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(54) **LASER FABRICATION OF CONTINUOUS NANOFIBERS**

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(57) **ABSTRACT**

This invention provides a continuous process of making continuous nanofibers of all kinds, such as SiC, BN, AlN, and C. Laser heating a vapor of feed-material made of all atomic elements needed to grow chosen nanofibers results in growth of nanofibers onto seed-nanostructures attached to a filament, which is then pulled up continuously at a rate controlled by a rate of growth of the nanofibers. More feed-material is supplied at a rate sufficient to enable the nanofibers to grow longer continuously without limit. Laser light focused into a doughnut shape provides a photon density gradient, which constrains the nanofibers to grow parallel to each other and in the form of cylinders, so that industrially useful structures like cables and cylinders can be made in one low cost operation and in large quantities.

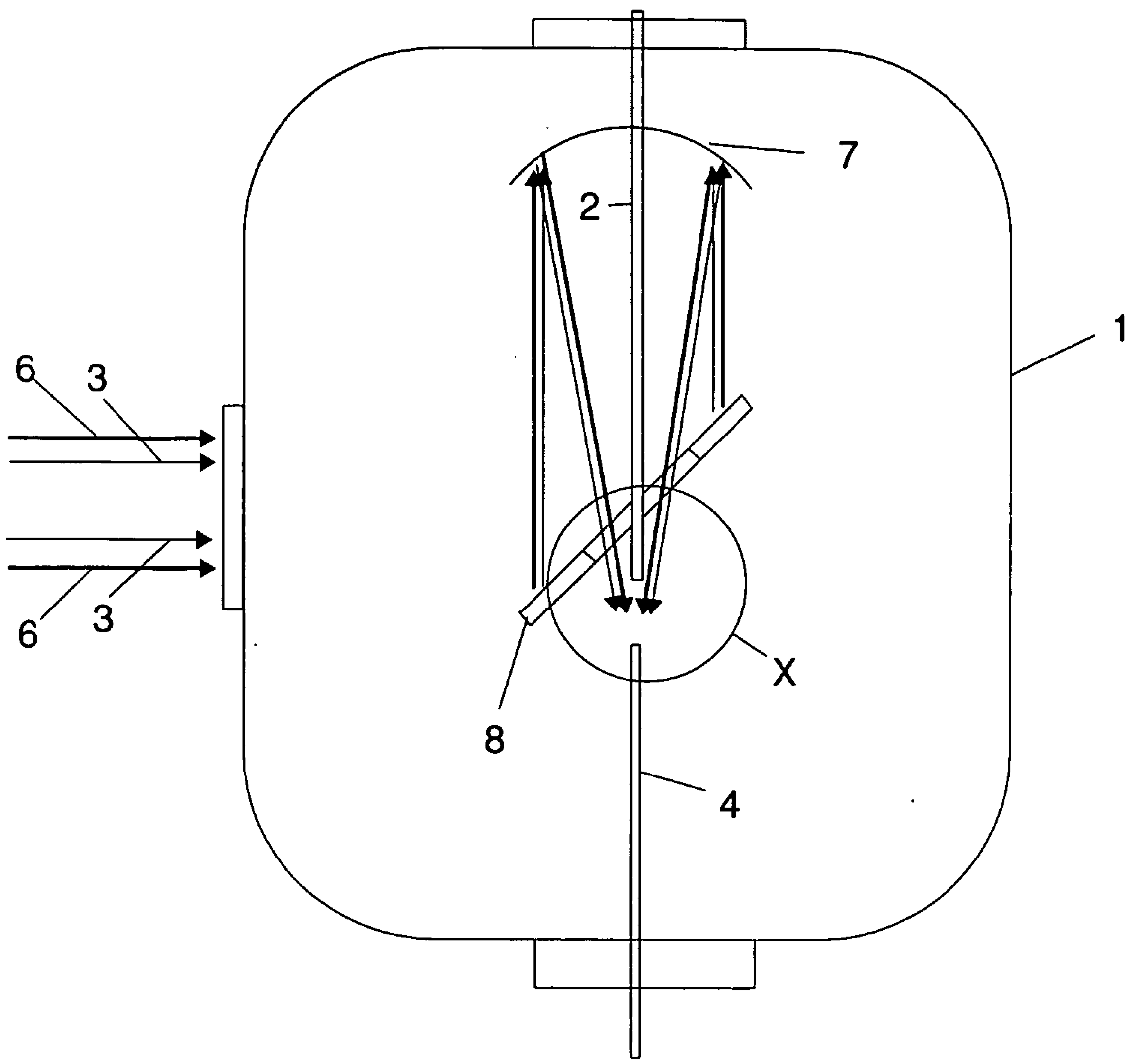

Fig. 1a

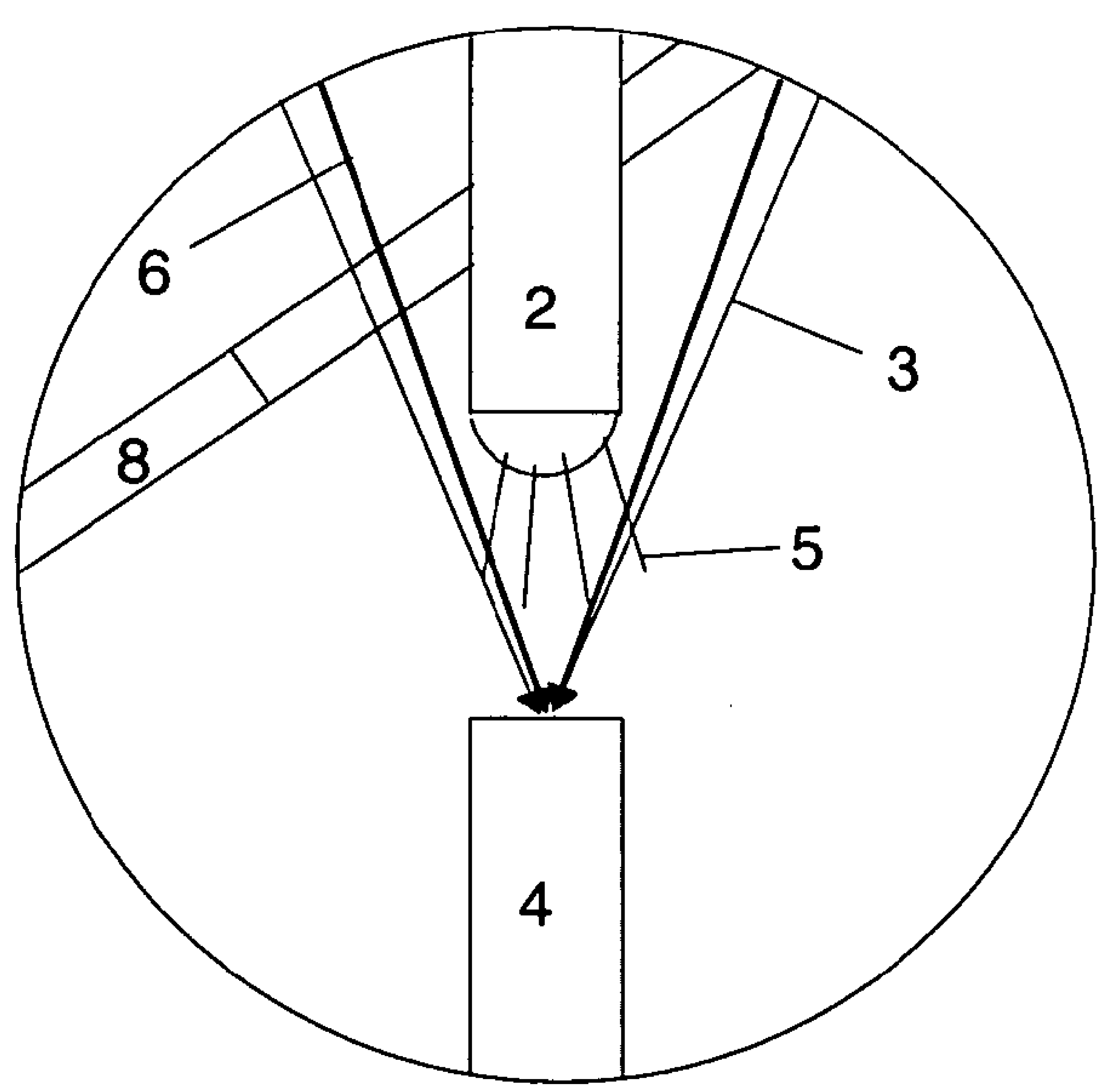

Fig. 1b

LASER FABRICATION OF CONTINUOUS NANOFIBERS

BACKGROUND OF THE INVENTION

[0001] This invention relates to a continuous-flow process of making continuous-length nanofibers by laser vaporization.

[0002] The fantastic properties and applications of nanotubes have been described in a presentation of a new field called "Fractal Tube Reinforcement Microengineering" by Russell in 32nd *International SAMPE Technical Conference*, p. 224 (Nov. 5-9, 2000). There has