(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 December 2007 (21.12.2007)

PCT

(10) International Publication Number
WO 2007/145647 A3

(51) International Patent Classification:
C23C 16/455 (2006.01)

(21) International Application Number:
PCT/US2006/034733

(22) International Filing Date:
6 September 2006 (06.09.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/220,454 6 September 2005 (06.09.2005) US

(71) Applicant and
(72) Inventor: **LEMAIRE, Charles, A.** [US/US]; 13195 Flamingo Court, Apple Valley, MN 55124 (US).

(74) Agent: **LEMAIRE, Charles, A.**; Lemaire Patent Law Firm, PLLC, P.O. Box 1818, Burnsville, MN 55337 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, 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, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *with amended claims*

(88) Date of publication of the international search report:
14 August 2008

Date of publication of the amended claims:
25 September 2008

(15) Information about Correction:
Previous Correction:
see Notice of 14 February 2008

(54) **Title:** APPARATUS AND METHOD FOR MAKING FULLERENE NANOTUBE FORESTS, FILMS, THREADS AND COMPOSITE STRUCTURES

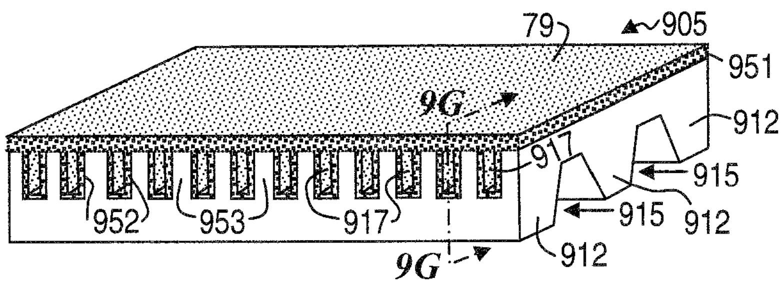

Fig. 9F

(57) Abstract: The present invention provides apparatus and methods for growing fullerene nanotube forests, and forming nanotube films, threads and composite structures therefrom. In some embodiments, an interior-flow substrate (977) includes a porous surface (79) and one or more interior passages (917) that provide reactant gas to an interior portion of a densely packed nanotube forest as it is growing. In some embodiments, a continuous-growth furnace is provided that includes an access port for removing nanotube forests without cooling the furnace substantially. In other embodiments, a nanotube film can be pulled from the nanotube forest without removing the forest from the furnace. A nanotube film loom is described. An apparatus for building layers of nanotube films on a continuous web is described.

WO 2007/145647 A3

AMENDED CLAIMS

received by the International Bureau on 18 July 2008 (18.07.08)

1. An apparatus comprising an interior-flow substrate having a first nanoporous surface layer formed thereon, the first nanoporous surface layer having a first major face in fluid communication with the first nanoporous surface layer, an interior flow system having a plurality of channels configured to deliver gasses to the nanoporous layer from a side of the first nanoporous surface layer other than the first major face, and a nanotube-synthesis catalyst on the first major face of the first nanoporous layer.

2. The apparatus of claim 1, wherein the interior flow system includes a first plurality of gas passages having a depth as measured in a direction perpendicular to the first major face greater than their width as measured in a direction parallel to the first major face, and having a length as measured in a along an end-to-end path that is parallel to the first major face and adjacent the first nanoporous layer.

3. The apparatus of claim 2, wherein the substrate is a side-flow substrate wherein each one the first plurality of gas passages provide fluid communication to the first nanoporous layer from one or more sides adjacent the first major face.

4. The apparatus of claim 1, wherein the interior flow system includes a first plurality of gas passages each having a depth as measured in a first direction that is perpendicular to the first major face greater than their width as measured in a second direction that is parallel to the first major face, and having a length along a third direction that is parallel to the first major face and perpendicular to the second direction, and a second plurality of gas passages that extend to a maximum distance more distal from the first major face than the maximum distance of the first plurality of gas passages from the first major face, and wherein each of the second gas passages is in fluid communication with a plurality of the first plurality of gas passages, in order to form a flow-through substrate.

5. The apparatus of claim 1, further comprising:

a furnace having a temperature control and heating unit operable to maintain an effective temperature for nanotube synthesis;

a substrate-holding mechanism;

a gas-flow system operable to deliver one or more reactant gasses to a side or face of the substrate other than the first major face and to exhaust spent gasses from a vicinity of the first major face; and

an access port through which nanotube product can be removed without interrupting a substantially continuous operation of the furnace at substantially its effective temperature for nanotube synthesis.

