adjusted to a flow rate higher or lower than about 1 standard liter/minute when taking into account the temperatures used to cause decomposition, nucleation, growth and crystallization. For example, when temperatures at the higher end of the ranges provided above are used, the carrier gas flow rate may be greater than 1 standard liter/minute because the aerosol droplet may be exposed to the temperatures for a shorter period of time while still achieving the desired decomposition, nucleation, and growth. Conversely, carrier gas flow rates less than 1 standard liter /minute may be used when the aerosol is exposed to lower temperatures. The same types of adjustments may be made to the pressure of the carrier gas.

The above described process of exposing the aerosol droplets to a series of different temperatures may be performed at atmospheric conditions. The process does not necessitate the use of a vacuum or elevated pressure within the tube furnace. Additionally, it can be seen that the process is substantially continuous. Precursor solution may be continuously introduced into the ultrasonic transducer and the aerosol droplets may be continuously passed through the multi-temperature furnace.

After the aerosol droplets have been converted into nanocrystals via exposure to the multiple temperature zones for the required periods of time, the nanocrystals may pass out of the multi-temperature furnace. In some embodiments, the nanocrystals may still be suspended in the solvent of the aerosol droplet. Accordingly, the nanocrystals may be collected in a bubbler containing a solvent. Any solvent for collecting the nanocrystals may be used. In some

embodiments, the solvent is trichloroethylene. In some embodiments, the nanocrystals may also be collected via deposition on a substrate. Any suitable substrate may be used for collecting nanocrystals.

The above described method may be carried out to simultaneously produce a plurality of
5 nanocrystals having similar diameters. In some embodiments, the plurality of nanocrystals produced have diameters ranging from 2 nm to 50 nm. The specific size of the nanocrystals formed may be selected from within this range by, as discussed in greater detail above, varying such parameters as the precursor concentration and the ultrasonic transducer frequency. Furthermore, the nanocrystals formed may have a uniformity in size. In some embodiments, the
10 standard deviation of nanocrystal diameter is no more than 15% of the mean diameter, and more preferably, no more than 10% of the mean diameter. The nanocrystals produced may also be non-agglomerated and demonstrate consistent, highly favorable morphologies (*i.e.*, nearly spherical shapes with well-defined smooth edges). Additionally, the nanocrystals may all have a diamond cubic structure. Finally, the plurality of nanocrystals may be produced at a rate of
15 about 250 mg/hour, and in some embodiments, greater than 250 mg/hour.

Surface chemistry may be added to the nanocrystals prepared by the method described herein. Surfactants are one example of a material that may be used to alter the surface chemistry of the nanocrystals. Surfactants (*i.e.*, surface capping agents/ligands) are molecules that may chemically coordinate (covalently bind) to the surface of the nanocrystals, either during or after
20 nanocrystal synthesis. These molecules may be used to modulate the growth kinetics of the nanocrystals as well as to prevent agglomeration of bare nanocrystals after synthesis.

Furthermore, surfactants may be applied to nanocrystals to fine-tune the physico-chemical properties of the material for various technical applications (*e.g.*, to modulate the optical absorption/emission of individual nanocrystals). Any suitable surfactants may be used to alter nanocrystal surface chemistry. Exemplary surfactants include, but are not limited to, 1-alkenes
5 (*e.g.*, 1-octene), *n*-alcohols (*e.g.*, octanol), or oleyl amine.

In the above described method, surfactants can be introduced before, during, or after nanocrystal synthesis. When applied before nanocrystal synthesis, the surfactant may be mixed with the Group IV organic compound and non-aqueous solvent before nebulization to both modulate the growth kinetics of the nanocrystals (during the heating step) as well as to cap the
10 growth kinetics to prevent subsequent agglomeration. When applied during nanocrystal formation, the surfactant may be introduced to the aerosol droplets after being exposed to the heating temperature. Addition of surfactants during nanocrystal formation may cap the as-prepared nanocrystals prior to the cooling process or subsequent capture and prevent agglomeration. When the surfactant is added after nanocrystal synthesis, the surfactant can be
15 mixed with the solvent in the bubbler. Upon capture in the solvent, the nanocrystals may be capped in a post-process. The addition of the surfactant may prevent agglomeration after synthesis. The capture flask solution containing the solvent and surfactant may be held at an elevated temperature (about 50°C to about 200°C) to facilitate the chemical reaction of the surfactant with the nanocrystal surface. Regardless of when the surfactant is introduced, the
20 surfactant can also be used to fine-tune the physico-chemical properties of the individual (unagglomerated) nanocrystals after synthesis.