been great interest in using nanotubes as building blocks to construct all kinds of products with superior performance, but nanotubes have been far too costly and of insufficient length and quantity to be useful for most industrial applications. Smalley, et al. in U.S. Pat. No. 6,183,714 disclose pulse laser vaporization of carbon mixed with one or more Group VIII transition metals to make a carbon nanotube. They then use a second laser pulse to maintain this nanotube end in an annealing zone, which allows growth of ropes of nanotubes. These ropes, however, are not continuous-length ropes and not attached to anything that can be pulled or wound. So, this process is not continuous and must be stopped to recover nanotube ropes from condensed vapor.

[0003] Kalaugher reported in "Nanotubes go to great lengths", Nanotechweb.org (Mar. 11, 2004) that Windle and colleagues at Cambridge University have used chemical vapor deposition in a furnace of ethanol with ferrocene and thiophene and catalyzed with iron to make ribbons of carbon nanotubes. However, they do not disclose any way to apply tension to the nanofibers to constrain them to grow parallel to each other with controlled geometry to form useful structures.

[0004] So, there remains a need to make continuous-length nanofiber in parallel, controlled arrangements in order to make commercially useful structures economically in large quantities.

SUMMARY OF THE INVENTION

[0005] A main object of the instant invention is to provide a continuous laser fabrication process of making all kinds of nanofibers of unlimited length. This is accomplished herein by laser vaporization of a feed-material made of all of the elements required to grow a chosen kind of nanofiber in a reactor, such that new nanofibers of the chosen kind grow onto seed-nanostructures attached to a filament. More feed-material is supplied to the reactor as needed to support the continuous growth of new nanofibers, which are pulled out and wound up at a rate controlled by their growth rate in a continuous-flow process.

[0006] Another object is to provide a process of controlling the growth of new nanofibers in order to make useful structures like cables and cylinders in one continuous operation. This is accomplished herein by applying tension to the growing nanofibers by focusing at least one laser light beam into the shape of a doughnut at a vapor of feed-material in a reaction zone. This provides a photon density gradient, which gathers atoms of the vapor together and constrains the growth of new nanofibers to be parallel to each other and to assume a cylindrical form. In another aspect an electrical field is applied to align the new nanofibers and constrain them into chosen shapes and useful structures.

[0007] These and other objects and advantages of the invention will be better understood from the following detailed description of preferred embodiments of the inventive process when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF DRAWINGS

[0008] **FIG. 1***a* is a schematic cross-sectional view of a laser-assisted continuous nanofiber reactor.

