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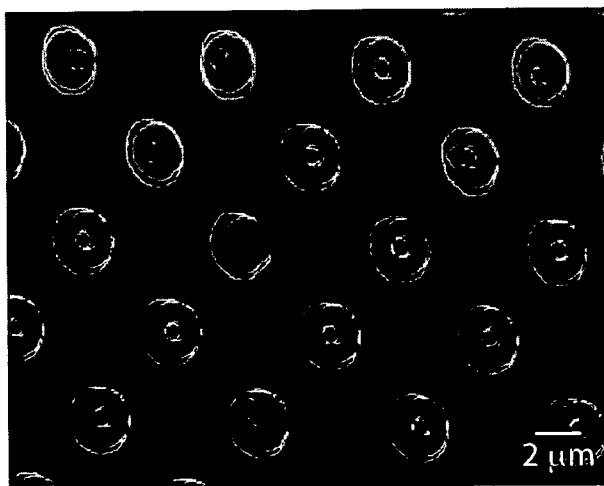
(43) International Publication Date
14 February 2008 (14.02.2008)

PCT

(10) International Publication Number
WO 2008/018923 A2

- (51) International Patent Classification: **Not classified**
- (21) International Application Number:
PCT/US2007/007101
- (22) International Filing Date: 22 March 2007 (22.03.2007)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/784,676 22 March 2006 (22.03.2006) US
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- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, 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, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— without international search report and to be republished upon receipt of that report

(54) Title: FABRICATION OF ISOLATED NANOSTRUCTURES AND/OR ARRAYS OF NANOSTRUCTURES



(57) Abstract: Methods for fabricating nanostructures and articles associated therewith are described. In some embodiments, an isolated nanostructure (e.g., a metal nanowire) or an array of nanostructures can be fabricated by depositing a material (e.g., a metal) on a surface having a plurality of protrusions or indentations. At least a portion of the deposited material may be embedded in an encapsulating material, and the encapsulating material can be cut, for instance, to form a thin slice that includes the deposited material at least partially embedded therein. In some instances, the slice can be positioned on a surface in a desired arrangement. The encapsulating material can be removed from the surface to form one or more isolated nanostructures of the deposited material. Advantageously, dimensions of the nanostructures can be controlled to, e.g., 15 nm, to form nanostructures having a variety of shapes and geometries (e.g., wires, rings, and cylinders). Nanostructures can also be formed in a variety of materials, including metals, ceramics, and polymers.

In addition, nanostructures can also be fabricated over large areas (e.g., greater than 1 mm²). In some cases, these nanostructures are positioned in association with other components, e.g., to form a functional component of a device.

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**FABRICATION OF ISOLATED NANOSTRUCTURES AND/OR ARRAYS OF
NANOSTRUCTURES**

RELATED APPLICATIONS

5 This application claims priority to U.S. Provisional Application No. 60/784,676, entitled, "Fabrication of Isolated Nanostructures", filed March 22, 2006.

FEDERALLY SPONSORED RESEARCH

 This invention was sponsored by the National Institutes of Health grant no.
10 GM065364 and the National Science Foundation, grant nos. DMR-9809363, and PHY0017795. The government has certain rights to the invention.

FIELD OF INVENTION

 The present invention relates to methods for fabricating nanostructures and
15 articles associated therewith and, more specifically, to methods for fabricating isolated nanostructures and/or arrays of nanostructures.

BACKGROUND

 Nanostructures with different geometries in a range of materials have been
20 successfully synthesized using chemical methods; however, these nanostructures may not be uniform in size and geometry. The integration of these nanostructures into devices, e.g., optical devices, is also challenging due to the difficulty of selecting and manipulating specific nanostructures. Nanostructures fabricated by nanosphere lithography have been used for chemosensing and biosensing. This technique, although
25 very useful, can only produce nanostructures with limited flexibility in dimensions and geometries. Electron beam lithography is widely used to fabricate metal nanostructures for studying surface plasmon coupling and subwavelength optical waveguiding. Electron-beam lithography is, however, still not conveniently available to general users; and it is also challenging to fabricate structures with sub-30 nanometer width and with a
30 high aspect ratio. Advances in the field that could, for example, enable the fabrication of nanostructures with well-controlled dimensions would find application in a number of different fields.

