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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 September 2013 (12.09.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/134779 A1

(51) International Patent Classification:
H01Q 3/01 (2006.01) *B82B 1/00* (2006.01)
H01Q 1/24 (2006.01)

(21) International Application Number:
PCT/US2013/030268

(22) International Filing Date:
11 March 2013 (11.03.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/609,109 9 March 2012 (09.03.2012) US

(71) Applicant: **AYON, Arturo, A.**; 7815 Dashwood, San Antonio, TX 78240 (US).

(72) Inventors; and
(71) Applicants : **STRICKLAND, Diana, L.** [US/US]; 9035 Cross Mountain Trail, San Antonio, TX 78255 (US). **KOTHA, Ramakrishna** [IN/US]; 8-3-231/W/26, Plot #26, Womens CO-OP Area, Krishna Nagar Yousufguda, Hyderabad, Andhra Pradesh 500045 (IN).

(74) Agent: **BORCHERS, William, R.**; Jackson Walker LLP, 112 E. Pecan, Suite 2400, San Antonio, TX 78205 (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, BN, 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, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, 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, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, 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, RS, SE, SI, SK, SM,

[Continued on next page]

(54) Title: SELF-ALIGNED TUNABLE METAMATERIALS

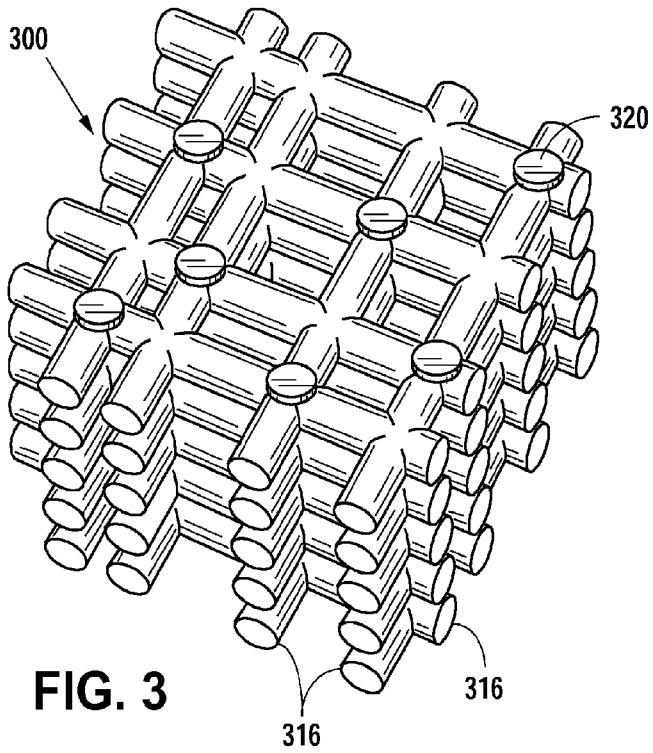


FIG. 3

(57) Abstract: [0055] A self-aligned tunable metamaterial is formed as a wire mesh. Self-aligned channel grids are formed in layers in a silicon substrate using deep trench formation and a high-temperature anneal. Vertical wells at the channels may also be etched. This may result in a three-dimensional mesh grid of metal and other material. In another embodiment, metallic beads are deposited at each intersection of the mesh grid, the grid is encased in a rigid medium, and the mesh grid is removed to form an artificial nanocrystal.

WO 2013/134779 A1

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

TITLE: SELF-ALIGNED TUNABLE METAMATERIALS

BACKGROUND

Field of the Disclosure

[0001] This disclosure relates to the field of tunable metamaterials, and more particularly to self-aligned arrays of nanomaterials.

Description of the Related Art

[0002] Metamaterials are synthetic, composite materials with periodic structures, known for their ability to create electromagnetic or acoustic properties that are not found in nature and that may determine how the material interacts with various types of radiation. Metamaterials may direct radiation either due to the external shape of a metamaterial structure or by spatially indexing the metamaterial. Conventional methods of forming metamaterial periodic and spatially indexed arrays in the nanoscale range, such as ion beam methods, are limited by processing options, materials, and ultimately, economic feasibility, and may be poorly suited to gain widespread industrial applicability. Therefore, there is a need in the art for an industrial method of producing desired tunable nanowire arrays in sufficient quantities and at relatively low cost.

BRIEF DESCRIPTION OF THE DRAWINGS

[0003] **FIG. 1** is a prior art representation of an empty-space-in-silicon process;

[0004] **FIG. 2A** is a block diagram of selected elements of an embodiment of a structure for forming a self-aligned metamaterial;

[0005] **FIG. 2B** is a block diagram of selected elements of an embodiment of a structure for forming a self-aligned metamaterial;

[0006] **FIG. 2C** is a block diagram of selected elements of an embodiment of a structure for forming a self-aligned metamaterial;

[0007] **FIG. 3** is a block diagram of selected elements of an embodiment of a self-aligned metamaterial;

[0008] FIG. 4 is a flow chart of an exemplary method of producing a self-aligned metamaterial; and

[0009] FIG. 5 is a perspective view of an artificial nanocrystal.

DESCRIPTION OF THE EMBODIMENT(S)

[0010] Various types of metamaterials are known that possess bulk electromagnetic properties different from materials observed in nature. These properties may create specific dispersion characteristics within the metamaterial, or they may control the way the metamaterial reflects, refracts, absorbs, scatters or transmits radiation.

[0011] Metamaterials are also known that direct electromagnetic radiation. The ability to direct radiation can result from an outer form or shape of a given material, for example, as in a conventional lens. Another way to control the path of radiation can result from the internal structure of a material. Spatial indexing, as used herein, refers to a patterned structure of a material that enables tuning of the electromagnetic properties of the material in space. For example, the geometry of an array structure and/or the constituent material composition may be varied in space. In one embodiment, a smooth increase of an array periodicity in a given direction may result in a gradual alteration of a metamaterial's permittivity in the given direction. Such spatially indexed properties of a metamaterial may be realized in 2-D and/or 3-D and may encompass tailoring the metamaterial for different kinds of properties and/or combinations of properties varying in space, as desired. One example of a spatially indexed metamaterial may exhibit a smooth increase in array periodicity in a single given direction. In other examples, the smooth increase in array periodicity may be present in two or three directions.

[0012] Control of bulk properties may be accomplished by positioning particles in periodic or non-periodic arrays with dimensions much smaller than an operational wavelength of electromagnetic radiation. The shape, placement and/or orientation of the particles, as well as constituent materials of the particles and/or a host material in which the particles reside, may determine the bulk properties of the array structure. The bulk properties may be tuned for a desired interaction in a particular range of wavelengths (or frequencies) of electromagnetic radiation. For example, for long wave infrared frequencies and higher, the array structure may be formed in nanoscale dimensions. Below infrared frequencies, the array structure may also be of nanoscale

dimensions. The array structures may be formed as grids, meshes, or crystal-like lattices in nanoscale dimensions that may be 2-D and/or 3-D in scope.

[0013] The novel and non-obvious fabrication processes, as described in further detail herein, provide various means for forming the array structure, as well as placing particles composed of desired constituent materials at desired locations in the array structure. Various dimensions, features, and compositions may be employed for tuning the array structure to interact with radiation of a desired frequency and/or frequency range(s). The control of bulk properties realized using the methods described herein may enable applications such as absorbers, waveguides, sensors, reflectors, phase control devices, radiation concentrators, cloaking devices, imaging devices, and electromagnetic pulse protectors, among others.