A comparison of the results achieved by the method described above to the results achieved by a previously known method for producing Group IV nanocrystals is set forth in Example 1 and further demonstrates the significant improvements achieved by the method described herein, and more specifically, by the specific temperature regime used to decompose, nucleate, grow and crystallize the Group IV nanocrystals.

A system capable of carrying out the above described method is illustrated in Fig. 2. The system 100 includes a precursor solution vessel 110 for containing a precursor solution. The precursor solution vessel 110 is in fluid communication with a syringe pump 120. The syringe pump 120 is in fluid communication with an ultrasonic transducer 130. Accordingly, the precursor solution may be introduced into the ultrasonic transducer 130 by way of the syringe pump 120. Once the precursor solution is introduced into the ultrasonic transducer 130, the ultrasonic transducer nebulizes the precursor solution to create a plurality of aerosol droplets. The aerosol droplets include organic precursor molecules suspended in non-aqueous solvent. A carrier gas vessel 140 that contains carrier gas may be in fluid communication with a mass flow controller 150. The mass flow controller 150 may be in fluid communication with ultrasonic transducer 130 such that a controlled amount of carrier gas may be passed from the carrier gas vessel 140 to the ultrasonic transducer 130. The carrier gas introduced into the ultrasonic transducer 130 may be contacted with the aerosol droplets to thereby transport the aerosol droplets into a tube furnace 160. The tube furnace 160 has a generally vertical orientation, and the carrier gas and aerosol droplets are introduced into the tube furnace 160 from the bottom end of the tube furnace 160. The tube furnace may include three temperature zones 161, 162 and

163, and the carrier gas and aerosol droplets may pass through each zone. As the aerosol droplets pass through zone 161, decomposition of the Group IV compound and nucleation and growth of the isolated Group IV atoms may occur. In zones 162 and 163, nanoparticles formed in zone 161 may be crystallized. The nanocrystals formed in the tube furnace 160 ultimately
5 pass out of the top end of the tube furnace, where they may then be collected in a bubbler 170 containing solvent or deposited on a substrate.

10

15

Examples

Example 1

The above-described method was carried out twice to form Si nanocrystals. In both trials, the volume output was 250 mg/hour. In the first trial, the mean diameter of the greater
5 than one hundred nanocrystals measured was 6.27 nm and the standard deviation was 0.42 nm. In the second trial, the mean diameter of the greater than one hundred nanocrystals measured was 12.67 nm and the standard deviation was 1.14 nm. A magnified view of the Si nanocrystals produced in both trials is shown in Figs. 5 (6.27 nm) and 6 (12.67 nm).

The gas-phase non-thermal RF plasma synthesis method described in detail in U.S. Patent
10 No. 7,446,335 was carried out twice to form silicon nanoparticles. The volume output for the two trials ranged between about 10 mg/hour to about 50 mg/hour. In the first trial, the mean diameter of the particles measured was 6.2 nm and the standard deviation was 1.8 nm. In the second trial, the mean diameter of the particles was 13.6 nm and the standard deviation was 5.8 nm.

15 Thus, as can be seen, the above-described method provides a throughput rate that is from 5 to 25 times higher than the throughput of the previously know method. Furthermore, the size uniformity of the nanocrystals formed by the above-described method was better than the size uniformity of the previously known method as evidenced by the smaller standard deviations calculated. This was especially true for larger nanocrystals (~13 nm), where the standard
20 deviation was roughly 5 times smaller for the above-described method.

Example 2

The above-described method was carried out twice to form Ge nanocrystals. In both trials, the volume output was 250 mg/hour. In the first trial, the mean diameter of the 834 nanocrystals measured was 7.6 nm and the standard deviation was 1.1 nm. In the second trial, the mean diameter of the 797 nanocrystals measured was 13.3 nm and the standard deviation was 1.97 nm.

