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(54) Title: METHOD FOR THERMALLY DRAWING NANOCOMPOSITE-ENABLED MULTIFUNCTIONAL FIBERS

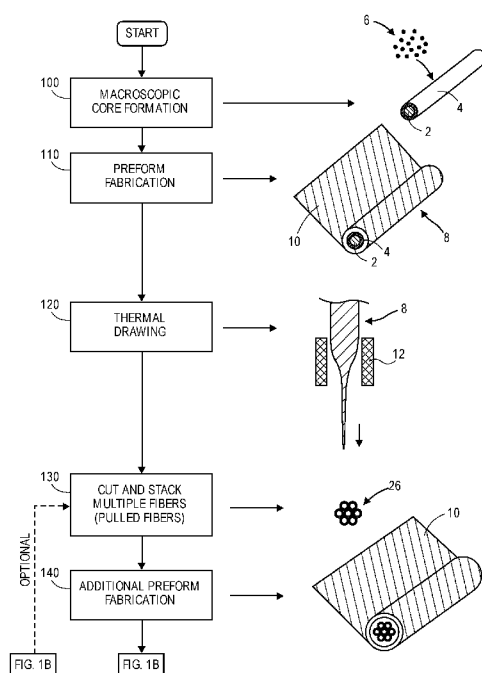


FIG. 1A

(57) Abstract: A method of thermally drawing fibers containing continuous crystalline metal nanowires therein includes forming a preform comprising an inner core and an outer cladding, wherein at least one of the core and cladding has nanoelements dispersed therein. The preform is drawn through a heated zone to form a reduced size fiber. A second preform is then created from a plurality of fibers created from the reduced size fiber. The second preform is then drawn through the heated zone to form an elongated fiber containing continuous crystalline metallic nanowires therein having a maximum cross-sectional dimension of less than 100nm. Optionally, a third or additional preforms are created from fibers made from the previous thermal drawing operation that are then drawn through the heated zone to form a fiber containing even smaller crystalline metal continuous nanowires therein. In some embodiments, only a single pass through the heated zone may be needed.

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METHOD FOR THERMALLY DRAWING NANOCOMPOSITE-ENABLED MULTIFUNCTIONAL FIBERS

Related Application

[0001] This Application claims priority to U.S. Provisional Patent Application No. 62/110,363 filed on January 30, 2015, which is hereby incorporated by reference in its entirety. Priority is claimed pursuant to 35 U.S.C. § 119 and any other applicable statute.

Statement Regarding Federally Sponsored

Research and Development

[0002] This invention was made with Government support under award number 1449395, awarded by the National Science Foundation. The Government has certain rights in the invention.

Technical Field

[0003] The technical field generally relates to methods and devices used in the thermal drawing of fibers having nanoparticles contained in the core, cladding, or both.

Background of the Invention

[0004] Long fibers with embedded functionalities have great potentials for numerous applications. Ongoing research on ultra-long functional fibers include, for example, microstructured photonic crystal fibers, optical micro/nano fibers, electronics in fibers, fiber-based metamaterials, fibers as a novel platform for sensing devices, studying chemical reactions, multi-material functional fibers, and more recently fibers as a platform for fabrication of nanowires and nanoparticles. The trend of combining a multitude of functionalities into a single long fiber demands the incorporation of a multiplicity of solid materials each with disparate physical properties. Significant progress has been made along this direction by thermal drawing of macroscopic multi-materials preforms. Materials that have distinctively different electrical and optical properties are integrated into a single fiber by means of a preform-based thermal drawing technique. Various electronic and optoelectronic devices have been realized in kilometer long fibers. Large-scale fabrics woven from such fibers have also been demonstrated. The capability of this technique towards scalable nanofabrication has been explored, however, with mixed success.

[0005] There exists a strong demand for low-cost and scalable manufacturing methods and techniques of these fibers having continuous nanowires contained therein. For example, such nanowires may be made from generally inert metals such as gold (Au), silver (Ag), and platinum (Pt) and used in short-haul electrical interconnect bundles and front-end sensing/recording multi-electrode arrays. Additional existing and emerging applications include, for instance, high resolution semiconductor/thin-film resistivity probes, electrical cellular phenotyping, neural/cardiac electrical signal recording, etc., representing a large global commercial market. Despite the huge potential economic and technological impact that high-volume production of fibers with continuous metallic nanowires will bring about, there has been little success for their reliable and scalable manufacturing; mostly due to the fluid instability induced by the low viscosity of molten metals and its large interfacial energy with the cladding.

[0006] Thermal drawing is a very promising approach to realize volume and low-cost nano-production of fibers with nanowires without harnessing costly lithography. However, there are significant scientific and manufacturing barriers that must be overcome. A successful thermal drawing of fibers from a macro preform made of multi-materials is fundamentally limited by at least the following constraints: (1) the viscosity of the most viscous constituent material (i.e. the cladding) should fall between $10^{3.5}$ and 10^7 Poise at the drawing temperature in order for the process to be controllable. Amorphous materials, such as glass and polymers, are typically used as the support (cladding) to contain other core materials for cross-sectional stability; (2) the softening or melting temperature of the core material(s) should be lower than or overlap with the drawing temperature. If a crystalline material is to be drawn, low vapor pressure is desired and its boiling should be avoided; (3) chemical reactions between the cladding and core materials should be avoided unless intentionally designed (e.g., for in-fiber synthesis purposes); (4) it is desired that cladding and core materials exhibit good adhesion/wetting with each other during and after drawing to avoid cracks, bubbles and fluid instability of the core material(s); and (5) the cladding and core materials should have relatively compatible thermal expansion coefficients in the temperature range up to the drawing temperature.

[0007] These constraints pose severe challenges to find suitable material combinations for multifunctional polymers or glass fibers drawn with metal nanowires. At present, most crystalline metal nanowires or even micro-wires are beyond the capability of current manufacturing techniques, due to the fluid instability induced by a low viscosity of molten metals and the large interfacial energy with the cladding materials.

[0008] Fibers with metal microwires are routinely produced by thermal drawing. The softening temperature of the cladding determines the types of metals that can be drawn within. Low melting temperature metals such as tin (Sn), bismuth (Bi), indium (In), and their respective alloys have been thermally drawn in polymer cladding (e.g., polyethersulphone (PES), polysulfone (PSU), and polyethylenimine (PEI) at which the softening temperature is below 300 °C). The resulting metal fibers with rectangular or circular cross sections have critical dimensions ranging from tens to hundreds of micrometers; they are not in the nanometer range. Fibers with metal microwires are also thermally drawn along with other functional materials (usually semiconductors or conductive polymers) and serve as conductive electrodes in multi-material functional fibers, which are in turn utilized as, for example, 1D photodetectors, thermal sensors, piezoelectric transducers, chemical sensors, and capacitors. The smallest diameter reported for metal-based wires that can be reliably drawn into infinitely long arrays is around 4 μm and is achieved from a low melting temperature Sn_{0.95}Ag_{0.05} alloy with PES cladding. See Yaman et al., Arrays of indefinitely long uniform nanowires and nanotubes, *Nature Materials*, vol. 10, pp. 494-501 (2011). Beads, discontinuities, and structural deformation were observed upon further size reduction. Others have demonstrated that thermally drawn functional fibers embedding in wires with diameter approaching 1 μm. See Tuniz et al., Fabricating Metamaterials Using the Fiber Drawing Method, *Journal of Visualized Experiments*, vol. 68, 2012.