SUMMARY OF THE INVENTION

Methods and articles associated with fabricating nanostructures are provided.

In one aspect, the invention provides a series of methods. In one embodiment, a method of fabricating a nanostructure comprises providing an article having a surface, depositing a first material on at least a portion of the surface of the article, encapsulating
5 at least a portion of the first material in an encapsulating material, cutting the encapsulating material in a direction that intersects at least a portion of the first material, thereby forming a cut portion, and removing the encapsulating material from the cut portion, thereby forming an isolated nanostructure comprising the first material.

In another embodiment, a method of fabricating a nanostructure comprises
10 providing a substrate formed in an article material having a surface defining a plurality of indentations, depositing a first material on at least a portion of the surface of the substrate, cutting the substrate in a direction that intersects at least a portion of the first material, thereby forming a cut portion, removing any substrate from the cut portion, and forming an isolated nanostructure comprising the first material.

In another embodiment, a method of positioning a plurality of isolated
15 nanostructures on a surface comprises providing a structure comprising a plurality of nanostructures positioned in a particular arrangement in association with a first material, at least a portion of each nanostructure embedded in the first material, positioning the structure on a surface, removing the first material from the surface, and allowing the
20 plurality of nanostructures to remain on the surface in the particular arrangement, wherein each nanostructure is physically isolated from another nanostructure in the particular arrangement.

In another embodiment, a method of making a device comprising a nanostructure comprises providing a precursor article having three principle intersecting axes, wherein
25 at least a first dimension of the precursor article, along a first axis passing through the precursor article, is smaller than 1 micron and at least a second dimension of the precursor article, along a second axis perpendicular to the first axis passing through the precursor article, is larger than 100 microns, separating, from the precursor article, a nanostructure, wherein the nanostructure has three principle intersecting axes, wherein at
30 least a first dimension of the nanostructure, along a first axis passing through the nanostructure, is smaller than 1 micron and at least a second dimension of the nanostructure, along a second axis perpendicular to the first axis passing through the nanostructure, is smaller than 1 micron, and positioning the nanostructure in association

with a plurality of other components to form a functional component of a functional device.

In another embodiment, a method of fabricating a nanostructure comprises providing a supporting article, positioning a precursor article in supported relationship
5 with the supporting article, and separating, from the precursor article, a nanostructure, wherein the nanostructure has three principle intersecting axes, wherein at least a first dimension of the nanostructure, along a first axis passing through the nanostructure, is smaller than 1 micron and at least a second dimension of the nanostructure, along a
10 second axis perpendicular to the first axis passing through the nanostructure, is smaller than 1 micron.

In another embodiment, a method of forming a composite structure is provided. The method comprises providing a first structure comprising a plurality of first nanostructures positioned in a particular arrangement in association with a first material, at least a portion of each first nanostructure embedded in the first material, and
15 positioning a dielectric material adjacent the first structure. The method also includes positioning a second structure adjacent the dielectric material such that the dielectric material is positioned between the first and second structures, wherein the second structure comprises a plurality of second nanostructures positioned in a particular arrangement in association with a second material, at least a portion of each second
20 nanostructure embedded in the second material, and allowing the plurality of first and second nanostructures to remain in their respective arrangements, wherein each nanostructure is not in direct physical contact with another nanostructure in the arrangements.

In another aspect, the invention provides a series of articles. Articles may include
25 ones that are made by a process of any preceding method.

In one particular embodiment, a composite structure is provided. The composite structure includes a first conductive nanostructure, wherein the first nanostructure has three principle intersecting axes, wherein at least a first dimension of the first nanostructure, along a first axis passing through the first nanostructure, is smaller than
30 500 nm and at least a second dimension of the first nanostructure, along a second axis perpendicular to the first axis passing through the first nanostructure, is smaller than 500 nm. The composite structure also includes a second conductive nanostructure positioned adjacent but not in physical contact with the first nanostructure, wherein the second

nanosstructure has three principle intersecting axes, wherein at least a first dimension of the second nanosstructure, along a first axis passing through the first nanosstructure, is smaller than 500 nm and at least a second dimension of the second nanosstructure, along a second axis perpendicular to the first axis passing through the second nanosstructure, is smaller than 500 nm. A dielectric material may be positioned between the first and second nanosstructures. The first and second nanosstructures may be positioned less than 1 micron apart.