[0009] **FIG. 1***b* is an enlarged view of section X in **FIG. 1***a* showing nanofibers attached to filament.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0010] In a first embodiment seed-nanostructures are placed in a reactor **1** shown in **FIG. 1***a*, which is capable of sustaining pressure. The pressure in the reactor **1** depends on the type of nanofibers to be built and controls their rate of growth to a manageable rate. The seed-nanostructures comprise nanotubes of any type and chemical composition including fullerenes and nanotube ropes together with catalyst nanoparticles, such as a mixture of Co and Ni. The catalyst nanoparticles are, alternatively, any of the transition elements or combinations thereof. In another example, seed-nanostructures comprise elements from which nanofibers are built. Nanostructures are defined to be structures less than 1 micron in thickness. An electric charge is imparted to an assembly of these seed-nanostructures relative to a filament **2** in the reactor **1** by means of a static charge generator until they become aligned relative to each other. Oxygen and water vapor are evacuated and inert gas is injected in the reactor **1**. The preferred inert gas is a gas selected from the group consisting of argon, helium, and any combination of these. Each lower tip of at least one filament **2** is heated by reflecting at least one input laser light beam **3** from mirror **8** to focusing mirror **7** and focusing the laser beam **3** on the lower tip by the focusing mirror **7** until the lower tip becomes molten hot. A preferred filament is one made of sapphire having a tapered lower tip. Another preferred filament is a nanofiber. The filament **2** may be made of any other material. The lower tip of the at least one filament **2** is then moved out of a path of the focused laser beam **3** toward the seed-nanostructures such that they become attached to the filament **2**. In one example the seed-nanostructures become attached to the filament **2** by embedding themselves into the molten tip. In another example they are adhered to the filament **2** by means of an applied adhesive. In another example they become attached by means of the electrostatic charge placed on them. A preferred laser emits a light beam **3** with a power of at least 10 mW in the visible frequency range. Visible light lasers are available from New Lamda Corp., Clearwater, Fla. Feed-material **4** is provided in the reactor **1**, which comprises all elements needed to build new nanofibers **5** including a total of at most 5 atom % of at least one transition element. More preferably the feed-material **4** comprises all elements needed to build new nanofibers **5** including a total of at most 3 atom % of at least 3 transition elements. Two examples of highly effective transition element combinations in catalyzing new nanofiber growth are 1 atom % each of Ni, Fe, & Co, and Y, Ir, & Pt. In this paper atom % is defined as the percentage of atoms relative to all other atoms present. Most preferably only a negligible amount of transition elements are included and only in the beginning of the inventive process, because this costly part of the process is minimized. In one example the feed-material **4** is in a solid state. In a second example the feed-material is in a liquid state. In a third example the feed-material is in a gas state. Examples of feed-material **4** are carbon, hydrocarbons, fullerenes, SiC, BN, AlN, and any combination of these. The feed-material **4** is then heated to form vapor. A preferred way to heat the feed-material **4** is by means of at least one infrared laser beam **6**. Infrared lasers are available from New Lambda Corp., Clearwater, Fla. In other examples electric arc, plasma arc, and radio frequency induction are used as means to heat the feed-material **4**. The vapor is heated by means of the focused laser beam **3** sufficiently so that new nanofibers grow in a local region of the focus of the beam **3**. A preferred reaction temperature of the vapor is 500° C. to 1400° C. More preferably the reaction temperature of the vapor is 600° C. to 1250° C. The at least one laser beam **3** creates a photon density gradient, which gathers atoms and molecules from the vapor together and constrains them to assemble into new nanofibers **5**. In this paper, nanofiber is defined as any fiber that has a thickness of less than 1 micron. The new nanofibers **5** include single-wall nanotubes. In another example the new nanofibers **5** include multi-wall nanotubes. In another example the new nanofibers **5** include a mixture of single-wall and multi-wall nanotubes. The well-known technology of using a photon density gradient from highly focused light to manipulate matter is documented by Plewa et al. in "Processing Carbon Nanotubes with Holographic Optical Tweezers", Physics-.nyu.edu/grierlab/nanotube3b (Feb. 14, 2004), and by Dholakia et al. in "Optical tweezers: the next generation", Nanotechweb.org/articles/feature/1/10/2/1 (October 2002). The lower tip of the filament **2** is then raised to a position just above the focus of the beam **3** such that new nanofibers form from the vapor on the seed-nanostructures. The new nanofibers **5** are structurally continuous with the seed-nanostructures. In one example the new nanofibers **5** are chemically identical with the seed-nanostructures. In another example the new nanofibers **5** are made of different elements than the seed-nanostructures. The filament **2** is then pulled out with the new nanofibers **5** attached as shown in **FIG. 1***b* at a rate controlled to match a rate of new nanofiber growth. Tension is provided on the new nanofibers **5** as they grow by at least one tensioning means. This constrains the new nanofibers **5** to grow parallel to each other. Feed-material **4** is continuously provided, as required, to allow continuous growth of new nanofibers **5** in a continuous-flow process. The means of providing tension is by focusing the at least one laser beam **3** into a toroid or doughnut shape. Preferably 3 laser beams **3** are used together to manipulate the nanofiber growth. This further constrains the new nanofibers **5** to assemble in a substantially cylindrical shape, so that cables, cylinders and hollow cylinders and other structures are manufactured in one efficient operation. Bonding agents may be used in this process to bond the new nanofibers **5** comprising these structures. Another means of providing tension and manipulating the new nanofibers **5** to control a final product geometry is by applying an electric field to the new nanofibers by an electric field generator. As the filament **2** is pulled out with the new nanofibers **5** attached it is wound up onto a spool, for example. The length of the new nanofibers **5** is not limited. The chemical make-up of the new nanofibers **5** depends on the type of feed-material used. Examples of new nanofibers **5** are C, SiC, BN, AlN, and any combination of these.