Example 3

Figs. 3A-E show representative transmission electron microscopy (TEM) images of Ge nanocrystals produced by the process described herein. The Ge nanocrystals (NCs) have mean diameters (A) 3.1 ± 0.4 nm; (B) 4.0 ± 0.6 nm; (C) 7.0 ± 1.6 nm; (D) 9.7 ± 2.0 nm; (E) 11.1 ± 3.6 nm synthesized at 700°C from 25, 35, 45, 55 and 65 μ L of TPG per 100 mL of toluene, respectively. Note that the Ge NCs have a near spherical morphology that is characteristic of particles synthesized by aerosol decomposition process. Additionally, the NCs are not agglomerated, but show a uniform distribution with easily defined boundaries after the drop-casting process from (trichloroethylene) (TCE) for TEM imaging. The NC mean diameter increases from about 3.1 nm to 11.1 nm as the volume of TPG in the precursor solution is increased from 25 μ L to 65 μ L per 100 mL toluene, respectively. Similarly, the standard deviations from measurement of over 1000 particles per TEM image range from about 10% to 30% and increase with NC size.

Example 4

High-resolution TEM (HRTEM) and X-ray diffraction (XRD) are utilized to verify that Ge nanocrystals are single crystal with a diamond cubic structure. Fig. 4A shows high resolution TEM images of Ge nanocrystals with about 13 nm and 10 nm diameter synthesized from 55 and 65 gL of TPG per 100 mL of toluene, respectively. The Ge NCs exhibited single crystal domains over a range of sizes as shown in Fig. 4A, where representative images of nanocrystals have approximate diameters of 10 nm and 13 nm.

Example 5

Fig. 4B shows a powder X-ray diffraction spectrum of a representative Ge nanocrystal. The diffraction peaks correspond to a diamond cubic Ge nanocrystal. The characteristic XRD pattern identifies diamond cubic structure with reflections that match the expected {111}, {220}, and {311} diffraction peaks of bulk Ge. As compared to conventional liquid synthesis where the particles or nanocrystals appear coarse with inconsistent morphologies, Ge NCs produced by UAP are nearly spherical with well-defined, smooth edges. The irregular nature of particles produced by conventional liquid phase processes may result from uncontrolled ripening during the stirred reaction or insufficient temperatures for atomic restructuring during growth.

In view of the many possible embodiments to which the principles of the disclosed invention may be applied, it should be recognized that the illustrated embodiments are only preferred examples of the invention and should not be taken as limiting the scope of the invention. Rather, the scope of the invention is defined by the following claims. We therefore
5 claim as our invention all that comes within the scope of these claims.

CLAIMS

What is claimed is:

1. A method comprising:

5 contacting a Group IV organic compound with a non-aqueous solvent to form a precursor solution;

 nebulizing the precursor solution to form one or more aerosol droplets;

 exposing the one or more aerosol droplets to a first temperature greater than 550°C to form Group IV nanoparticles; and

10 cooling the nanoparticles at a temperature below the first temperature to form nanocrystals.

 2. The method as recited in claim 1, wherein the first temperature is in the range of from 550°C to 900°C and cooling the nanoparticles comprises sequentially exposing the
15 nanoparticles to a second temperature in the range of from 550°C to 700°C and a third temperature in the range of from 230°C to 400°C.

 3. The method as recited in claim 2, wherein the Group IV organic compound is an organic compound comprising silicon.

20

4. The method as recited in claim 3, wherein the organic compound comprising silicon is selected from the group consisting of diethylsilane, tetraethylsilane, tetrapropylsilane, trisilane, phenylsilane, diphenylsilane, and triphenylsilane.

5 5. The method as recited in claim 3, wherein the first temperature is in the range of from 650°C to 900°C and the third temperature is in the range of from 250°C to 400°C.

6. The method as recited in claim 5, wherein the one or more aerosol droplets are exposed to each of the first, second, and third temperatures for a period of time ranging from 0.6
10 seconds to 1.0 seconds.

7. The method as recited in claim 3, wherein prior to exposing the one or more aerosol droplets to the first temperature, the one or more droplets are contacted with a carrier gas comprising argon and hydrogen.

15 8. The method as recited in claim 2, wherein the Group IV organic compound is an organic compound comprising germanium.

9. The method as recited in claim 8, wherein the organic compound comprising
20 germanium is selected from the group consisting of tetrapropylgermane, tetraethylgermane, diphenylgermane, and tetramethylgermane.

10. The method as recited in claim 8, wherein the first temperature is in the range of from 550°C to 750°C and the third temperature is in the range of from 230°C to 380°C.

11. The method as recited in claim 10, wherein the one or more aerosol droplets are
5 exposed to each of the first, second, and third temperatures for a period of time ranging from 0.6 seconds to 1.0 seconds.

12. The method as recited in claim 8, wherein prior to exposing the one or more aerosol droplets to the first temperature, the one or more droplets are contacted with a carrier gas
10 comprising argon.