Other advantages and novel features of the present invention will become apparent from the following detailed description of various non-limiting embodiments of the invention when considered in conjunction with the accompanying figures. In cases where the present specification and a document incorporated by reference include conflicting and/or inconsistent disclosure, the present specification shall control. If two or more documents incorporated by reference include conflicting and/or inconsistent disclosure with respect to each other, then the document having the later effective date shall control.

BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying figures, which are schematic and are not intended to be drawn to scale. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention. In the figures:

FIG. 1 shows a method of fabricating isolated nanosstructures, according to one embodiment of the invention;

FIGS. 2A and 2B are SEM images of isolated nanosstructures fabricated by the method shown in FIG. 1, according to another embodiment of the invention;

FIG. 3 shows another method of fabricating isolated nanosstructures, according to another embodiment of the invention;

FIGS. 4A-4O are SEM images of various isolated nanosstructures, according to another embodiment of the invention;

FIGS. 4P and 4Q are schematic diagrams of stacked nanostructures according to another embodiment of the invention;

FIG. 5 shows another method of fabricating isolated nanostructures, according to another embodiment of the invention;

5 FIGS. 6A and 6B are SEM images of isolated nanostructures, according to another embodiment of the invention;

FIG. 7A shows an experimental setup for measuring scattering spectra of single nanostructures, according to another embodiment of the invention;

10 FIG. 7B shows scattering spectra of four randomly-selected nanostructures, according to another embodiment of the invention;

FIGS. 8A-8C shows dark field optical images of gold nanowires having different dimensions, according to another embodiment of the invention;

FIGS. 8D-8F show scattering spectra of the gold nanowires of FIGS. 8A-8C, respectively, according to another embodiment of the invention;

15 FIGS. 9A-9C show Finite-Difference Time-Domain simulations of scattering spectra of gold nanowires, according to another embodiment of the invention;

FIG. 9D shows a comparison between scattering spectra obtained from experiments and simulations, according to another embodiment of the invention

20 FIG. 10 shows a method of fabricating nanostructures, according to another embodiment of the invention;

FIG. 11A shows a photograph of patterned square-loop shaped nanostructures, according to another embodiment of the invention;

FIG. 11B shows a dark-field optical microscopy image of the nanostructures of FIG. 11A, according to another embodiment of the invention;

25 FIG. 11C shows an SEM image of an array of closed-loop holed nanostructures, according to another embodiment of the invention;

FIG. 11D shows an IR transmission spectrum measured through an array of the nanostructures shown in FIG. 11B, according to another embodiment of the invention;

30 FIG. 12A shows a dark-field optical image of L-shaped gold nanostructures on a CaF_2 substrate, according to another embodiment of the invention;

FIGS. 12B-12D show transmission spectra of the nanostructures of FIG. 12A using different incidents of light polarization, according to another embodiment of the invention;

FIG. 13 shows a transmission spectrum of L-shaped nanostructures with polarization parallel to either of the two arms of the nanostructure, according to another embodiment of the invention;

FIG. 14A shows a bright-field optical image of an epoxy article including U-shaped nanostructures positioned on a hole of a copper sheet, according to another embodiment of the invention;

FIG. 14B shows an SEM image of the U-shaped nanostructures of FIG. 14A, according to another embodiment of the invention;

FIGs. 14C-14E show transmission spectra of the U-shaped nanostructures of FIGs. 14A and 14B of different polarization directions of incident light, according to another embodiment of the invention;

FIG. 15 shows a transmission spectrum of a 100 nanometer thick epoxy article, according to another embodiment of the invention;

FIG. 16A shows a SEM image of U-shaped nanostructures supported on a CaF_2 substrate, according to another embodiment of the invention;

FIG. 16B shows a transmission spectrum of the U-shaped nanostructures of FIG. 16A, according to another embodiment of the invention; and

FIGs. 17A and 17B are images of a composite structure including stacked nanostructures separated by a dielectric film, according to another embodiment of the invention.