[0014] One example structure for realizing a spatially indexed metamaterial is an array structure, such as a grid, mesh, or lattice, that may be implemented as a 3-D framework. Such an array structure may be realized in one embodiment using nanowires to form the framework. The tunability of such a 3-D nanowire array may be achieved by modulating dimensional properties, such as wire thickness, array spacing, etc., as well as through selection of the material(s) for the nanowire array. Voids and/or empty space may also be used to tune the properties of the metamaterial, as will be discussed in further detail below.

[0015] While conventional semiconductor processing methods may be useful to produce array structures on a 2-D surface of a flat substrate, such methods may be excessively costly and laborious in the nanoscale range. Furthermore, many conventional processing methods do not generally scale up to a 3-D approach. Thus, producing 2-D and/or 3-D nanoscale array structures with specific tunable properties using conventional methods, for example by forming layer upon layer in a successive manner, may not be economically feasible and may be unsuitable for widespread industrial exploitation. As will be described herein, a novel and patentably distinct method for forming 2-D and 3-D nanoscaled arrays is disclosed that relies on self-alignment through inherent thermodynamic properties of a silicon substrate.

[0016] In the following description, details are set forth by way of example to facilitate discussion of the disclosed subject matter. It should be apparent to a person of ordinary skill in the

field, however, that the disclosed embodiments are exemplary and not exhaustive of all possible embodiments.

[0017] Throughout this disclosure, a hyphenated form of a reference numeral refers to a specific instance of an element and the un-hyphenated form of the reference numeral refers to the element generically or collectively. Thus, for example, widget 12-1 refers to an instance of a widget class, which may be referred to collectively as widgets 12 and any one of which may be referred to generically as a widget 12.

[0018] Turning now to the figures, **FIG. 1**, is a prior art representation of empty-space-in-silicon process **100**, sometimes also known as silicon-on-nothing [*see* T. Sato, *et al.*, Electrochem. Soc. Proc. 539, 2000-17 (2000)]. The process **100** is an example of a method of producing self-aligned structures in a silicon substrate. In operation **101**, deep reactive etching (also known as DRIE) is performed on an etched single crystal silicon substrate to produce a deep channel of desired dimensions (i.e., width and depth). In operation **102**, several intermediate states of a single annealing step are shown that may result in self-organization (i.e., self-alignment) of empty bubbles in the bulk silicon that become buried upon healing of the top silicon surface. The annealing may be performed under hydrogen at relatively high temperatures (e.g., at about 1100°C) and at ambient pressures of about 10 Torr. Such processing conditions promote silicon migration and formation of voids or channels, depending upon the etch geometry.

[0019] Referring now to **FIG. 2A**, a block diagram of selected elements of an embodiment of structure **200-1** for forming a self-aligned metamaterial is shown. Structure **200-1** is shown as a cut-away view and may be representative for structures of various dimensions and/or may represent a repeating element in a larger super-structure (not shown). Structure **200-1** shows a pattern formed in photoresist **202** at the surface of a crystalline silicon substrate **204** that has been etched to produce deep channels **206** of a desired geometry. The dimensions of the geometry, including width **208** and depth **210** may be determined at this step for tuning final dimensions of a 3-D nanowire array, as will be subsequently demonstrated. For example, width **208** may be determined by patterning photoresist **202** accordingly, while depth **210** may be determined by process etch parameters. A number of deep channels **206** as well as spacing between deep channels **206** may also be determined by patterning

photoresist **202**. In this manner, tuning of a 3-D nanowire array may be performed using 2-D patterning and etching techniques.

[0020] FIG. 2A is a block diagram of a prior-art embodiment of structure **200-2** for forming a self-aligned metamaterial. Structure **200-2** is similar to structure **200-1** (see **FIG. 2A**) but is shown after an annealing step that has transformed deep channels **206** into channel grids **216**, which are self-aligned along the original mask pattern in photoresist **202**. The annealing step may be varied to control a number and arrangement of linear channels **212**, in various embodiments. It is noted that in certain embodiments, linear channels **212** may be formed in a single horizontal layer (not shown) buried beneath a surface of structure **200-2**, which may result in a 2-D array structure (not shown). It is further noted that the dimensions of linear channels **212** also correspond to those of deep channels **206** and of the mask pattern, accordingly. In some embodiments, crystalline silicon substrate **222** itself may be used as a metamaterial with anisotropic bulk permittivity that may have a value of one (1) or a low value. In various embodiments, crystalline silicon substrate **222** may exhibit a spatially indexed permittivity that may vary in a regular or irregular manner in space.

[0021] FIG. 2C is a block diagram of selected elements of an embodiment of structure **200-3** for forming a self-aligned metamaterial is shown. Structure **200-3** is similar to structure **200-2** (see **FIG. 2B**) but is shown with an orthogonal pattern of channels forming a grid pattern in photoresist **214**, which has resulted in a stack of channel grids **216**. In certain embodiments, substrate **218** having channel grids **216** may serve as a metamaterial with desired bulk properties and/or as a spatially indexed metamaterial.

[0022] Also formed in structure **200-3** are vertical wells **220**, which may also be formed using a patterning/etch technique or another method to remove material at a particular location. Vertical wells **220** may penetrate substrate **218** vertically to a desired depth (obscured from view in structure **200-3**) to intersect one or more channel grids **216**. Vertical channels (not shown) may also be formed that do not intersect channel grids **216**. Either with or without intersections, substrate **218** may be used in various embodiments to form metamaterials with isotropic and/or anisotropic bulk permittivity at may have a value of one (1) or a low value. In different embodiments, substrate **218** may exhibit a spatially indexed permittivity that may vary in a regular or irregular manner in space.

As shown in **FIG. 2C**, vertical wells **220** are open at a top surface of substrate **218**, which may extend empty space within channel grids **216** in 3-D. In certain embodiments, vertical wells **220** may provide a route for subsequent deposition steps that fill the array. In other embodiments, vertical wells are formed in a subsequent processing step after channel grids **216** have been formed and/or filled with another material, as will be described below in more in detail. In yet other embodiments, vertical wells **220** may be etched at angles other than normal to channel grids **216**, for example by rotating substrate block **218**. This process may be used, for example, to create a Bragg diffraction grating.

[0023] After channel grids **216** and/or vertical wells **220** have been formed, substrate **218** may be sectioned vertically to reveal ends of channel grids **216**, exposing an inner surface of channel grids **216** to an external atmosphere. In this state, structure **200-3** may be subject to a deposition process (e.g., metallic vaporization, evaporation, sputtering, electroless deposition, and/or electroplating) to form a solid structure within channel grids **216** and/or vertical wells **220**. Different materials may be deposited within channel grids **216** from those deposited within vertical wells **220** to form a nanoscale composite material. In certain embodiments, a partial deposition may result in a tubular (i.e., hollow) lattice structure being deposited within channel grids **216** and/or vertical wells **220**. In one embodiment, a relatively thin deposited metal layer creates a material with permittivity tailored in three dimensions that is substantially zero or near zero (also referred to as epsilon near zero or ENZ). In other instances, a full deposition may result in a solid structure being formed in an interior volume defined within channel grids **216** and/or vertical wells **220**.