[0009] Higher melting temperature metals such as Au, copper (Cu), zinc (Zn), and their respective alloys require cladding materials with higher softening temperatures. Pyrex glass (with softening point ~800 °C) and fused silica (with softening point ~1700 °C) are the materials of choice in this regime, though not excluding their usage to draw metals with low melting temperature. In fact, larger sized, metal microwire fabrication by thermal drawing in a glass cladding, known as the Taylor-wire process, has been in practice for decades. However, similar to the case with polymer cladding, manufacturing reliability suffers as the diameter of metal wire approaches less than 1 μm. Au microwires of 4 μm diameter have been fabricated over a length of several centimeters and this continuous length shrank to ~20 μm as their diameter reduced to 260 nm. See Tyagi et al., Plasmon Resonances on Gold Nanowires Directly Drawn in A Step-index fiber, *Optics Letters*, vol. 35, pp. 2573-2575 (2010). Pb-Sn alloys and Bi nanowires (drawn in glass cladding) with diameter down to 50 nm were reported with a length reaching 1 m with no experimental evidence provided to support their continuity over the claimed 1 m drawn length. See Badinter et al., Exceptional Integration of Metal or Semimetal Nanowires in Human-hair-like Glass Fiber, *Materials*

Letters, vol. 64, pp. 1902-1904 (2010). Similarly, fabrication of discontinuous $\text{Cu}_{0.93}\text{P}_{0.07}$ with a diameter of 500 nm has been reported using Pyrex glass cladding. See Zhang et al., Mass-Productions of Vertically Aligned Extremely Long Metallic Micro/Nanowires using Fiber Drawing Nanomanufacturing, *Advanced Materials*, vol. 20, pp. 1310-1314 (2008). On the other hand, and again being consistent with that of using polymer cladding, thermally drawn continuous Cu microwire of 4 μm in diameter has been demonstrated which enables single mode visible light guidance by metallic reflection in a photonic crystal fiber See Hou et al., Metallic Mode Confinement in Microstructured Fibres, *Optics Express*, vol. 16, pp. 5983-5990 (2008).

[0010] Fiber drawing via laser-based heat source pulling of short pieces of Pt microwires has been used to fabricate quartz-sealed Pt nanowires. The resultant fibers were tapered down to 10 nm in diameter yet with a length of only 5 mm. See Percival et al., Laser-pulled Ultralong Platinum and Gold Nanowires, *RSC Adv.*, vol. 4, pp. 10491-10498 (2014). Since such tapering method is confined to a narrow (length) region of wires, it is hard to extend it to pull wires that are tens of centimeters long. Alternatively, a polyol process, which is the synthesis of metal-containing compounds in ethylene glycol, was used to fabricate Ag nanowires with length up to 230 μm and diameter of 60-90 nm. See Araki et al., Low Haze Transparent Electrodes and Highly Conducting Air Dried Films with Ultra-long Silver Nanowires Synthesized by One-step Polyol Method, *Nano Research*, vol. 7, pp. 236-245 (2014) and Jiu et al., Facile Synthesis of Very-long Silver Nanowires for Transparent Electrodes, *J. Mater. Chem. A*, vol. 2, pp. 6326-6330 (2014). Polyvinylpyrrolidone (PVP) and ethylene glycol (EG) were used as the capping and reducing agent, respectively, which also mandated a few more steps in manufacturing.

[0011] From the above-described literature citations, despite the fact that reliable drawing of indefinitely long amorphous semiconductor and polymer nanowires has been achieved, it is clear that there exists a fundamental size limit to the diameter of thermally drawn crystalline metal wires below which the metal wires become inherently unstable and extremely difficult to control, if not impossible, by current manufacturing techniques. Capillary fluid instability poses severe challenges for scale-up manufacturing processes. It is clear that there exists a fundamental size limit to the diameter of thermally drawn metal wires below which the metal wires become inherently unstable and extremely difficult to control, if not impossible, by current manufacturing techniques. There is a great and unmet need to break the fundamental limits and technical barriers to enable a reliable way to manufacture

nanometer sized (diameter from tens to hundreds of nanometers) crystalline metal wires with a continuous length.

Summary

[0012] In one aspect of the invention, a method of thermally drawing fibers containing continuous crystalline metal nanowires therein includes the steps of: (a) forming a preform comprising an inner core comprising the crystalline metal and an outer cladding, wherein at least one of the core and cladding having dispersed therein nanoelements; (b) drawing the preform through a heated zone to form a reduced size fiber; (c) forming a second preform created from a plurality of fibers from the reduced size fiber of (b); and (d) drawing the second preform of (c) through the heated zone to form another reduced sized fiber having a continuous length exceeding one meter and containing crystalline metal nanowires therein having a diameter less than 100 nm. In alternative embodiments, this last process may be repeated one or more times to further reduce the size of the crystalline metal nanowires.

[0013] In another aspect of the invention, a method of thermally drawing a fiber containing crystalline metal nanowires therein includes forming a preform comprising an inner core having a plurality of individual metal wires surrounded by an outer cladding, wherein at least one of the inner core and cladding comprise nanoelements dispersed therein. The preform is then drawn through a heated zone (e.g., a furnace) to form a reduced size fiber having a length of at least one meter and containing a plurality of continuous crystalline metal nanowires therein having a maximum cross-sectional dimension less than 100 nm.

[0014] In another embodiment, a nanoelectrode array includes a fiber having a distal end and a proximal end, the fiber having a plurality of crystalline metal nanowires each with a maximum cross-sectional dimension less than 100 nm embedded therein and terminating at a plurality of exposed electrodes at the distal end of the fiber, wherein the distal end of the fiber has a diameter that is $\ll$ than a diameter of the proximal end of the fiber.

[0015] In another embodiment, an article of manufacture includes a fiber having a distal end and a proximal end, the fiber having a plurality of crystalline metal nanowires embedded therein, each nanowire having a maximum cross-sectional dimension less than 100 nm, wherein the fiber has a length exceeding 1 meter.

Brief Description of the Drawings

- [0016] FIGS. 1A and 1B illustrate a flowchart illustrating one illustrative method of thermally drawing fibers containing continuous nanowires.
- [0017] FIG. 1C illustrates a cross sectional view of a fiber containing continuous crystalline metal nanowires therein.
- [0018] FIG. 2 illustrates another flow chart illustrating a thermal drawing process for creating a fiber according to one embodiment.
- [0019] FIG. 3 illustrates one exemplary method of creating a nanocomposite core using accumulative roll bonding (ARB).
- [0020] FIG. 4 illustrates a fiber embedded with crystalline metal nanowires used for cell-based assays.
- [0021] FIG. 5 illustrates an electrode-embedded fiber cell-based assay platform.
- [0022] FIG. 6A illustrates a schematic illustration of a preform made from a Sn-Si nanocomposite core and polyethersulphone (PES).
- [0023] FIG. 6B illustrates a photograph of an experimentally drawn tapered fiber within nanowires made from the Sn-Si nanocomposite.
- [0024] FIG. 6C illustrates a cross-sectional SEM image of the Sn nanowire.
- [0025] FIG. 6D illustrates a SEM image of the Sn nanowire after chemical etching of the PES cladding.
- [0026] FIG. 6E illustrates a pure Sn microwire with a diameter of about 10 μm after etching of the PES cladding.