[0011] In a second embodiment the seed-nanostructures are replaced with seed-nanotubes, which are comprised of nanotubes. In another example the seed-nanotubes are comprised of short sections of nanotube ropes. There are no transition elements used in this embodiment to catalyze formation of new nanofibers **5**. An electric charge is placed on the at least one filament **2** relative to the seed-nanotubes. In all other respects the process steps are the same in this embodiment as in the first embodiment.

[0012] While there is described herein certain specific process steps embodying the invention, it will be manifest to those skilled in the art that modifications may be made without departing from the spirit and the scope of the underlying inventive concept. The present invention shall not be limited to the particular processes herein shown and described except by the scope of the appended claims.

What is claimed is:

1. A process of making continuous nanofibers comprising the steps of:

providing seed-nanostructures in a reactor capable of maintaining a positive internal pressure; applying a static electric charge to an assembly of said seed-nanostructures in said reactor by means of a static electric charge generator sufficiently so that said seed-nanostructures become aligned relative to each other; removing oxygen and water and injecting inert gas in said reactor with said seed-nanostructures; heating each lower tip of at least one filament by focusing at least one laser light beam on said tip by means of at least one laser until said tip becomes molten hot; moving said tip of said filament out of a path of said beam toward said seed-nanostructures such that said seed-nanostructures become attached to said tip of said filament; providing feed-material comprised of all atomic elements from which new nanofibers are built; making a vapor from said feed-material by heating said feed-material; heating said vapor to a temperature sufficient to cause new nanofiber growth and gathering atoms of said vapor together in a local region of said laser light beam by focusing said beam from said laser; raising said tip of said filament to a position just above said beam such that said new nanofibers form from said vapor in a continuous structure with said seed-nanostructures; pulling out said filament with attached said new nanofibers at a rate controlled to match a rate of new nanofiber growth; providing tension on said new nanofibers as they grow by at least one tensioning means; and constraining said new nanofibers to grow substantially parallel to each other by said tensioning means.

2. The process of claim 1 wherein said process is a continuous-flow process such that said feed-material is continuously provided as required to allow continuous growth of said new nanofibers.

3. The process of claim 2 wherein the step of providing said feed-material further comprises including in said feed-material a total of at most 5 atom % of at least one transition element selected from the group consisting of all transition elements.