[0024] Mask **202** is depicted in structure **200** with lines removed for etching linear trenches. In other embodiments (not shown), the mask pattern and subsequent trenches may be curved. One specific embodiment may include curved patterns to form broken or split rings that allow magnetic and/or magnetoelectric structures to be formed. Arrays of these structures formed as planes of broken toroidal voids and subsequently metallized may represent omega structures (*e.g.*, omega-particle metamaterials), which may display negative permittivity and/or magnetoelectric properties. In combination with metallized vertical channels, such omega structures may exhibit negative index of refraction. Other magnetic structures, such as so-called Swiss rolls and/or oriented helix arrays resulting from tapered walls on deep channels **206** may also be formed in various embodiments.

Such magnetic and/or magnetoelectric structures may be used to tune the permeability or magnetoelectric bulk or spatially indexed parameters of the metamaterial.

[0025] Turning now to **FIG. 3**, a block diagram of selected elements of an embodiment of self-aligned metamaterial **300** is shown. The bulk or spatially indexed properties of self-aligned metamaterial **300** may be achieved by virtue of the dimensions and arrangement of an array structure. In certain embodiments, self-aligned metamaterial **300** is a nanowire array formed by depositing a desired material, as described previously, within channel grids **216** and/or vertical wells **220** (see **FIG. 2**C). Accordingly, vertical elements **320** may correspond to vertical wells **220**, while horizontal elements **316** may correspond to channel grids **216**. Prior to metallization, various process steps may be undertaken, such as additional etching and/or surface treatments. After metallization, the silicon substrate matrix may be etched away or otherwise removed to result in self-aligned metamaterial **300** as shown in **FIG. 3**. In certain embodiments, a subsequent deposition step may be performed to add a matrix, a surface layer, and/or a desired coating to the structure depicted in **FIG. 3**. For example, a ferroelectric coating may provide dynamic tunability to self-aligned metamaterial **300**.

[0026] Vertical elements **320** may be formed from the same material as horizontal elements **316** and may be selected to provide structural support and rigidity to self-aligned metamaterial **300**. In given embodiments (not shown), vertical elements **320** may be formed at every intersection of horizontal elements **316**. Since vertical elements **320** may be formed by different processing operations than horizontal elements **316**, it is noted that vertical elements **320** may also be formed from a different material than horizontal elements **316** for a variety of purposes and applications. For example, vertical elements **320** may be formed as beads or connectors that are insulators (such as SU8) or semiconductors, for example when horizontal elements **316** are conductors and may result in a semiconductor device formed within self-aligned metamaterial **300**. Vertical elements **320** may be flexible to provide desired elasticity or resonance, for example, when horizontal elements **316** are relatively stiff. Vertical elements **320** may also be made of metals, dielectrics, bi-metallics, ferroelectrics, and/or ferromagnetics in order to alter bulk properties. In particular embodiments, vertical elements **320** are formed to achieve deformable, reconfigurable, and/or dynamically controllable mobile structures. In other embodiments, active and/or dynamic materials may be

formed as 2-D or 3-D arrays of antennas driven through vertical elements **320** that are metallized. Individual elements in such arrays may be individually driven (or driven in groups) to create shaped radiation transmission/reception patterns, or may be phased to create steerable radiation beams. In other embodiments, horizontal elements **316** may be formed at least in part as ferroelectric dots that provide controllable features. For example, the ferroelectric dots may be individually voltage biased (or biased in groups) to form arrays that are dynamically tunable and may be spatially indexed along one or more directions or axes. In certain embodiments, horizontal elements **316** may be formed at least in part as magnetic dots and may form a material with permanent magnetization that is also tunable in one or more directions. When vertical elements **220** are etched at certain angles with respect to a substrate surface and subsequently metallized, a material with a very high index of refraction and special dispersion properties may be formed. Self-aligned metamaterial **300** may allow for economical and industrial scale production of a wide variety of novel 3-D array structures that have previously been inaccessible.

[0027] **FIG. 4** is a flow chart of an exemplary method of manufacturing a metamaterial according to the disclosure of the present disclosure. Elements depicted in method **FIG. 4** may be omitted or rearranged, as desired in different embodiments. **FIG. 4** provides an illustrative and non-limiting example of formation of self-aligned metamaterials, as previously discussed herein.

[0028] Manufacturing begins with a masked substrate block **200**, with mask **202**. In step **410**, a two-dimensional grid pattern is laid out on the mask. The grid pattern, including the length, width, and intersections of trace liens, is selected for a desired metamaterial property, such as a specific desired permittivity or resonant frequency. In some embodiments, the grid pattern is selected to be periodic. Further in some embodiments, the grid pattern may be a substantially rectilinear grid, as shown in **FIG. 2C**. In other embodiments, curved or other non-rectilinear grid patterns may be used, including wavy lines, circles, magnetic field lines, spirals, or randomized lines. In some embodiments, non-rectilinear patterns may be used to create artificial magnets.

[0029] The patter of step **410** may involve various geometries and designs, and is not limited to the linear examples presented herein for descriptive clarity (see FIGS. 2A-C, 3). Various types of patterning and etch processes may be employed to create deep channels in the silicon substrate. The

pattern features and dimensions may be selected for a desired configuration of the self-aligned metamaterial, as mentioned previously.

[0030] Once the two-dimensional grid pattern is laid out, in step **420** block **200** is etched using for example deep reactive etching. The etching depth is selected for a desired metamaterial property, and in particular may be selected to provide a desired number of grid layers. In an exemplary embodiment, deep reactive etching is carried out to a uniform depth throughout the two-dimensional grid pattern. However, those having skill in the art will recognize that in some embodiments, the etching depth can be selectively varied to create non-uniform channel depths, which may control desired properties of a metamaterial.

[0031] In step **430**, substrate block **200** is annealed to create a plurality of layered channel grids, each layer following the pattern of the two-dimensional grid pattern. The annealing process is known in the prior art, and may involve hydrogen annealing at relatively high temperature. Annealing creates bubbles that "heal" in layers into the desired pattern. Each channel grid thus formed is analogous to a two-dimensional network of tunnels, and each occupies a single vertical position in the substrate block. In an exemplary embodiment, each channel grid is substantially identical to each other channel grid because the deep reactive etch of step **420** is performed to a uniform depth throughout the block. The channel grids collectively are all vertically self-aligned with one another. At step **430**, the channel grids are not interconnected with each other, but rather lie in a parallel stack of several layers. Those with skill in the art will recognize that substances other than silicon may be used as a substrate, in which case, another type of anneal or thermodynamically self-aligned void array formation process may be used.

[0032] Etching step **440** is a common to a plurality of variations of the method disclosed herein. However, in some embodiments, intervening step **460** may be performed. In general, the method that follows the step-**440** branch, wherein etching step **440** immediately follows annealing step **430** is suitable for embodiments wherein the target metamaterial is a mesh structure. The step-**460** branch, wherein annealing step **430** is followed by a filling step **460** is suitable for embodiments wherein the target metamaterial is an artificial nanocrystal, or wherein vertical well portions of the metamaterial are to be constructed of material different from the material of the two-dimensional

grid. Those having skill in the art will appreciate that many combinations of the basic steps disclosed are possible.

[0033] Following the step-**440** branch, at step **440**, vertical wells **220** are etched substantially orthogonally to the channel wells. For example, in some embodiment, a vertical well is etched at every intersection formed by the two-dimensional grid pattern. In other embodiments, vertical wells may be selectively placed only at some intersections, or may be placed at non-intersecting points along trace lines. The arrangement of vertical wells is selected to impart the desired metamaterial property.