Detailed Description of the Illustrated Embodiments

[0027] FIGS 1A and 1B illustrate a flowchart illustrating one illustrative method of thermally drawing a fiber 50 (seen in FIG. 1B and 1C) containing continuous nanowires 52 (FIG. 1C). Referring to FIG. 1A, the method starts with operation 100 where a core 2 is formed with a cladding 4 surrounding the core 2. The core 2 is typically a metal, metal alloy, or metal matrix. The core 2 may be crystalline or amorphous material. The cladding 4 jackets or surrounds the core 4 and is typically made from an amorphous material such as a polymer, glass, or quartz, whose viscosity reduces gradually as temperature goes above the material's glass transition point. According to the invention, at least one or both of the core 2 and cladding 4 having nanoelements 6 that are incorporated therein. The nanoelements 6 may include nanoparticles, nanowires, nanoplates, nanoflakes, nanowhiskers or other geometries. The nanoelements 6 generally are nanometer sized particles wherein their largest

dimension is 100 nm or less. For example, the nanoelements 6 may have a size (e.g., diameter) within the range of 1-100 nm. While the nanoelements 6 may have any number of geometries currently the most commonly produced nanoelements 6 are nanoparticles that have spherical shapes. Of course, other shapes are contemplated to fall within the scope of the inventions described herein.

[0028] The core 2 and cladding 4 are prepared separately and then mechanically or thermally treated to yield a single nanocomposite preform. As seen in operation 110 of FIG. 1A, a preform 8 is fabricated, for example, by rolling the core 2 and cladding 4 in a sheet 10. The sheet 10 may be formed from the same material used in the cladding 4. The preform 8 is much larger and typically has a diameter on the order of about 1 cm although the invention is not limited by the size of the preform 8. For example, in FIG. 1A, the sheet 10 may be formed from a glass-based cladding material that forms a continuous phase with the one or more cores 2 embedded inside (in this embodiment the cladding 4 is also glass-based). Typically, vacuum consolidation may be performed in conjunction with high temperatures to bond the cladding 4 to the core 2. While FIG. 1A illustrates the preform 8 being formed with a single core 2 it should be understood that the preform 8 may be formed with a plurality of cores 2 (e.g., stacked or bundled cores 2).

[0029] The nanoelements 6 may be incorporated into the core 2 or cladding 4 using any number of solid and liquid state processing methods used for the preparation of bulk nanocomposites. These methods includes, for example, casting, extrusion, melting, sonication (e.g., with ultrasound), high-shear mixing, solution-based processes, severe plastic deformation, electroplating, electro-codeposition, sintering, and the like. FIG. 3 illustrates the formation of a nanocomposite core 2 using accumulative roll bonding (ARB) which is one method. In FIG. 3, in this particular embodiment, the nanoelements 6 are dispersed within a solution 16 using an ultrasonic transducer 18 or the like. For example, the solution may include a solvent such as acetone and the nanoelements 6 are silicon nanoparticles. The dispersion 20 containing the nanoelements 6 is then deposited on a metal foil 22 using a syringe 24 or other applicator. For example, the metal foil 22 may include Sn foil. Next, as seen in FIG. 3, another layer of metal foil 22 is placed on the deposited dispersion 20 and the entire structure is then introduced through a pair of rotating rollers 26 with a small gap to compress the structure. In the illustrated embodiment, this produces a Sn-Si nanocomposite core 2. A stock Sn-Si nanocomposite can also be produced by electrocodeposition. Cold extrusion, casting, or other methods are used to transform the stock Sn-Si nanocomposite into the desired shape of the core 2. While FIG. 3 illustrates the formation of a nanocomposite

core 2 that includes a metal plus nanoelements 6, in other embodiments, the nanoelements 6 are incorporated into the cladding 4 material.

[0030] For the manufacturing of fibers 50 embedded with crystalline metal nanowires (e.g., gold, platinum, or silver), suitable nanoelements 6 (e.g., ceramics, oxides, carbides or borides) can be mixed and dispersed into the metal core 2 in the macroscopic preform 8 to increase the viscosity of the molten metal; it also reduces the interfacial energy between the liquid metal of the core 2 and material of the cladding 4 to suppress the fluid instability during thermal drawing, thus allowing further size reduction of the metal core 2 to nanoscale sizes. The nanoelements 6 may also include semiconductor materials, high temperature metals, carbon, and ceramics. For metals, the presence of the nanoelements 6 suppresses the instability that would otherwise force the creation of the metal in the nanowires 52 to break and form droplets; thereby breaking the continuous nature of the elongate nanowire 52. The presence of the nanoelements 6 enables long length fibers 50 to be created that have long lengths (greater than 1 meter). As explained herein, the prior art has not been able to generate crystalline metal nanowires 52 having useful lengths (e.g., greater than 1 meter).

[0031] Referring back to FIG. 1A, in operation 120, the preform 8 is then thermally drawn through a furnace 12. The furnace 12 is part of a fiber drawing furnace which is well known and commercially available. The fiber drawing furnace operates using a furnace 12 that applies heat to the preform 8. The preform 8 is typically loaded above the fiber drawing furnace and upon insertion the preform 8 necks down on its own and the preform 8 end is cutaway and fixed to a fiber drawing mechanism (e.g., spool, wheel or the like). The fiber drawing furnaces enables one to control the temperature of the furnace 12 which is set at a designated value above the softening temperature of the glass part of the preform 8. The speed of the downward linear motion may be controlled by speed of the fiber drawing mechanism. The diameter (or other dimension) of the pulled fiber may be monitored during fiber formation. A load cell may be used as part of the fiber drawing furnace to measure and monitor the drawing force which is an indicator of fiber quality and processing condition because it is directly related to the viscosity of the softened material at the neck-down area 14. Tension monitoring can be incorporated into the system (along with measured diameter) and used as a feedback signal to adjust or modulate the drawing/feeding speed and temperature of the furnace 12.

[0032] Next, as seen in operation 130, the reduced diameter fibers that have been drawn through the furnace 12 are then cut and placed in a bundle 26 or stack and then jacketed by the same material 10 that was used to create the preform 8 as illustrated in operation 140.

This creates another preform 8' that is then subject to thermal drawing as seen in operation 150 in FIG. 1B. The newly formed preform 8' is run through the fiber drawing furnace as explained above. In this regard, the method provides for iterative size reduction as each pass through the furnace 12 reduces the diameter of the core 2 to form the wires. In one embodiment as illustrated in FIGS. 1A and 1B, two passes through the furnace 12 may be enough to generate a fiber 50 that has continuous crystalline metal nanowires therein. FIG. 2B illustrates the process ends after two passes through the furnace 12 whereby the final fiber 50 has the crystalline metal nanowires therein (step 160). The crystalline metal nanowires have nanometer sized dimensions, namely, a diameter less than 100 nm. In some embodiments, the nanowires may have non-circular cross-sectional shapes. In such instances, the longest cross-sectional dimension of the nanowire would be less than 100 nm. As seen in FIG. 1B (dashed line), optionally, additional preforms 8 may be created after the second preform 8' has been run through the furnace 12. The additional preforms 8' are created as previously explained whereby the drawn fibers are cut and bundled or stacked and a new preform is formed using the same cladding material 10. This new or additional preform 8' is then run through the furnace 12 again until the desired final feature size is achieved.

[0033] FIG. 2 illustrates a flowchart illustrating another illustrative method of thermally drawing a fiber 50 with cross-sectional views of the core 2, cladding 4, and preform 8 being illustrated. In this embodiment, a first preform 8 is formed that includes a core 2 and cladding 4. The nanoelements 6 are dispersed in the core 2, the cladding 4, or both the core 2 and the cladding 4. The initial preform 8 is subject to thermal drawing and cutting as seen in operation 200 which generates smaller-sized fibers 30. These fibers 30 are then bundled or stacked and wrapped in a cladding 4 to create another preform 8' and then subject to another thermal drawing and cutting operation as seen in step 210. Another set of fibers 30' is created with progressively smaller cores 2 and then bundled and stacked and wrapped in a cladding 4 to generate another preform 8''. The process of thermally drawing and cutting may be repeated any additional number of times as illustrated in step 220 to generate the final fiber 50 containing the nanowires 52 (FIG. 1C) contained therein.