6. The apparatus of claim 5, wherein the substrate is configured to have plurality of successive

nanotube forests grown and harvested by removing the nanotube forests so that additional nanotube forests can be grown from the substrate.

7. The apparatus of claim of 1, wherein the channels include a plurality of defined oblong channels generally parallel to the first major face.

8. The apparatus of claim of 1, wherein the channels in the interior flow system are larger than pores in the nanoporous surface layer.

9. The apparatus of claim of 1, wherein the channels include a plurality of channels some of which are larger channels and smaller channels adjacent the nanoporous layer.

10. The apparatus of claim of 1, wherein the channels include a plurality of channels that include channels adjacent the first nanoporous layer that are smaller in cross-sectional area than channels further from the first nanoporous layer.

11. A nanotube article comprising: a plurality of nanotube films stacked on a continuous web in each of one or more directions relative to a length-wise edge having the longest dimension of the web.

12. The article of claim 11, wherein the web is densified and wound on a take-up roll.

13. The article of claim 11, wherein the web and each of the plurality of nanotube films includes carbon fullerene nanotubes.

14. The article of claim 11, wherein the web includes woven nanotube films.

15. The article of claim 11, wherein the web includes a first set having a plurality of nanotube warp films positioned at a first angle to a length-wise edge of the web woven with a second set having a plurality of nanotube weft films positioned at a second angle, different than the first angle, to a length-wise edge of the web.

16. The article of claim 1, wherein the web includes crossed-but-not-woven nanotube films.

17. The article of claim 1, wherein the web includes a first set having a plurality of nanotube films parallel to one another crossed-but-not-woven with a second set having a plurality of nanotube films parallel to one another.

18. An apparatus for continuous fabrication of a carbon nanotube film comprising: a first film-transport mechanism having one or more nanotube-film-holding surfaces, and movable along a first fabrication path; and a layer-build-up mechanism operable to place carbon nanotube film across the

nanotube-film-holding surfaces while the holding surfaces are moving along the fabrication path.

19. The apparatus of claim 18, wherein the nanotube-film-holding surfaces include one or more adhesive surfaces along a surface of a flexible sheet belt, wherein the layer-build-up mechanism lays each film at a non-parallel non-perpendicular angle to a lengthwise edge of the sheet belt.

20. The apparatus of claim 19, wherein the belt is a continuous-loop made of a polymer material having the adhesive surfaces along its two opposite outer edges, and wherein the nanotube film is placed across the belt and held by the one or more adhesive surfaces.

21. The apparatus of claim 18, wherein the nanotube-film-holding surfaces include one or more adhesive surfaces along a surface of each of a plurality of separate spaced-apart endless-loop belts moved substantially piecewise parallel to one another.

22. The apparatus of claim 21, further comprising a second film transport mechanism having a plurality of spaced-apart adhesive surfaces on a sheet belt, and movable along a second fabrication path that connects to the first fabrication path in a manner to allow transfer of the nanotube film from the first film transport mechanism to the second film transport mechanism.

23. The apparatus of claim 8, wherein the layer-build-up mechanism includes a first set of one or more warp-film holders operable to hold a first set of warp films stretched to a first adhesive strip along a distal first edge of the first film-transport mechanism from the first set warp-film holders, and a second set of warp film holders operable to hold a second set of warp films stretched to the first adhesive strip, wherein the first film-transport mechanism includes a second adhesive strip along a second edge opposite the first edge, and a weft-film placement mechanism operable to place a weft film in a shed between the first set of warp films and the second set of warp films and attach opposite ends of the weft to the first and second adhesive strips respectively and then separate from the attached weft.

24. The apparatus of claim 23, wherein the first set warp-film holders moves in a direction opposite relative to the second set warp-film holders after deposition of a weft film placed from the first adhesive strip to the second adhesive strip, and wherein the warp-film holders successively attach a near end of each warp film to the second adhesive strip as it completes its weave and then separate from the attached warp.

25. The apparatus of claim 18, wherein the first film-transport mechanism includes a vacuum table, wherein the nanotube-film-holding surfaces are operable to hold and release nanotube film using a gas-pressure difference, the vacuum surface movable relative to layer-build-up mechanism to position itself for a predetermined film deposition layout.