DETAILED DESCRIPTION

In primary embodiments of the invention, a precursor material is provided and a nanostructure is formed by separating a portion of the precursor article (which becomes the nanostructure) from the precursor article. This separation can take place by positioning the precursor article in supported relationship with a supporting article, and effecting separation by slicing, cutting, or the like. The resulting nanostructure can take a variety of forms, as described in greater detail below. For example, the nanostructure can include at least one portion having an aspect ratio of at least 5:1, 10:1, 25:1, 50:1, 100:1, or greater where aspect ratio is the ratio between a dimension of the article along a first axis compared to a dimension of the article along a second axis perpendicular to the first axis. In all embodiments, the nanostructure can be positioned in association with a plurality of other components to form a functional component of a functional device.

Such a device can be, for example, an electronic device, a sensor, or essentially any other device that can utilize such a nanostructure. In some embodiments, the nanostructure, once formed by separation from a precursor article, is moved from a position and/or location from which it is separated to another position defining a location of such a functional device.

“Article” as used herein takes its common meaning as would be understood by those of ordinary skill in the art. That is, it is a piece of material, significantly more than just an isolated molecule or a relatively small number of molecules.

The present invention relates to methods for fabricating nanostructures and articles associated therewith and, more specifically, to methods for fabricating isolated and/or arrays nanostructures. In some embodiments, isolated nanostructures and/or arrays of nanostructures of the invention (e.g., metal nanowires) can be fabricated by depositing a material (e.g., a metal) on a surface having a plurality of protrusions or indentations. At least a portion of the deposited material may be embedded in an encapsulating material, and the encapsulating material can be cut, for instance, to form a thin slice that includes the deposited material at least partially embedded therein. In some instances, the slice can be positioned on a surface in a desired arrangement. If desired, the encapsulating material can be removed from the surface to form one or more isolated nanostructures of the deposited material. In other embodiments, the encapsulating material is not removed and an array of nanostructures (e.g., nanostructures that are positioned in a predetermined (e.g., ordered) arrangement) can be used to form a composite structure. Advantageously, dimensions of the nanostructures of the invention can be controlled to, e.g., 15 nm, to form nanostructures having a variety of shapes and geometries (e.g., wires, rings, and cylinders). Nanostructures can also be formed in a variety of materials, including metals, ceramics, and polymers. In addition, nanostructures of the invention can also be fabricated over large areas (e.g., greater than 1 mm²). In some cases, these nanostructures may be positioned in association with other components, e.g., to form a functional component of a device.

FIGS. 1A-1H show one method of fabricating isolated nanostructures and/or arrays of nanostructures (which may be isolated or embedded in an encapsulating material) according to an embodiment of the invention. In the embodiment illustrated in FIG. 1A, substrate 10 includes a plurality of protrusions 14 and indentations 16 that form the features of the substrate. The protrusions or indentations may be formed by any

suitable process, such as photolithography, molding, or etching, as described in more detail below. The dimensions of protrusions 14 and the spacing between the protrusions can be easily controlled by such processes. In FIG. 1A, the spacing between the features is denoted x . In some cases, this spacing can define a cross-sectional dimension of the nanostructures formed.

As illustrated in FIG. 2B, a material 20, which may be the material used to form the nanostructures, can be deposited on the surface of substrate 10. Material 20 may be deposited to cover all, or, portions, of the protrusions and/or indentations of the substrate. FIG. 1C shows the removal of protrusions 20 from the surface of the substrate, leaving material 20 remaining on the indentation portions. In other embodiments, however, removal of the protrusions may not be required. The widths of material 20 on the surface of the substrate may be defined by the spacing x between the protrusions in the original pattern of features on the substrate.

As shown in FIG. 1D, substrate 10 may be coated with an encapsulating material 26, which may be in the form of a pre-polymer. After curing the pre-polymer, and removing the polymer from the substrate, an article 28 which includes portions of material 20 can be formed, as shown in FIG. 1E. If desired, material 20 may be encapsulated in a material (e.g., encapsulating material 26) to form article 30 (FIG. 1F).