[0034] FIG. 2 illustrates the final fiber 50 that contains a proximal end 32 and a distal end 34. As seen in FIG. 2, the distal end 34 of the fiber 50 has a cross sectional dimension that is much smaller ($\ll$) than the cross sectional dimension of the proximal end 32 of the fiber 50. This construction has the advantage in that the proximal end 32 of the fiber 50 and the wires 52 contained therein can be easily interfaced with back-end electronic interfaces due to its

larger size. Numerous applications can be enabled by the fibers 50. These include, for example, applications for thermoelectric generators, battery electrodes, low current fuses, nano-electrode arrays, reinforcement for composite materials, sensors for material or sample study at the micro or nanoscale, metamaterials or plasmonic materials for telecommunication applications.

[0035] One particular example of a use for the fiber 50 is for cell-based assays. In particular, the nanowires 52 that are contained in the fiber 50 can terminate at electrodes 54 (FIG. 4) that are formed at the distal end 34 of the fiber 50. The electrodes 54 that are formed at the distal end 34 of the fiber 34 may be active electrodes in which current is applied to the cell or other sample or, alternatively, the electrodes 54 may be passive electrodes that are used more for detection purposes.

[0036] FIG. 4 illustrates one such example a fiber 50 that includes an electrode-embedded fiber with graded dimensions and material composition between the proximal end 32 and the distal end 34. That is to say the fiber 50 includes a distal 34 end having a very small diameter and a proximal end 32 that has a diameter that is much larger than that of the distal end 34. The distal end 34 of the fiber includes an array 36 of electrodes 54 that are exposed and made of biocompatible materials used for interfacing with biological cells 300. The dimension of every embedded wire 52 is gradually increased from nanoscale to macroscale (together with the surrounding insulation tubes) starting from the distal end 34 that contains the exposed electrodes 54 and moving proximally in the direction of the proximal end 32. In addition, the constituent metal of the embedded wires 52 can also be changed from something with biocompatibility at the distal end 34 to low resistivity for high fidelity off-chip signal routing. The wider proximal end 32 of the fiber 50 is connected to an interface device 56 that connects to 58 control circuitry such as a PCB for signal transmission, signal receiving, processing, and storage.

[0037] The electrode-embedded fiber 50 illustrated in FIG. 4 may be used for cellular electrophysiological measurements with sub-cellular spatial resolution and intracellular phenotyping capability. The electrode 54 dimension, inter-electrode arrangement, and material can be designed for different biological cell types and counts. Typically, the electrode 54 dimension is significantly smaller than a typical cell size ($\sim 10\text{-}100\text{ }\mu\text{m}$) so as to spatially confine the emanated electric field for highly localized measurements as illustrated in FIG. 3 inset. On the other hand, the electrodes 54 do not need to be unduly small (i.e. $<20\text{ nm}$) as the goal is to identify and track changes of intra-cellular components such as nucleus, mitochondria, chloroplasts, endoplasmic reticulum, Golgi, and even lysosome.

[0038] In the embodiment of FIG. 4, various pairs of electrodes 54 are used to extract the two dimensional spatial impedance distribution along the surface of the cell. An AC voltage V_{AC1} is applied across the E1-E2 pair such that the current emanated from one electrode penetrates the intracellular space above and in between the pair. A higher frequency directs the trans-cellular current to flow nearer to the top cell membrane (dashed traces) while a lower frequency does the opposite (solid traces). This is intuitive given that the higher frequency AC current can permeate the cell membrane and some capacitive subcellular components more effectively, and vice versa. As a result, the electrode-embedded fiber 50 has the ability to perform intracellular phenotyping in the depth (z) dimension by taking differential measurements over several different AC frequencies. Since the current always starts and ends with an electrode, the intracellular impedance right above an electrode can alternatively be extracted by using two nearby electrodes: by applying an AC voltage V_{AC2} across E3 and E5 to measure impedance above E4 as shown in the FIG. 4 inset.

[0039] For the electrodes 54 in the distal end 34, metals with known biocompatibility such as gold and platinum may be used; for the proximally extending remainder of the nano/macro electrodes 54, metals with low resistivity such as copper or silver may be used as illustrated starting at the transition 60. For the cladding 4, materials that are biocompatible, mechanically robust, and electrically insulating such as glass (for drawing high melting point metals) and polymer (for drawing low melting point metals) can be used. In addition, embedding air or vacuum insulation within the cladding 4 may optionally be used to further minimize inter-electrode crosstalk.

[0040] The electrode-embedded fiber 50 solves an important biotic/abiotic interfacing problem. Not only is the electrode-embedded fiber 50 adaptable to different cell types and counts requiring different phenotyping resolutions and surface areas, the electrode-embedded fiber 50 includes a proximal interface that is amenable to fit the same or similar PCB without re-design. In other words, the electrode-embedded fiber 50 is scalable, cheap and disposable while the PCB and chipset are reusable. The electrode-embedded fiber 50 also takes care of the dimension and material mismatch between the cell phenotyping surface and sampling/processing circuitries. In the larger context, the electrode-embedded fiber 50 approach generally tackles the nano-to-macro interfacing challenges for 2D interconnection electrode arrays. Air or vacuum insulation could be embedded inside the fiber 50 toward ideal electrical interconnection with minimal parasitic coupling. Note that only the cores of the produced fibers are needed, the cladding materials can be selectively etched away using organic solvents for polymer or HF solution for glass or quartz.

[0041] FIG. 5 illustrates an electrode-embedded fiber 50 cell-based assay platform. As seen in FIG. 5, cell culture plates 62 are provided with multiple wells 64. At the bottom of each well 64, several openings (not shown) are created for the electrode-embedded fibers 50 to plug in and then seal any resultant gap at the rim. The proximal end 32 of the electrode-embedded fibers 50 are connected to precision LCR meter (impedance measuring device) to perform impedance spectroscopy during platform validation and actual operation. Each well 64 may have a number of electrode-embedded fibers 50 that terminate or interface with the well surface. A cell or multiple cells 300 that sit atop the distal electrode array of the electrode-embedded fibers 50 may have hundreds or even thousands of separate electrodes that are covered by the cell.

[0042] Prior to any cell phenotyping experimentation, the assembled plates are exposed under UV and injected with buffer solution into the electrode-embedded fiber-plugged cell culture wells to check for leaks and sterility. In addition, one can obtain impedance spectra of the buffer solution without cells using several pairs of electrodes 54. The cell-based assay is able to examine cellular morphology, proliferation rate, attachment-adhesion-spreading, and intra-cellular content changes, which are useful early indicators of pharmaceutical or adverse cellular effects. The assay platform of FIG. 5 allows one to detect and quantify these cellular events in a real-time, label-free, and non-invasive manner.

[0043] The assay platform allows oncologists to perform assay-directed chemotherapy instead of empirically based therapy, i.e. drug selection based on clinical trial evidence. Although in principle many complex factors may also determine the outcomes of chemotherapy *in vivo*, the use of the assay platform of FIG. 5 could ultimately replace the multi-well assays and result in more rational and personalized treatment decisions in this highly fatal carcinoma disease. Compared to conventional assays, e.g. cell viability assays (MTT and ATP assays), the electrode-embedded fiber assays can provide more informative cellular data as additional safeguards to predict *in vivo* response.