[0034] In some embodiments, where a complete wire mesh is desired, vertical wells **220** may be etched at every intersection, and each vertical well will pass through each layer, so that a network of vertical wells joins every intersection of each layer to the corresponding intersections of each other layer. In other embodiments, a plurality of vertical wells are provided, at least some of which will pass through more than one layer, so that individual wells join two or more layers to one another. The result is a three-dimensional network containing a plurality of substantially identical channel grids joined to one another by a plurality of vertical wells, called herein a 3-D cavity mesh.

[0035] In step **444**, the 3-D cavity mesh is filled with a material. This step may include, for example, deposition of a metal along the walls of each channel so that a network of hollow "tubes" is formed. In other embodiments, the 3-D channel mesh may be completely filled with metal, resulting in a solid wire mesh metamaterial such as self-aligned metamaterial **300**. This exemplary metamaterial is composed entirely of one substance, and metamaterial properties are affected by the substance itself as well as the final arrangement of the mesh.

[0036] The filling step may involve exposing vertical edges of the channel grid so that they can be metallized. The horizontal grid pattern may include vertical intersections. In certain embodiments, metallization in may be replaced with another desired deposition process and type of material.

[0037] In step **450**, the substrate **200** is removed from around metamaterial **300** only if it is desirable or beneficial to do so. For example, if metamaterial **300** is a wire mesh to be used as an

antenna at infrared frequencies, it may be beneficial to leave substrate **200** in place. However, in antennas at other frequencies, it may be beneficial or necessary to chemically remove substrate **200**. In step **454**, metamaterial **300** may optionally be encased for example in a resin. The desirability of encasing in resin will depend on the metamaterial and the desired properties. In some embodiments, encasing metamaterial **300** in resin may defeat some or all of the desired metamaterial properties.

[0038] Similar methods may be used to make mixed-material metamaterials. For example, the process as described above may be suitable for making a metamaterial antenna. The process can be modified slightly to make a metamaterial filter for example by making metamaterial **300** in three separate blocks, two of which are made of conductive metal and one of which is made of a dielectric. By joining three separate blocks in the pattern conductor-dielectric-conductor, a high-frequency passband can be produced and used to filter unwanted frequencies.

[0039] Returning to the step-**460** branch of **FIG. 4**, at step **460**, the two-dimensional channel grids are filled with a first material. This may be done in the same manner as described in step **444**.

[0040] In step **464**, vertical wells are etched. This method is similar as to that described in step **440**. In step **464**, selection of an appropriate etchant and process is necessary because an existing wire mesh is already in place. For example, if a chlorinated chemical process is used, the existing wire pieces may vertically block the etch, so that "walls" of substrate material are left between layers of wire mesh. To avoid formation of walls, a fluorinated chemical etch process may be used instead to ensure a clean etch around each individual wire and between wires. The result is a line of exposed wire intersections running down the well.

[0041] In step **470**, a second material may deposited on exposed intersections. For example, if the wire mesh is made of aluminum, a gold beat may be deposited on each exposed junction. This can be accomplished for example by electrically or chemically "growing" the beads on the junctions according to methods known in the art.

[0042] In step **474**, after beads of the second material are deposited or "grown" on the exposed junctions, the remainder of each well may be filled with a desired fill material, such as resin. Those with skill in the art will recognize that other combinations are possible to select for

desired metamaterial properties. For example, vertical wells may be filled with the first material after beads of the second material are deposited on the junctions.

[0043] In step **480**, once the vertical wells are filled in, the wire mesh has sufficient three-dimensional structure that substrate **200** can be removed. The result is a wire mesh similar to metamaterial **300**, with a plurality of beads of a second material deposited on intersections throughout, and vertical structure provided by a third material such as resin.

[0044] In step **484**, the new wire mesh may be encased in a material such as resin, which may be the same resin as the resin of the third material in step **474**. The resin encasing provides mechanical structure.

[0045] In step **490**, the first material of step **460** is removed. For example, in an exemplary embodiment, the first material is aluminum, the second material is gold, and the third material is resin. Thus, before step **490**, a wire mesh of aluminum is encased within a resin body. At each intersection in the wire mesh there is a gold bead. In step **490**, terminal ends of the aluminum wires may be exposed to a reactive chemical such as nitric acid, fluoric acid, or an aluminum etchant. In this case, it is important to select a second material that is not reactive with or is less reactive with the chemical agent, such as gold. The chemical agent dissolves the aluminum wire mesh, but does not destroy the gold beads. Any spaces left by the dissolved aluminum may then be back-filled with additional resin.

[0046] The result of step **490** is an artificial resin crystal having a plurality of gold beads dispersed throughout the resin in a pattern selected for a desired metamaterial property. For example, the gold beads may impart a desired resonant frequency.

[0047] Although a series of steps have been disclosed in **FIG. 4** in an exemplary order, those with skill in the art will recognize that the order of some steps may be varied, and that some steps may be optional to certain embodiments. For example, a first exemplary process may include, in order, steps **410** → **420** → **430** → **440** → **444** and optionally either or both of **450** and **454**. The result of this exemplary method is a uniform wire mesh that is optionally left inside the substrate or optionally encased in a polymer resin or other casing material.

[0048] A second exemplary process may include, in order, steps **410** → **420** → **430** → **460** → **464** → **470** → **474** and optionally steps **480**, **484**, and **490**. The result of this process may be an exemplary artificial nanocrystal (**FIG. 5**).

[0049] A third exemplary process may include, in order, steps **410** → **420** → **430** → **460** → **464** → **474** and optionally step **480** and **484**. The result of this process is a three-dimensional mesh wherein the each mesh grid is upheld by a material different from the grid material, for example a wire mesh with structural resin providing vertical support between layers.

[0050] A fourth exemplary process includes following the method of **FIG. 4**, but etching the substrate deep enough to form one or more two-dimensional wire meshes after the annealing and metalizing operations. In this example, steps **440** and **464** (etching vertical wells) are unnecessary. The wire meshes may remain buried in the substrate or may be exposed to the surface of the. This process is useful for buried in-plane propagation, for example in electro-optical circuits, and also may be used as a method of creating integrated or printed circuits. In this exemplary embodiment, the substrate remains substantially in place. Advantageously, wires thus formed will have circular cross sections rather than rectangular cross sections, which may impart desired properties including isotropy in a wave's behavior. Furthermore, in an exemplary electro-optical circuit, a wire mesh could be used in optical transmission lines to affect the propagation phase. This is important when using nanoantennas to transmit optical signals because such antennas, when arrayed, must be fed with the correct phase by transmission lines to achieve the desired radiation pattern. In electro-optical circuits (or any on-chip circuits), space is at a premium. The ability to array antennas in whatever space and direction is available, limited only by the desired pattern, is therefore helpful.

[0051] A fifth exemplary process includes etching and annealing vertical wells without constructing the grid pattern. In this case, a plurality of wells may be etched in a desired pattern, and the wells then annealed, so that a three-dimensional matrix of bubbles is formed in the substrate. The bubbles may be useful in tuning permittivity or spatial indexing. They can also create broadband negative refraction materials. In some cases, creation of a bubble matrix may be combined with other exemplary methods to further select a desired metamaterial property.

[0052] **FIG. 5** is a perspective view of an exemplary artificial nanocrystal **500** manufactured according to the process of **FIG. 4**. Nanocrystal **500** is formed with a structural body of resin **510**, and has placed therein a plurality of beads **520**. The beads may be placed for example in an ordered or periodic pattern selected for a particular resonance. In some embodiments, an artificial nanocrystal **500** will have a much sharper resonance curve than a natural crystal. If nanocrystal 500 is an electromagnetic of photonics crystal, the the useful frequencies will be set by the wavelengths equivalent to repeated unit cell size. Electromagnetic or photonics crystals are often used to create a bandgap so that radiation at a selcted frequency will not propagate. Defects may also be introduced throughout the material, for example by chemical etching additional vertical wells, which may serve as "light tunnels."