13. The method as recited in claim 1, wherein the non-aqueous solvent comprises toluene, pentane, hexane, heptane, octane, decane, tridecane, methanol, ethanol, octanol, heptanol, acetone.
15

14. The method as recited in claim 1, wherein the precursor solution is nebulized by ultrasonic vibrations .

15. The method as recited in claim 1, wherein the nanocrystals are formed at a rate of
20 about 250 mg/hour.

16. The method as recited in claim 1, wherein the nanocrystals are formed at a rate of greater than 250 mg/hour.

17. The method as recited in claim 1, wherein the Group IV compound and the non-
5 aqueous solvent are contacted at a rate of from 10 microliters to 15 milliliters of Group IV compound per 100 milliliters of solvent.

18. A plurality of simultaneously-produced nanocrystals having a mean diameter in the range of from 2 to 50 nm and a standard deviation of no more than 15% of the mean
10 diameter.

19. The plurality of nanocrystals as recited in claim 18, wherein the standard deviation is no more than 10% of the mean diameter.

15 20. The plurality of nanocrystals as recited in claim 18, wherein the nanocrystals are Si nanocrystals or Ge nanocrystals.

21. A Group IV nanocrystal produced by a method comprising:
contacting a Group IV organic compound with a non-aqueous solvent to form a
20 precursor solution;
nebulizing the precursor solution to form one or more aerosol droplets;

exposing the one or more aerosol droplets to a first temperature greater than 550 °C to form nanoparticles; and;

cooling the nanoparticles at a temperature below the first temperature to form nanocrystals.

5

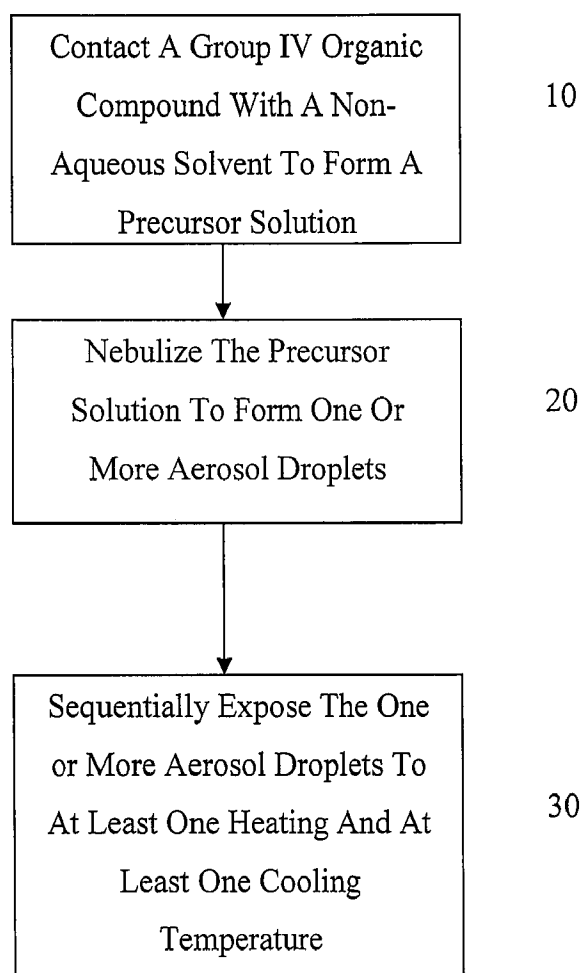
22. The method as recited in claim 3, wherein the first temperature is in the range of from 815°C to 835°C, the second temperature is in the range of from 615°C to 635°C, and the third temperature is in the range of from 315°C to 335°C.

10

23. The method as recited in claim 8, wherein the first temperature is in the range of from 715°C to 735°C, the second temperature is in the range of from 615°C to 635°C, and the third temperature is in the range of from 295°C to 315°C..