[0044] FIG. 6A illustrates a schematic of the macro preform that was experimentally tested with a Sn-Si nanocomposite core and PES cladding. About 2 volume % of Si nanoparticles (NPs) with a diameter of 80 nm were incorporated into the Sn matrix through electroplating. The macro Sn-Si nanocomposite preform was then cladded with PES for thermal drawing. The consolidated preform was fed into a cylindrical furnace at constant feeding speed (50 $\mu\text{m}/\text{sec}$) at 275 $^{\circ}\text{C}$ with a constant drawing speed of around 6 m/min. Next, the drawn fibers were cut, stacked and reconsolidated from the first draw following the procedure shown in FIGS. 1A and 1B. The iterative size reduction enabled by thermal

drawing gives rise to the micro-to-nano metal wires. After drawing, some polymer claddings were dissolved in Dichloromethane (DCM) to expose the metal wires for scanning electron microscopy (SEM) characterization. FIG. 6B illustrates a photographic image of the drawn electrode-embedded fiber made from the Sn-Si nanocomposite. FIG. 6C illustrates a cross-sectional SEM image of the Sn nanowire. As one moves closer to the distal end, the narrower the wire becomes. FIG. 6D illustrates a SEM image of the Sn nanowire after chemical etching of the PES cladding. FIG. 6E illustrates a pure Sn microwire with a diameter of about 10 μm after etching of the PES cladding. In the thermal drawing method, the nanoelements incorporated either are pushed to the metal/polymer interface during drawing, and serve as the interfacial energy modifier, or stay inside the metal matrix and increase the viscosity of the molten metal.

[0045] While embodiments of the present invention have been shown and described, various modifications may be made without departing from the scope of the present invention. The invention, therefore, should not be limited except to the following claims and their equivalents.

What is claimed is:

1. A method of thermally drawing fibers containing continuous crystalline metal nanowires therein comprising:

a) forming a preform comprising an inner core comprising the crystalline metal and an outer cladding, wherein at least one of the core and cladding having dispersed therein nanoelements;

b) drawing the preform through a heated zone to form a reduced size fiber;

c) forming a second preform created from a plurality of fibers from the reduced size fiber of (b); and

d) drawing the second preform of (c) through the heated zone to form another reduced sized fiber having a continuous length exceeding one meter and containing crystalline metal nanowires therein having a diameter less than 100 nm.

2. The method of claim 1, wherein the nanoelements comprise nanoparticles, nanowires, nanoplates, nanoflakes, or nanowhiskers.

3. The method of claim 1, further comprising forming a third preform created from a plurality of fibers of (d) and drawing the third preform through the heated zone to form another reduced sized fiber having a continuous length exceeding 1 meter and containing crystalline metal nanowires therein having a diameter less than 100 nm.

4. The method of claim 3, further comprising forming a one or more additional preforms created from a plurality of fibers formed by the third preform and drawing the one or more additional preforms through the heated zone to form another reduced sized fiber having a continuous length exceeding 1 meter and containing crystalline metal nanowires therein having a diameter less than 100 nm.

5. The method of claim 1, wherein the nanoelements have a diameter or major cross-sectional dimension within the range of 1 to 100 nm.

6. The method of claim 1, wherein the nanoelements comprises a metal.

7. The method of claim 1, wherein the nanoelements comprise a ceramic.

8. The method of claim 1, wherein the core comprises one of gold, platinum, or silver.
9. The method of claim 1, wherein the cladding comprises a polymer.
10. The method of claim 1, wherein the cladding comprises a glass.
11. The method of claim 1, further comprising sintering the reduced sized fiber having metal nanowires therein.
12. The method of claim 1, further comprising cutting the fiber, wherein the cut fiber has a distal end and a proximal end and the diameter of the distal end is $\ll$ the diameter of the proximal end.
13. A method of thermally drawing a fiber containing crystalline metal nanowires therein comprising:
 - forming a preform comprising an inner core having a plurality of individual metal wires surrounded by an outer cladding, wherein at least one of the inner core and cladding comprise nanoelements dispersed therein; and
 - drawing the preform through a heated zone to form a reduced size fiber having a length of at least one meter and containing a plurality of continuous crystalline metal nanowires therein having a maximum cross-sectional dimension less than 100 nm.
14. The method of claim 13, wherein the nanoelements comprise one or more of nanoparticles, nanowires, nanoplates, nanoflakes, or nanowhiskers.
15. The method of claim 13, wherein the nanoelements have a diameter or major cross-sectional dimension within the range of 1 to 100 nm.
16. The method of claim 13, wherein the nanoelements comprises a metal.
17. The method of claim 13, wherein the nanoelements comprise a ceramic.

18. The method of claim 13, wherein the core comprises one of gold, platinum, or silver.

19. The method of claim 13, wherein the cladding comprises a polymer.

20. The method of claim 13, wherein the cladding comprises a glass.

21. A nanoelectrode array comprising:

a fiber having a distal end and a proximal end, the fiber having a plurality of crystalline metal nanowires each with a maximum cross-sectional dimension less than 100 nm embedded therein and terminating at a plurality of exposed electrodes at the distal end of the fiber, wherein the distal end of the fiber has a diameter that is $\ll$ than a diameter of the proximal end of the fiber.

22. The nanoelectrode array of claim 21, further comprising a circuit interface device coupled to the proximal end of the fiber.

23. The nanoelectrode array of claim 21, wherein the distal end of the fiber is disposed in a well, channel, or reservoir of a microfluidic device.

24. The nanoelectrode array of claim 21, wherein the composition of the metal nanowires changes along the length thereof with the exposed electrodes comprising a first metal and a proximal portion that is located proximally with respect to the exposed electrodes comprises a second, different metal.

25. An article of manufacture comprising:

a fiber having a distal end and a proximal end, the fiber having a plurality of crystalline metal nanowires embedded therein, each nanowire having a maximum cross-sectional dimension less than 100 nm, wherein the fiber has a length exceeding 1 meter.