[0053] The novel and patentably distinct methods of producing metamaterials described herein may also be used for producing other complex electromagnetic media, such as photonic crystals and/or electromagnetic crystals. The methods described herein may be applicable to produce materials having repeated structural dimensions that are smaller than and/or about the same size as an operational wavelength of radiation. Other applications include electromagnetic filters configured to block specific wavelengths of radiation; for example, a filter could be configured to block wavelengths in common communication-band frequencies but pass visible light.

[0054] While the subject of this specification has been described in connection with one or more exemplary embodiments, it is not intended to limit the claims to the particular forms set forth. On the contrary, the appended claims are intended to cover such alternatives, modifications and equivalents as may be included within their spirit and scope.

7. The method of claim 1 wherein the grid pattern is non-rectilinear.

8. A wire mesh metamaterial constructed according to the process of claim 1.

9. The method of claim 1 wherein the operation of depositing a first material in the channel grids precedes the step of etching a plurality of vertical wells and further comprising:

depositing a second material on a plurality of intersecting lines of the first material exposed by the vertical wells;

depositing a third material in the vertical wells;

removing the substrate block;

encasing the multi-layer wire mesh in a rigid medium;

removing the first material; and

back-filling voids in the rigid medium left by the removal of the first material.

10. An artificial nanocrystal constructed according to the method of claim 9.

11. The method of claim 9 wherein depositing the second material comprises electrochemical deposition.

12. The method of claim 9 wherein the first material and the third material are the same.

13. The method of claim 9 wherein the first material is aluminum and the second material is gold.

14. The method of claim 9 wherein etching the vertical wells comprises etching with a fluorechemical process.

15. An artificial self-aligned nanocrystal comprising a plurality of nanoparticles suspended in a rigid substrate, the nanoparticles arranged to impart to the nanocrystal a characteristic resonant frequency.

16. The artificial nanocrystal of claim 15 wherein the nanoparticles are gold beads.

17. The artificial nanocrystal of claim 15 wherein the rigid substrate is a polymer.

18. A method of manufacturing an artificial nanocrystal comprising:

deeply etching a two-dimensional horizontal grid pattern into a substrate block, the two-dimensional grid pattern and depth of the etch being compatible with an array of beads having a programmed resonant frequency;

annealing the substrate to form a plurality of channel grids, each channel grid being characterized by the two-dimensional grid pattern and each channel grid being substantially identical to and vertically aligned with each other channel grid;

metallizing the channel grids to form a plurality of two-dimensional wire grids, each wire grid having a plurality of intersections;

etching a plurality of vertical wells in the substrate block to expose the intersections, the vertical wells being etched orthogonal to the wire grid and each vertical well being etched at a depth selected to expose at least two intersections;

depositing a conductive metal bead on each exposed intersection;

filling the vertical wells with a rigid structural medium; and

chemically removing the two-dimensional wire grids.

19. The method of claim 18 further comprising:

chemically removing the substrate block to leave a three-dimensional mesh structure;

encasing the three-dimensional mesh structure in the rigid structural medium;

20. The method of claim 18 further comprising filling voids left by removal of the wire grid with a rigid structural medium.

21. The method of claim 18 wherein the two-dimensional grid pattern and the depth of the vertical wells are selected to place the metal beads substantially equidistant from each other throughout the artificial nanocrystal.

22. An artificial nanocrystal manufactured according to the method of claim 18.

23. A method of manufacturing a metamaterial comprising:

etching a two-dimensional horizontal grid pattern into a substrate block, the two-dimensional grid pattern and depth of the etch being selected for a desired metamaterial property;

annealing the substrate to form a channel grid, the channel grid being characterized by the two-dimensional grid pattern; and

depositing a material in the channel grid to form a single-layer wire mesh.

WHAT IS CLAIMED IS:

1. A method of manufacturing a metamaterial comprising:

etching a two-dimensional horizontal grid pattern into a substrate block, the two-dimensional grid pattern and depth of the etch being selected for a desired metamaterial property;

annealing the substrate to form a plurality of channel grids, each channel grid being characterized by the two-dimensional grid pattern and each channel grid being substantially identical to and vertically aligned with each other channel grid;

etching a plurality of vertical wells in the substrate block, each vertical well substantially orthogonally intersecting at least two channel grids; and

depositing a first material in the channel grids to form a multi-layer wire mesh.

2. The method of claim 1 further comprising depositing the first material in the vertical wells.

3. The method of claim 1 further comprising depositing a second material in the vertical wells.

4. The method of claim 1 further comprising removing the substrate block.

5. The method of claim 1 wherein depositing the first material comprises depositing a metal on the edges of the channels whereby hollow metallic tubes are formed.

6. The method of claim 1 wherein depositing the first material comprises filling the channels with the first material whereby solid wires are formed.

7. The method of claim 1 wherein the grid pattern is non-rectilinear.

8. A wire mesh metamaterial constructed according to the process of claim 1.

9. The method of claim 1 wherein the operation of depositing a first material in the channel grids precedes the step of etching a plurality of vertical wells and further comprising:

depositing a second material on a plurality of intersecting lines of the first material exposed by the vertical wells;

depositing a third material in the vertical wells;

removing the substrate block;

encasing the multi-layer wire mesh in a rigid medium;

removing the first material; and

back-filling voids in the rigid medium left by the removal of the first material.

10. An artificial nanocrystal constructed according to the method of claim 9.

11. The method of claim 9 wherein depositing the second material comprises electrochemical deposition.

12. The method of claim 9 wherein the first material and the third material are the same.

13. The method of claim 9 wherein the first material is aluminum and the second material is gold.

14. The method of claim 9 wherein etching the vertical wells comprises etching with a fluorechemical process.

15. An artificial self-aligned nanocrystal comprising a plurality of nanoparticles suspended in a rigid substrate, the nanoparticles arranged to impart to the nanocrystal a characteristic resonant frequency.

16. The artificial nanocrystal of claim 15 wherein the nanoparticles are gold beads.

17. The artificial nanocrystal of claim 15 wherein the rigid substrate is a polymer.

18. A method of manufacturing an artificial nanocrystal comprising:

deeply etching a two-dimensional horizontal grid pattern into a substrate block, the two-dimensional grid pattern and depth of the etch being compatible with an array of beads having a programmed resonant frequency;

annealing the substrate to form a plurality of channel grids, each channel grid being characterized by the two-dimensional grid pattern and each channel grid being substantially identical to and vertically aligned with each other channel grid;

metallizing the channel grids to form a plurality of two-dimensional wire grids, each wire grid having a plurality of intersections;

etching a plurality of vertical wells in the substrate block to expose the intersections, the vertical wells being etched orthogonal to the wire grid and each vertical well being etched at a depth selected to expose at least two intersections;

depositing a conductive metal bead on each exposed intersection;

filling the vertical wells with a rigid structural medium; and

chemically removing the two-dimensional wire grids.

19. The method of claim 18 further comprising:

chemically removing the substrate block to leave a three-dimensional mesh structure;

encasing the three-dimensional mesh structure in the rigid structural medium;

20. The method of claim 18 further comprising filling voids left by removal of the wire grid with a rigid structural medium.