15

1/6

**FIGURE 1**

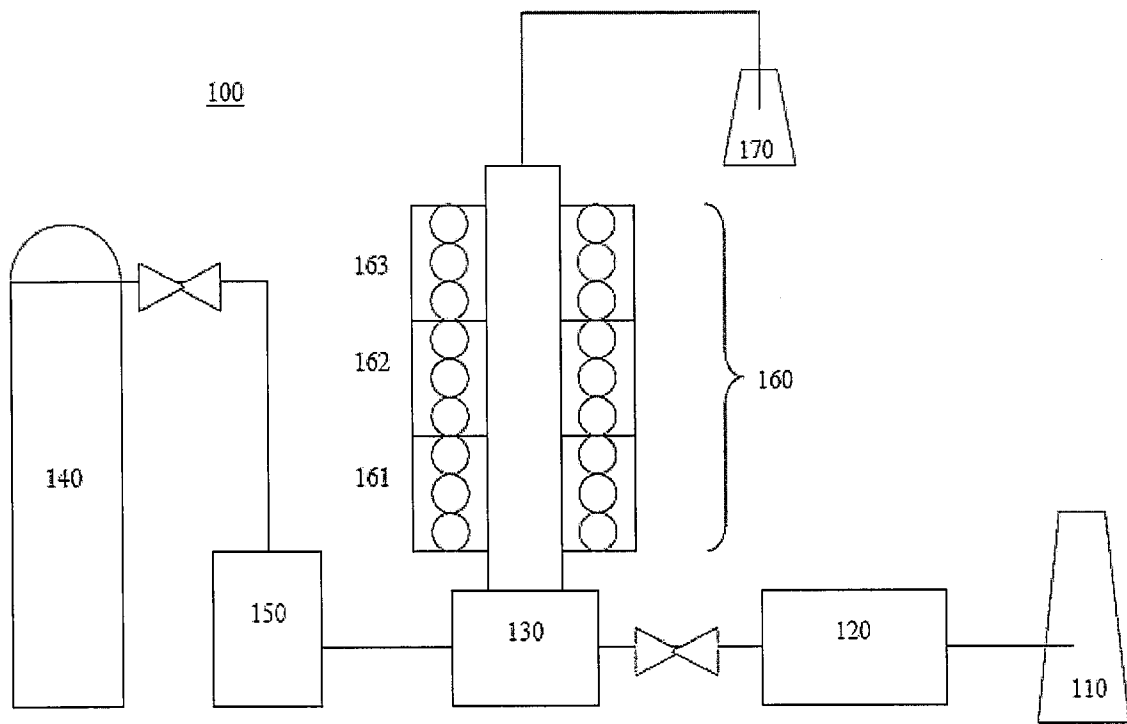


FIGURE 2

3/6

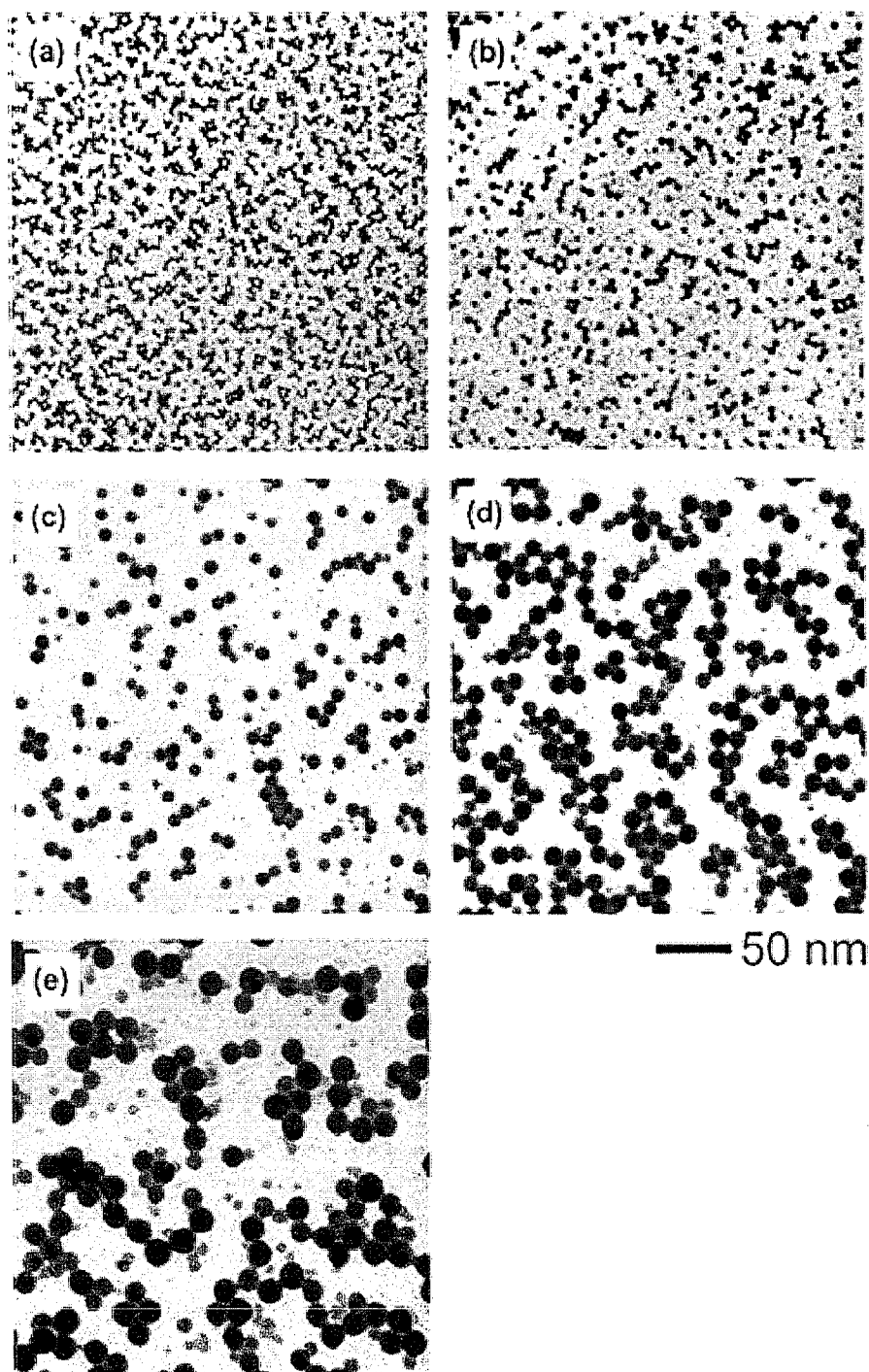


FIGURE 3

4/6

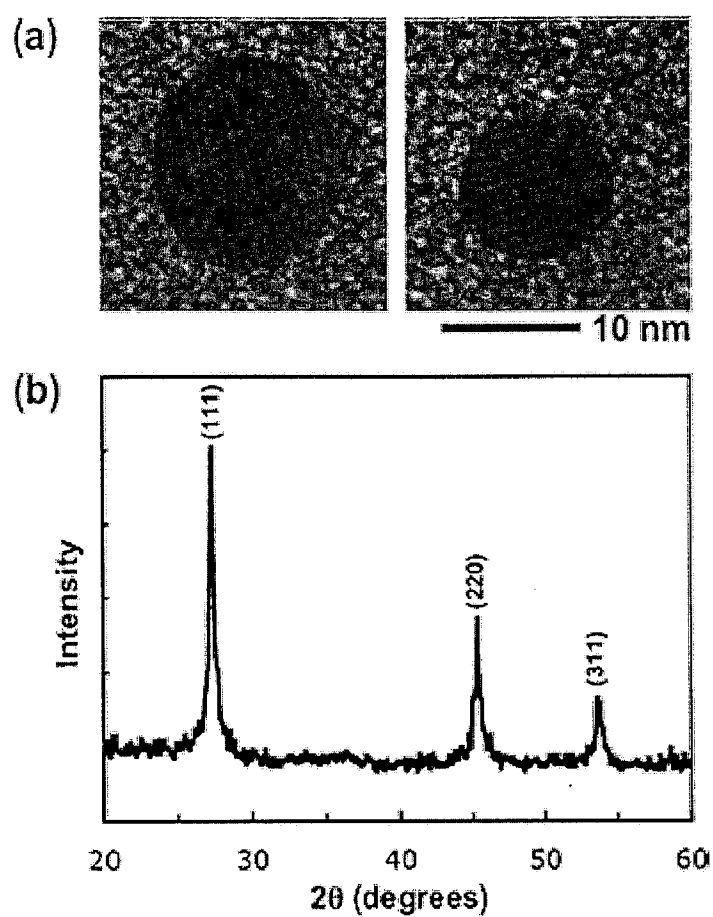


FIGURE 4

5/6

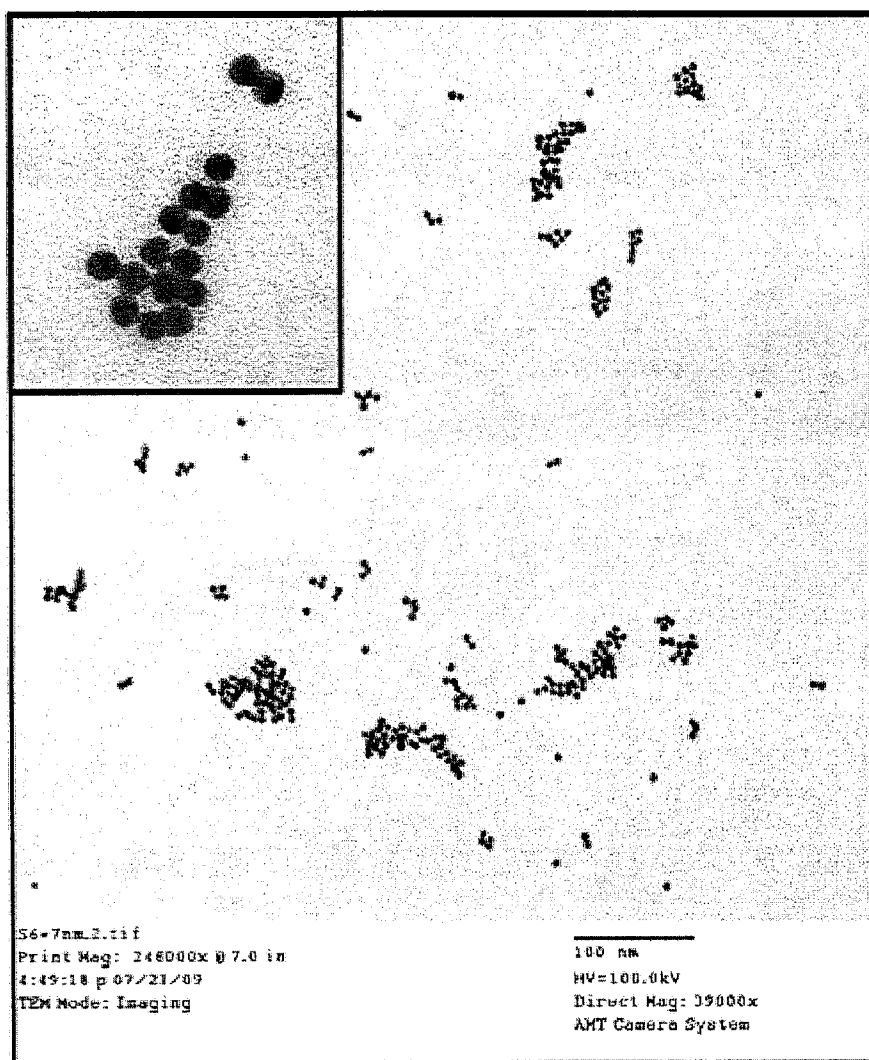


FIGURE 5

6/6

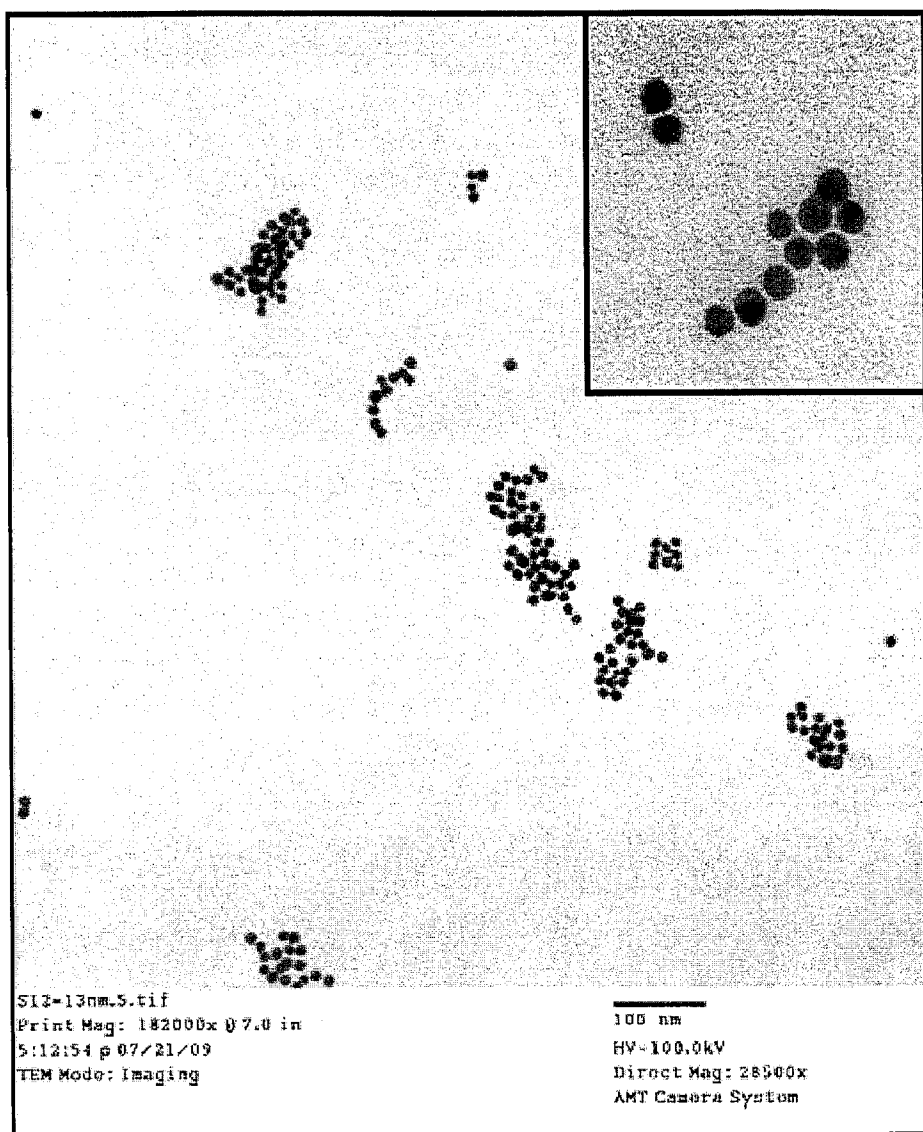


FIGURE 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 09/52565

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C01G 23/00, 25/00, 27/00 (2009.01)

USPC - 423/69; 977/773, 777

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)

IPC(8) - C01G 23/00, 25/00, 27/00 (2009.01)

USPC - 423/69; 977/773, 777

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

IPC(8) - C01G 23/00, 25/00, 27/00 (2009.01) (text search only)

USPC - 423/69; 977/773, 777 (text search only)

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

(USPT, PGPB, EPAB, JPAB); Google Patent, Google Scholar, Dialog Web