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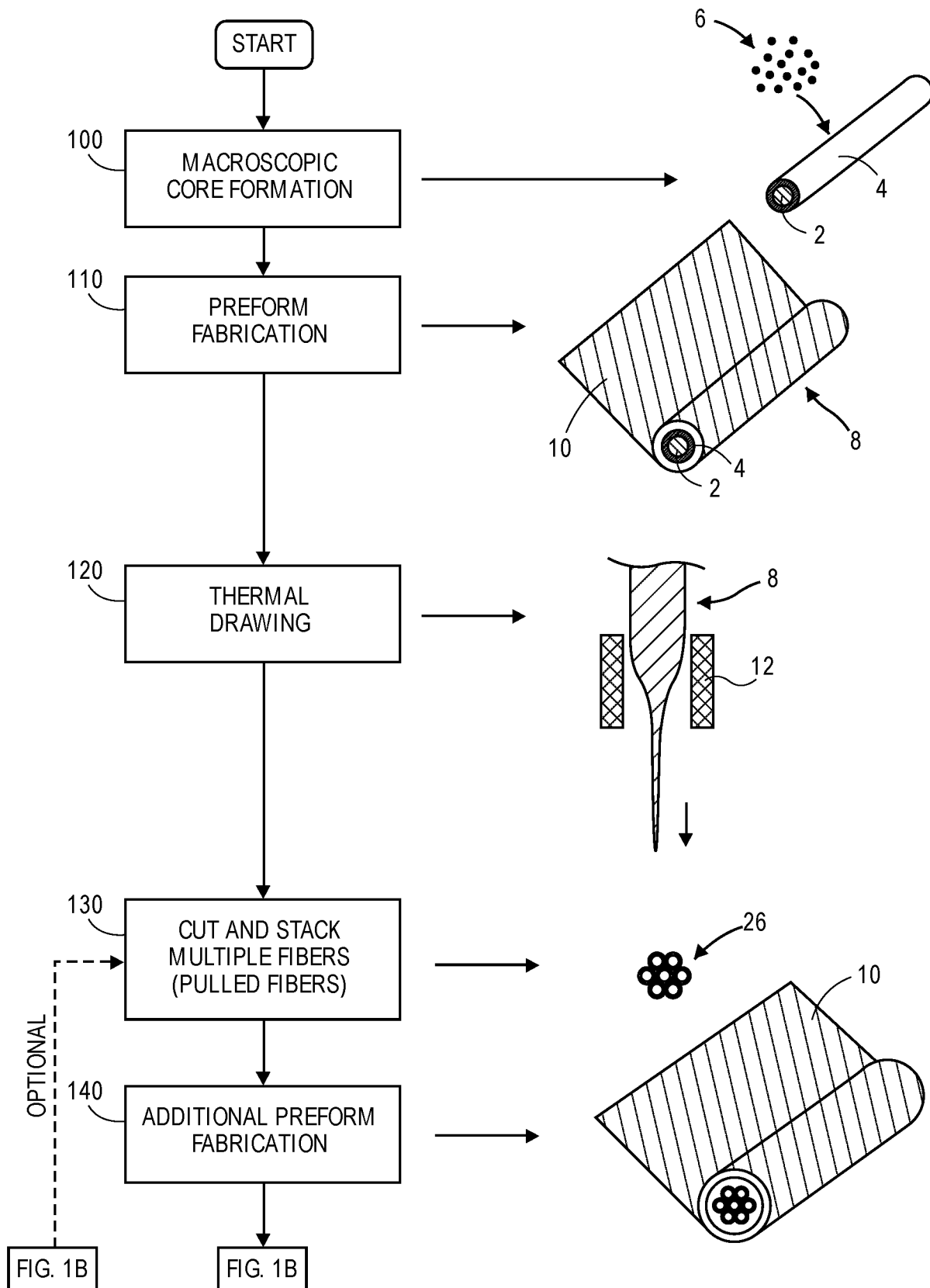
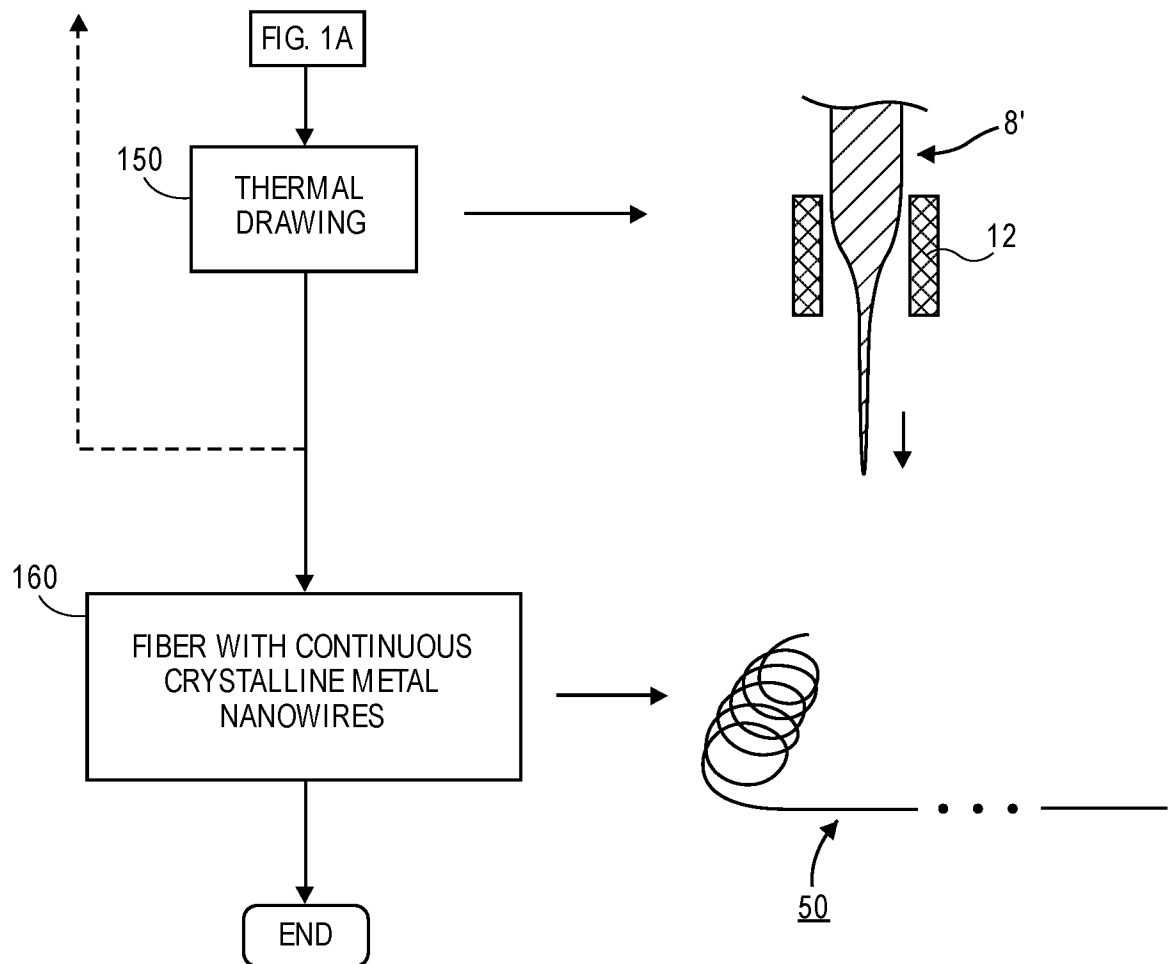
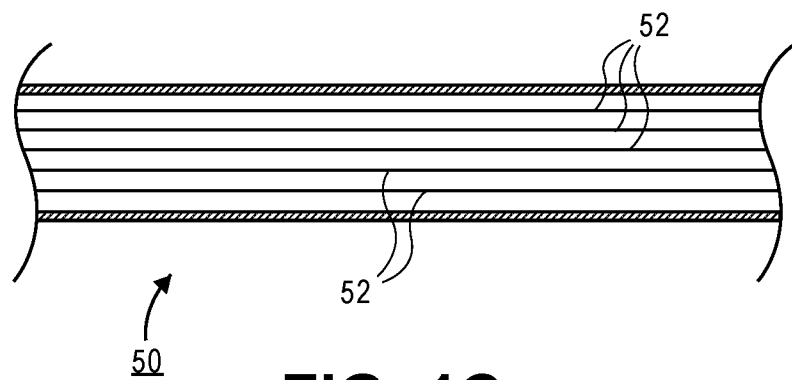
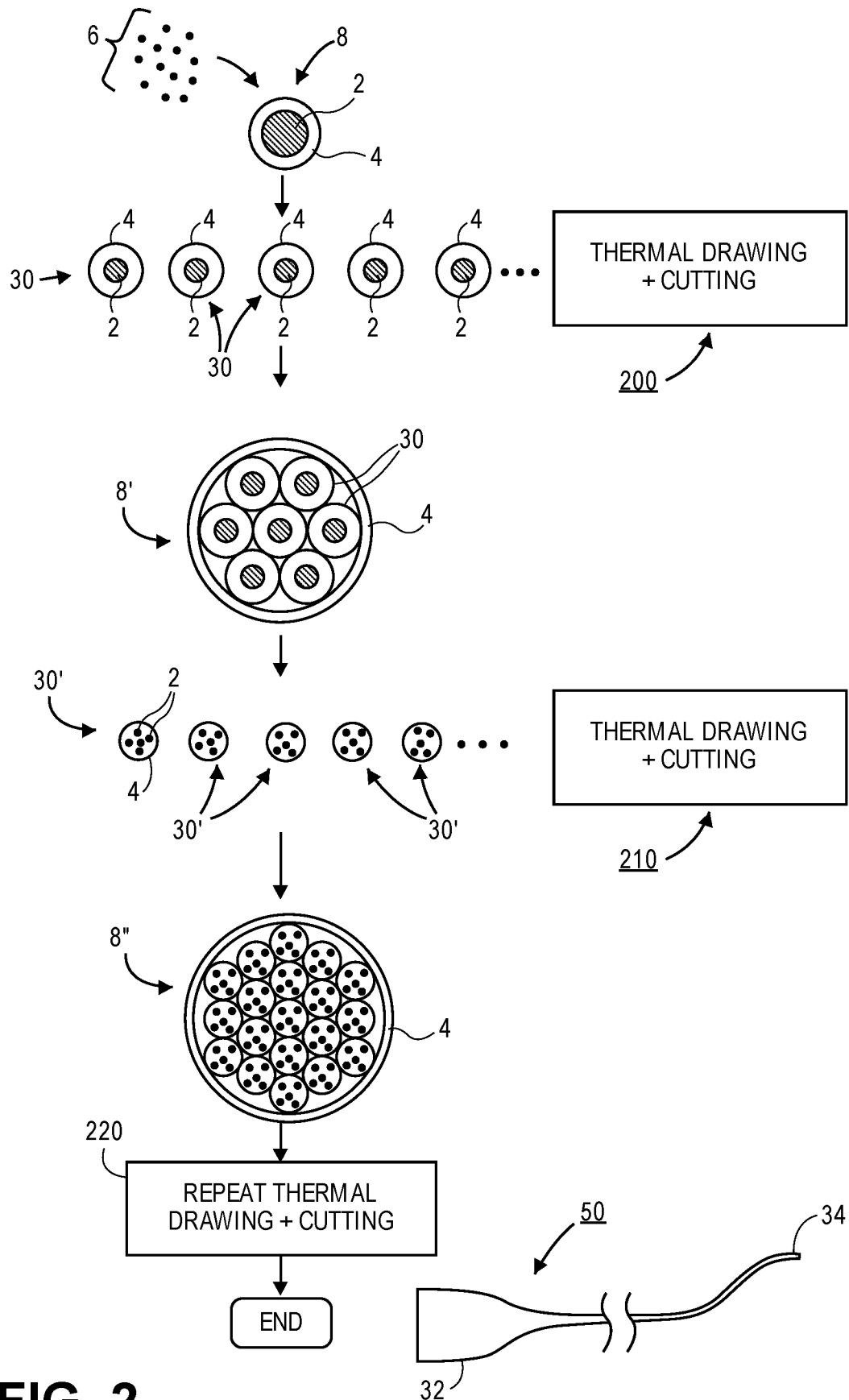