4. The process of claim 3 wherein the step of providing tension further comprises converging said laser light beam such that a photon density gradient is provided having a toroidal shape, said laser being a visible light laser, and the step of constraining said new nanofibers to grow substantially parallel to each other further comprises constraining said new nanofibers to assemble into a cylindrical shape by means of said photon density gradient.

5. The process of claim 4 wherein the step of providing tension further comprises applying an electrical field to said new nanofibers by means of an electric field generator.

6. The process of claim 4 wherein the step of providing feed-material further comprises providing carbon feed-material, including in said feed-material a total of at most 3 atom % of at least three transition elements selected from the group consisting of all transition elements, and said new nanofibers are carbon nanofibers.

7. The process of claim 5 wherein the step of providing feed-material further comprises providing carbon feed-material, including in said feed-material a total of at most 3 atom % of at least three transition elements selected from the group consisting of all transition elements, and said new nanofibers are carbon nanofibers.

8. The process of claim 6 wherein the step of pulling up said filament further comprises winding said filament together with attached said new nanofibers, and the step of heating said feed-material further comprises heating said feed-material by means of an infrared laser.

9. The process of claim 7 wherein the step of pulling out said filament further comprises winding said filament together with attached said new nanofibers, and the step of heating said feed-material further comprises heating said feed-material by means of at least one infrared laser.

10. The process of claim 5 wherein the step of providing feed-material further comprises providing boron nitride in said feed-material.

11. The process of claim 5 wherein the step of providing feed-material further comprises providing silicon carbide in said feed-material.

12. The process of claim 5 wherein the step of providing feed-material further comprises providing aluminum nitride in said feed-material.

13. A process of making continuous nanofibers comprising the steps of:

providing seed-nanotubes in a reactor; applying a static charge to at least one filament in said reactor by means of a static charge generator sufficiently so that said seed-nanotubes become aligned relative to each other; removing oxygen and water and injecting inert gas in said reactor; heating each lower tip of said at least one filament by focusing at least one laser light beam on said tip by means of at least one laser until said tip becomes molten hot; moving said tip of said filament out of a path of said beam toward said seed-nanotubes such that said seed-nanotubes become attached to said tip of said filament; providing feed-material including all elements from which new nanofibers are built; making a vapor from said feed-material by heating said feed-material by at least one heating means; heating said vapor to a temperature sufficient to cause new nanofiber growth and gathering atoms of said vapor together in a local region of said laser light beam by focusing said beam from said laser; raising said tip of said filament to a position just above said beam such that new nanofibers form from said vapor in a continuous structure with said seed-nanotubes; pulling out said filament with attached said new nanofibers at a rate controlled to match a rate of new nanofiber growth; providing tension on said new nanofibers as they grow by converging said laser light beam such that a photon density gradient is provided having a toroidal shape; and constraining said new nanofibers to grow substantially parallel to each other in a substantially cylindrical shape by means of said photon density gradient.

14. The process of claim 13 wherein said process is a continuous-flow process such that said feed-material is continuously provided as required to allow continuous growth of said new nanofibers.

15. The process of claim 14 wherein the step of providing tension further comprises applying an electric field to said new nanofibers by means of an electric field generator.

16. The process of claim 15 wherein the step of pulling out said filament further comprises winding said filament together with attached said new nanofibers, and the step of heating said feed-material further comprises heating said feed-material by means of an infrared laser.

17. The process of claim 13 wherein the step of providing feed-material further comprises providing feed-material that comprises a carbon material selected from the group consisting of carbon, and silicon carbide, and any combination of these.

18. The process of claim 16 wherein the step of providing feed-material further comprises providing feed-material that comprises a carbon material selected from the group consisting of carbon, silicon carbide, and any combination of these.

19. The process of claim 13 wherein the step of providing feed-material further comprises providing feed-material that comprises a nitride selected from the group consisting of boron nitride, and aluminum nitride, and any combination of these.

20. The process of claim 16 wherein the step of providing feed-material further comprises providing feed-material that comprises a nitride selected from the group consisting of boron nitride, and aluminum nitride, and any combination of these.

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