21. The method of claim 18 wherein the two-dimensional grid pattern and the depth of the vertical wells are selected to place the metal beads substantially equidistant from each other throughout the artificial nanocrystal.

22. An artificial nanocrystal manufactured according to the method of claim 18.

23. A method of manufacturing a metamaterial comprising:

etching a two-dimensional horizontal grid pattern into a substrate block, the two-dimensional grid pattern and depth of the etch being selected for a desired metamaterial property;

annealing the substrate to form a channel grid, the channel grid being characterized by the two-dimensional grid pattern; and

depositing a material in the channel grid to form a single-layer wire mesh.

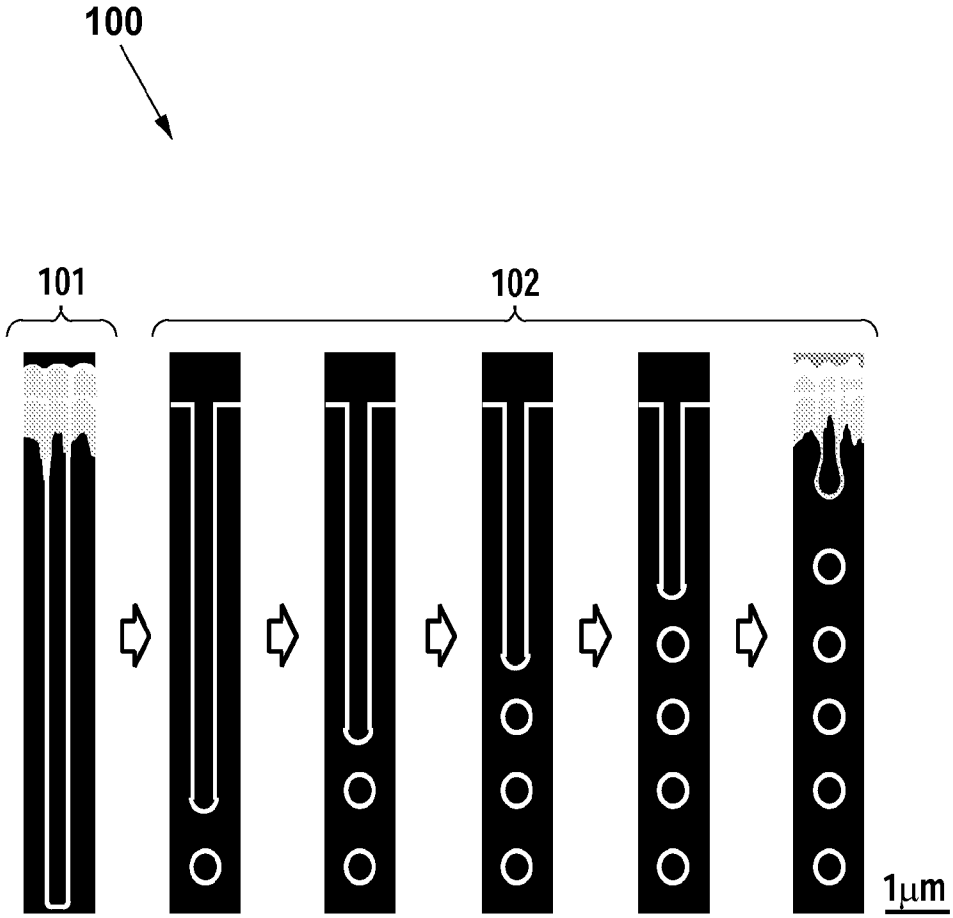


FIG. 1
(PRIOR ART)