FIG. 1A

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**FIG. 1B****FIG. 1C**

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**FIG. 2**

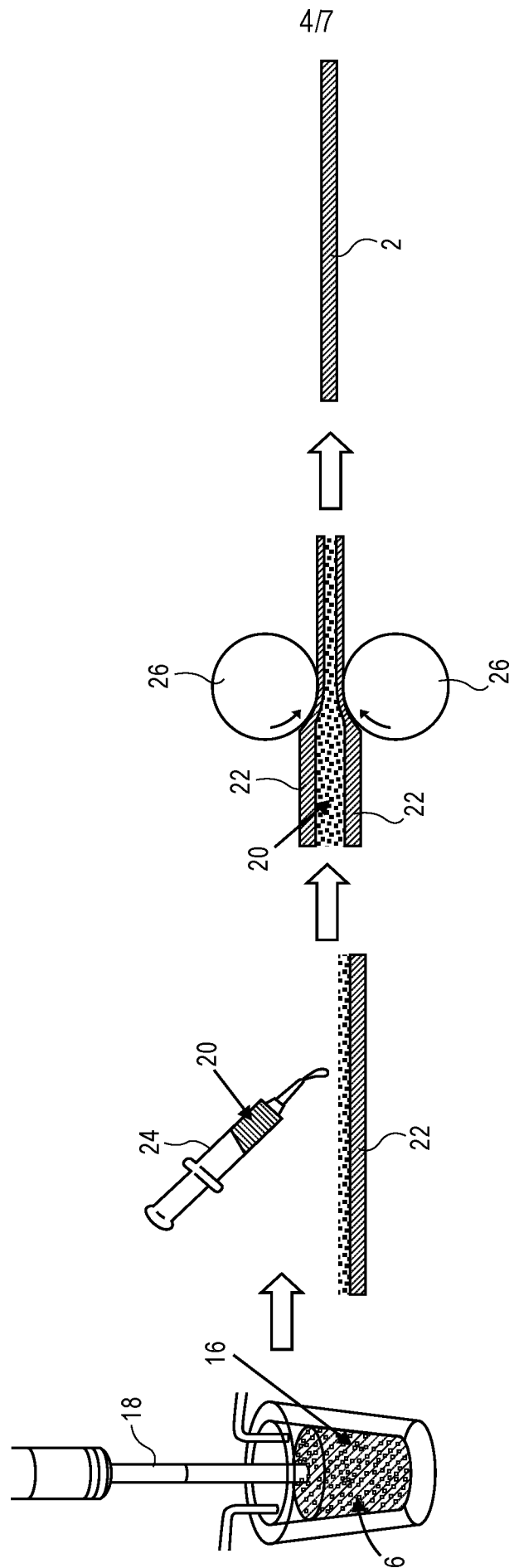
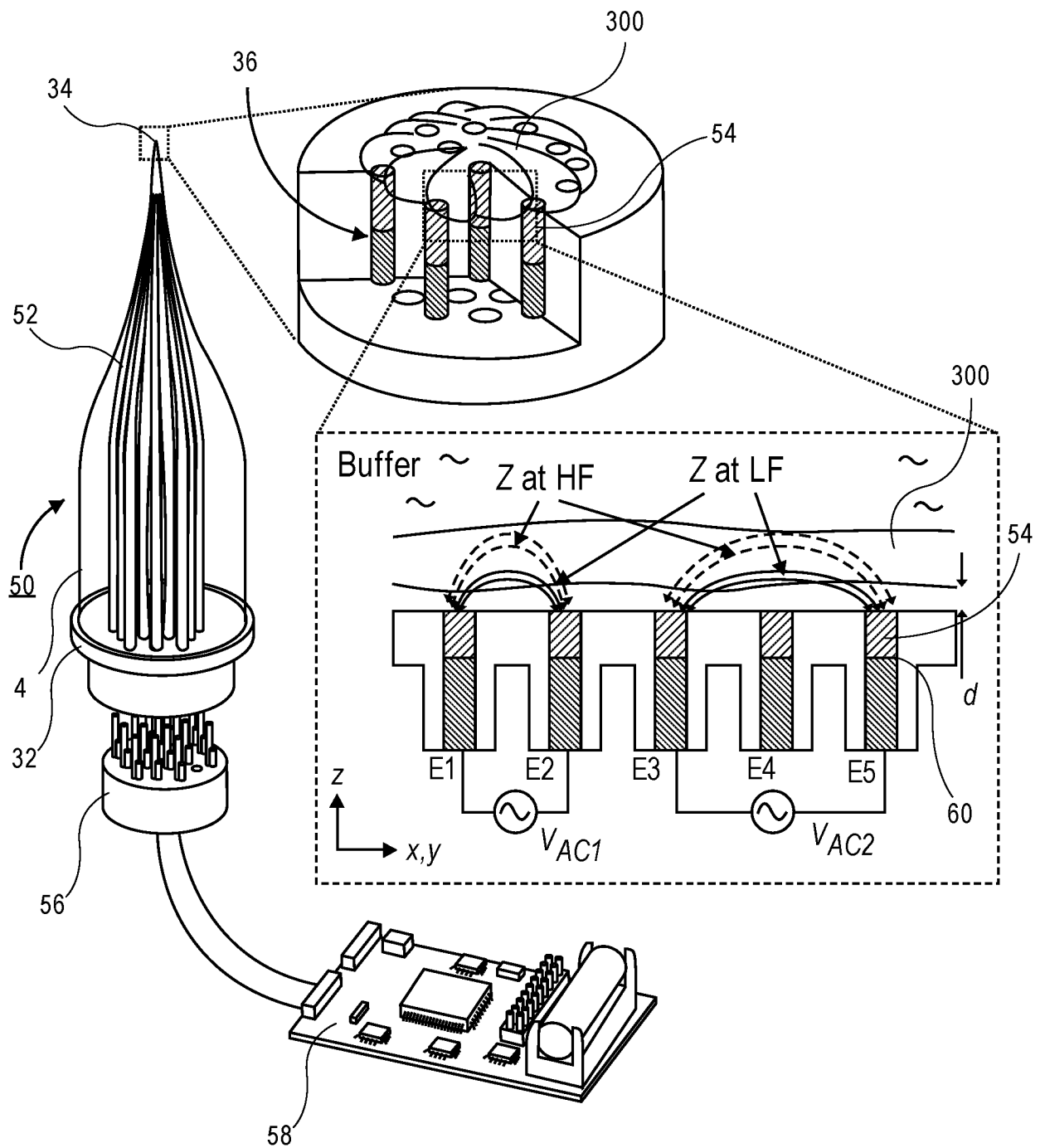