Search terms on extra sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/0111319 A1 (Bastide et al.) 17 May 2007 (17.05.2007) (Abstract, para [0031], [0032], [0042], [0047], [0049], [0050], [0053], [0057], [0059], [0066], [0067]).	1, 13-17, 21
Y		2-12, 22-23
Y	US 2006/0051505 A1 (Kortshagen et al.) 09 Mar 2006 (09.03.2006) (para [0010], [0048], [0050], [0079], [0081] [0085], Fig. 11).	2-12, 22-23

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

* 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

16 Nov 2009 (16.11.2009)

Date of mailing of the international search report

01 DEC 2009

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 09/52565

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

Group I: claims 1-17 and 21-23

Group II: claims 18-20

see extra sheet for details

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-17, 21-23

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Observations where unity of invention is lacking (Continuation of Box III)

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: claims 1-17 and 21-23: directed to nebulizing a solution of a Group IV organic compound, exposing the resultant one or more aerosol droplets to a temperature greater than 550 deg C to form Group IV nanoparticles, and cooling to form nanocrystals.

Group II: claims 18-20: directed to a plurality of simultaneously-produced nanocrystals having a specified size distribution.

The inventions listed as Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group I does not include the specified size distribution of nanocrystals, as required by Group II.

Group II does not include the inventive concept of nebulizing a solution of a Group IV organic compound, exposing the resultant one or more aerosol droplets to a temperature greater than 550 deg C to form Group IV nanoparticles, and cooling to form nanocrystals, as required by Group I.

Groups I and II share the technical feature of nanocrystals; however, this shared technical feature does not represent a contribution over the prior art of US 2004/0217335 A1 (Sterzel) 4 November 2004. Sterzel (Abstract) teaches a nanocrystalline material. As nanocrystals were known, they cannot be considered a special technical feature that would otherwise unify the groups.

Groups I and II therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.

Box B - FIELDS SEARCHED (continued) - Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Search terms:

nanocrystal, nanocrystallinity, germanium, Ge, Si, silicon, Group IC, nanoparticle, temperature, heating, cooling, solvent, diethylsilane, tetraethylsilane, tetrapropylsilane, trisilane, phenylsilane, diphenylsilane, triphenylsilane, tetrapropylgermane, tetraethylgermane, diphenylgermane, tetramethylgermane, argon, hydrogen, carrier gas, aerosol, nebulizer, droplets, toluene, pentane, hexane, heptane, octane, decane, tridecane, methanol, ethanol, octanol, heptanol, acetone, ultrasonic