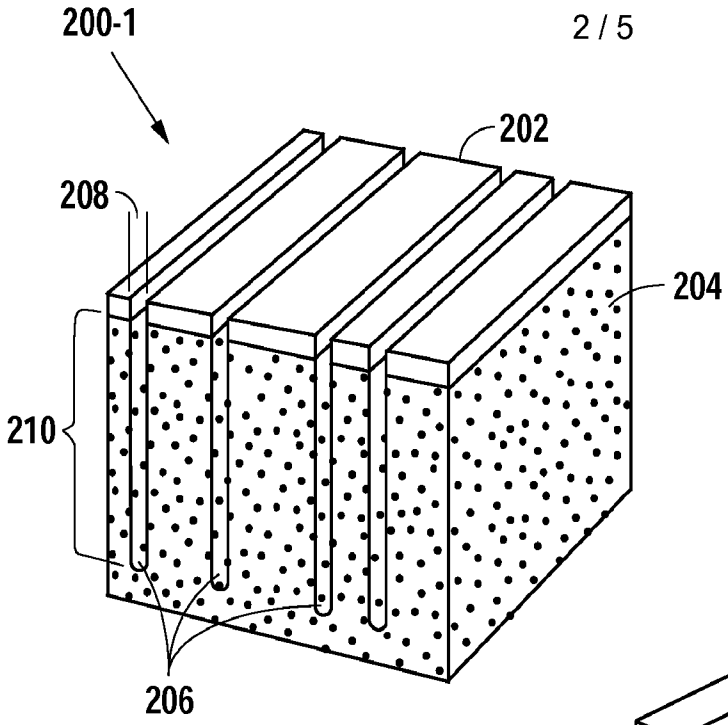


FIG. 2A

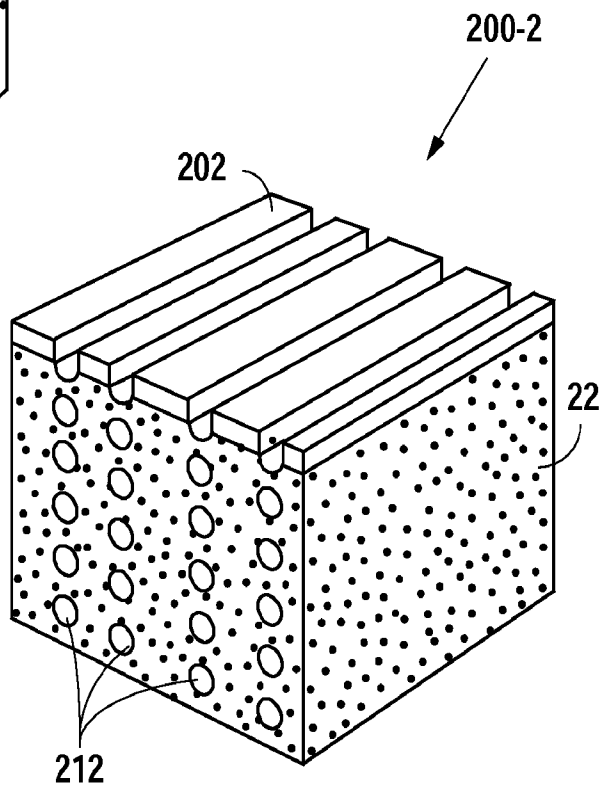


FIG. 2B

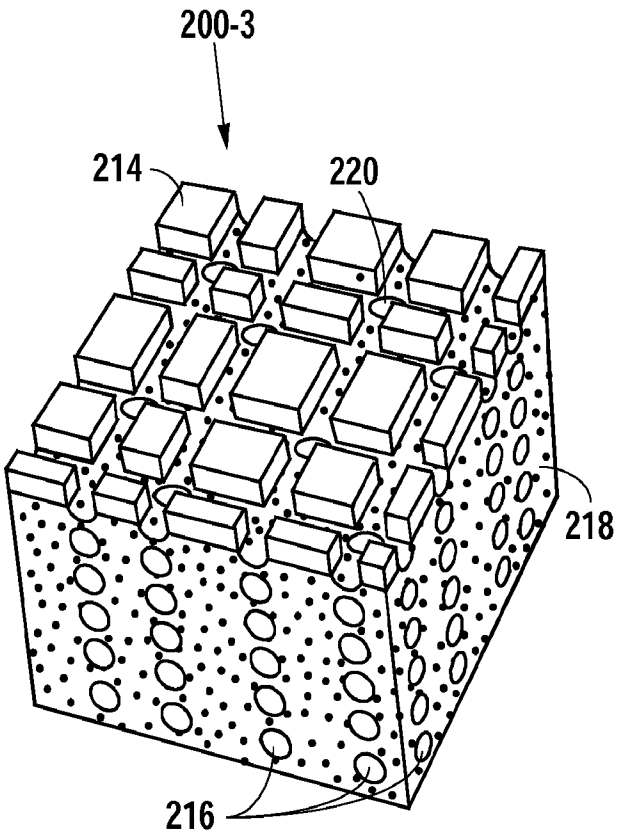


FIG. 2C

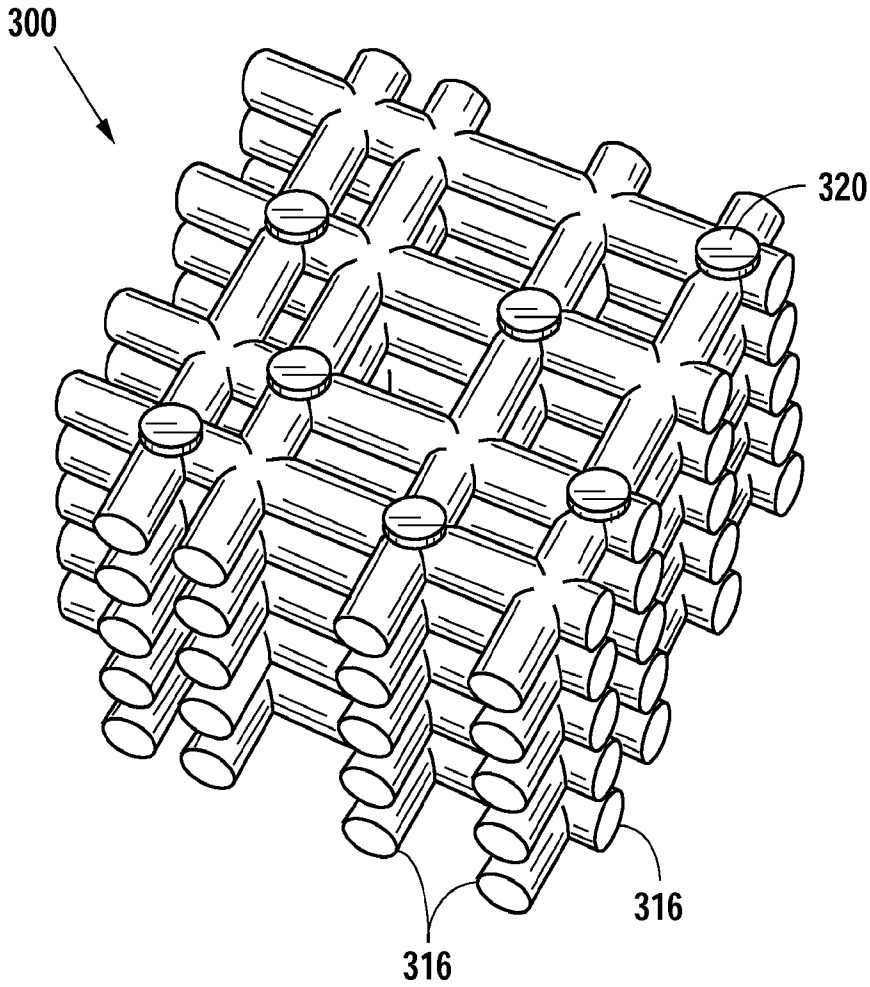


FIG. 3

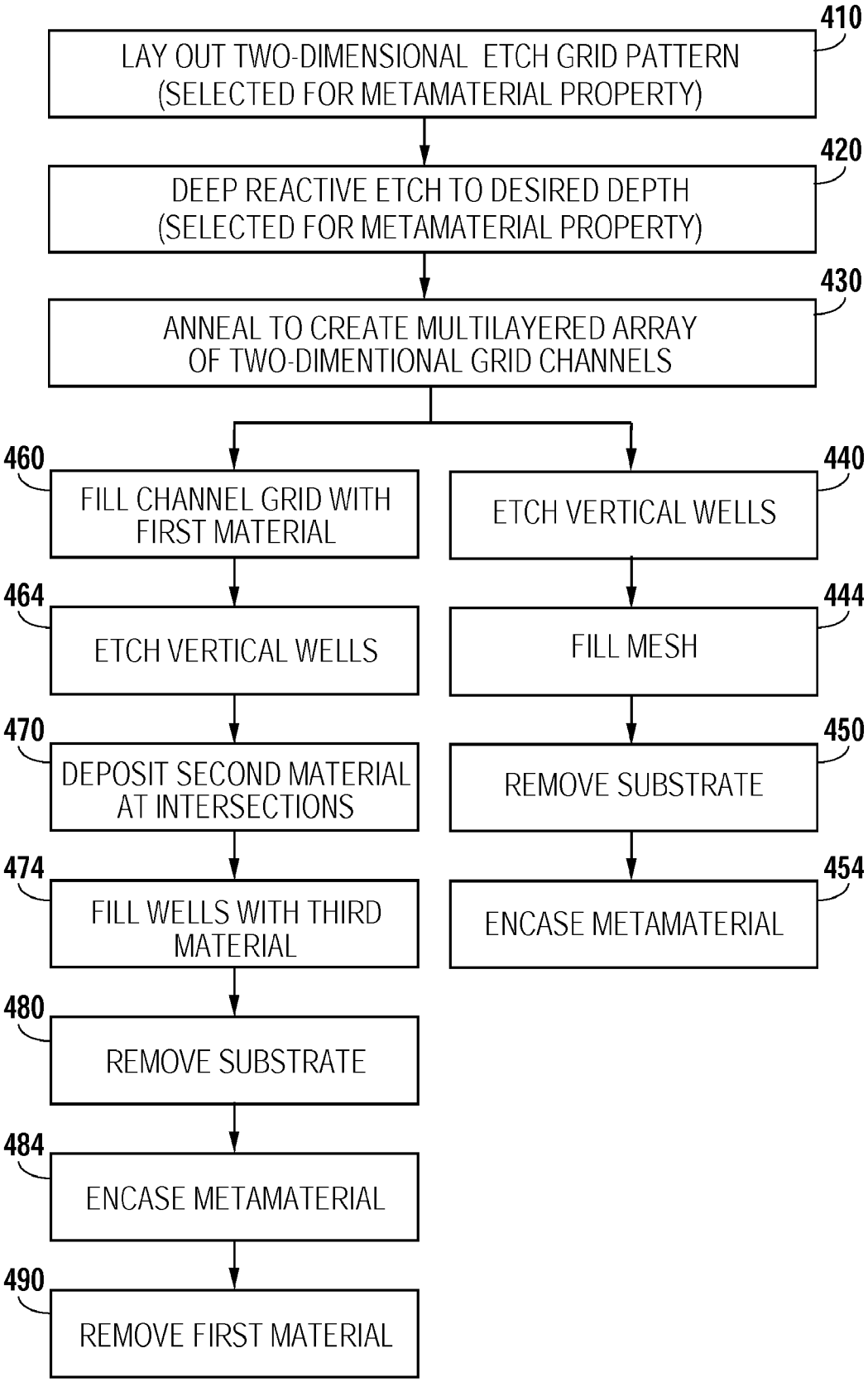

410
LAY OUT TWO-DIMENSIONAL ETCH GRID PATTERN (SELECTED FOR METAMATERIAL PROPERTY)
420
DEEP REACTIVE ETCH TO DESIRED DEPTH (SELECTED FOR METAMATERIAL PROPERTY)
430
ANNEAL TO CREATE MULTILAYERED ARRAY OF TWO-DIMENTIONAL GRID CHANNELS
460
FILL CHANNEL GRID WITH FIRST MATERIAL
464
ETCH VERTICAL WELLS
470
DEPOSIT SECOND MATERIAL AT INTERSECTIONS
474
FILL WELLS WITH THIRD MATERIAL
480
REMOVE SUBSTRATE
484
ENCASE METAMATERIAL
490
REMOVE FIRST MATERIAL
440
ETCH VERTICAL WELLS
444
FILL MESH
450
REMOVE SUBSTRATE
454
ENCASE METAMATERIAL

FIG. 4

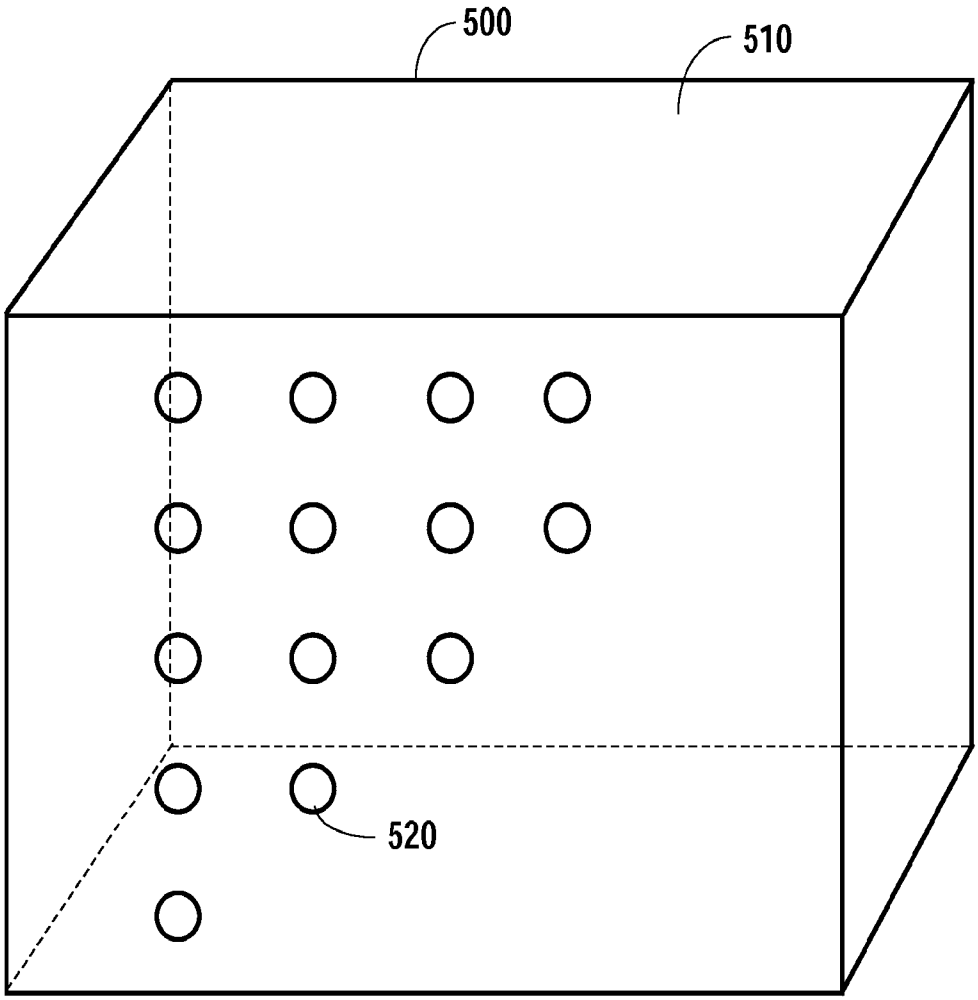


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/030268

A. CLASSIFICATION OF SUBJECT MATTER

H01Q 3/01(2006.01)i, H01Q 1/24(2006.01)i, B82B 1/00(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)
H01Q 3/01; H01L 21/306; H01Q 15/02; H01Q 1/24; B82B 1/00

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: etching, depositing, metamaterial, intersection, multi-layer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010-0248449 A1 (HILDRETH et al.) 30 September 2010 See abstract, paragraphs [0035]-[0065], claims 1-13 and figures 3-4G.	23
A		1-22
Y	GALISTEO, J. F. et al. Self-assembly approach to optical metamaterials. Pure and Applied Optics. 20 January 2005, Vol. 7, No. 2, S244-S254. See pages S245-S252 and figure 15.	23
A	AMIR TAL. Three-Dimensional Micron-Scale Metal Photonic Crystals Via Multi-Photon Direct Laser Writing And Electroless Metal Deposition. 2007, The Master of Science in the College of Optics and Photonics at The University of Cetral Florida. See pages 18-45 and figures 4-5, 4-7.	1-23