FIG. 3

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**FIG. 4**

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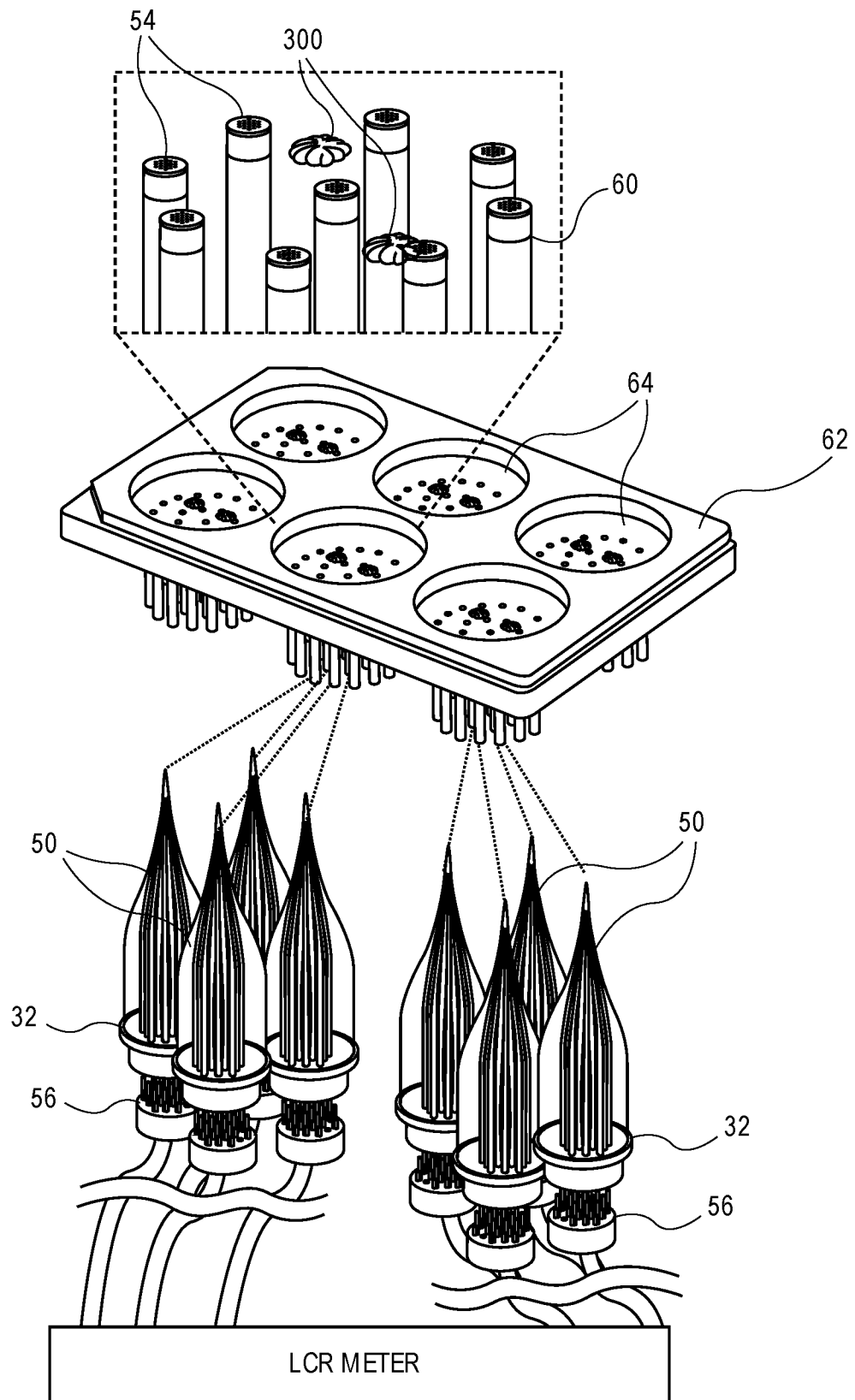


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/014262**A. CLASSIFICATION OF SUBJECT MATTER****D06M 11/83(2006.01)i, D06M 11/42(2006.01)i, D02G 3/36(2006.01)i**

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)

D06M 11/83; B29C 55/30; C03B 37/022; H01B 7/00; B29B 9/00; D02G 3/36; D02G 3/04; D02G 3/00; H01B 13/06; D06M 11/42

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: thermally drawing, nanowire, metal, core, cladding, preform, heat zone, reduce size, diameter, continuous length**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007-0245774 A1 (DUTTA, BIPRODAS) 25 October 2007 See abstract; claims 1-4, 10; paragraphs [0002], [0017], [0051]-[0054], [0064], [0067]; and figure 1.	1-25
A	US 2011-0097581 A1 (DENG, DAOSHENG et al.) 28 April 2011 See abstract; claims 1-12; and figures 1A-3.	1-25
A	US 2014-0262433 A1 (POSTECH ACADEMY-INDUSTRY FOUNDATION) 18 September 2014 See abstract; claims 1-13; and figures 1-5.	1-25
A	US 2013-0202888 A1 (MASSACHUSETTS INSTITUTE OF TECHNOLOGY et al.) 08 August 2013 See abstract; claims 1-9, 19-21; and figure 1B.	1-25
A	WO 2013-032936 A1 (THE TRUSTEES OF COLUMBIA UNIVERSITY IN THE CITY OF NEW YORK) 07 March 2013 See abstract; and claims 1-39.	1-25



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

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"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

13 May 2016 (13.05.2016)

Date of mailing of the international search report

13 May 2016 (13.05.2016)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

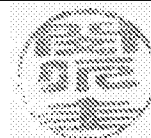
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/014262

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