A	US 2008-0165079 A1 (SMITH et al.) 10 July 2008 See paragraphs [0123]-[0128], [0161]-[0174] and figures 15(a)-15(c), 23(a)-23(e).	1-23

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

☒ See patent family annex.

* 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 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	Date of mailing of the international search report
25 June 2013 (25.06.2013)	**27 June 2013 (27.06.2013)**

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer
KANG, Sung Chul
Telephone No. 82-42-481-8405

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/030268

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KAHYN HUR et al. Three-Dimensionally Isotropic Negative Refractive Index Materials from Block Copolymer Self-Assembled Chiral Gyroid Networks. WILEY-VCHVERLAG GMBH & CO., KGAA. Angew. Chem. Int. Ed. 09 December 2011, Volume12, Issue 50, pages 12191-12195. See page 2, lines 28-78 and figure 1.	1-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/030268

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2010-0248449 A1	30.09.2010	US 8278191 B2	02.10.2012
		WO 2010-114887 A1	07.10.2010
US 2008-0165079 A1	10.07.2008	CN 101389998 A	18.03.2009
		CN 101389998 B	04.07.2012
		CN 102798901 A	28.11.2012
		EP 1771756 A2	11.04.2007
		EP 1771756 A4	15.05.2013
		JP 04795344 B2	19.10.2011
		JP 2008-507733 A	13.03.2008
		JP 2011-254482 A	15.12.2011
		KR 10-1192907 B1	18.10.2012
		KR 10-1250059 B1	02.04.2013
		KR 10-2007-0050051 A	14.05.2007
		KR 10-2012-0123746 A	09.11.2012
		US 2010-0067091 A1	18.03.2010
		US 2011-317275 A1	29.12.2011
		US 7538946 B2	26.05.2009
		US 8040586 B2	18.10.2011
		WO 2006-023195 A2	02.03.2006
		WO 2006-023195 A3	30.10.2008