Article 30 may be cut, e.g., with a microtome or another suitable apparatus, to form cut portions 34. The cut portions may have a thickness z , which can be controlled down to, e.g., 15 nanometers, in some embodiments. The cut portions may include a plurality of nanostructures 38 embedded therein. In some embodiments, a cut portion is a precursor article for a plurality of isolated nanostructures (e.g., nanostructures that are not embedded (either partially or completely) in a material).

In some cases, one or more cut portions can be positioned on a surface, and encapsulating material 26 may be removed (partially or completely) from the surface, as discussed in more detail below. As shown in FIG. 1H, the pattern of isolated nanostructures 38 on surface 40 (e.g., a silicon surface, a TEM grid, or a single crystal CaF_2 surface) may be defined by the original pattern of material 20 deposited on substrate 10. The nanostructures may have dimensions of x , y and z , the length x of the nanostructure defined by the spacing between the protrusions (FIG. 1A), the width y defined by the thickness of material 20 deposited on substrate 10 (FIG. 1B), and the height z defined by the thickness of the cut portions (FIG. 1G).

FIGS. 2A and 2B show SEM images of isolated nanostructures formed by the method described in FIG. 1. FIG. 2A shows gold nanowires with dimensions of 2 microns (x) $\times$ 40 nanometers (y) $\times$ 50 nanometers (z). The insets show high magnification images of the same samples. FIG. 2B shows gold nanowires with dimensions of 2 microns (x) $\times$ 10 nanometers (y) $\times$ 100 nanometers (z). As illustrated in these embodiments, dimensions of the nanostructures can be controlled by varying the thickness of materials deposited on a substrate and the thicknesses of portions cut from an article. Advantageously, nanostructures having high aspect ratios can be fabricated using the methods of fabrication described herein. The aspect ratio of a nanostructure is the ratio of minimum lateral dimension of any raised portion of the structure to the height of the structure. FIG. 2B shows nanostructures having an aspect ratio of 10:1. In other embodiments, nanostructures (including isolated nanostructures) having aspect ratios of at least 5:1, at least 10:1, at least 20:1, at least 50:1, or at least 100:1 can be fabricated by methods of the invention.

FIGS. 3A-3H show another method of fabricating isolated nanostructures and/or arrays of nanostructures according to another embodiment of the invention. As illustrated in FIGS. 3A and 3B, substrate 50, which includes a plurality of features 52 (e.g., protrusions), may be formed using mold 56, which includes a plurality of inverse features 58 (e.g., indentations). The mold may be brought into contact with material 60 (e.g., a pre-polymer), and the material may fill, or coat, at least a portion of the indentations of the mold. Although not required, the material may be molded against surface 62. Layer 64, which may include an adhesive layer (e.g., silver) may optionally be deposited on the surface prior to molding. Upon curing of material 60 in the mold, removal of the mold can produce substrate 50 with a plurality of features 52.

As illustrated in FIG. 3C, material 70, which may be the material in which the nanostructures are formed, can be deposited on substrate 50. All, or portions, of material 70 can be encapsulated in an encapsulating material 72, as shown in FIG. 3D. Next, surface 62 can be removed from substrate 50. In some cases, this removal can be aided by the differential adhesion between layer 64 and surface 62 (e.g., layer 64 may be more adhesive to surface 62 than to encapsulating material 72). Of course, this differential adhesion may depend on the material properties of the surface and encapsulating material, and these materials may be chosen accordingly.

FIG. 3F shows article 74 after the removal of layer 64. In order to form embedded nanostructures, article 72 may be cut, e.g., in the direction of arrows 76, to form one or more cut portions 80. The cut portions can include a plurality of nanostructures 82 embedded therein. If desired, cut portion 80 may be positioned on surface 84, and encapsulating material 72 may be separated or removed (partially or completely) to form a plurality of isolated nanostructures 82 on the surface. Advantageously, a plurality of nanostructures can be fabricated in a single step (e.g., in a single cutting step). In addition, these nanostructures can be positioned essentially simultaneously on a surface in a single step.

It should be understood that while in some embodiments the encapsulating material (e.g., encapsulating material 72 of FIG. 3F) is removed from the isolated nanostructures, in other embodiments, the encapsulating material is not removed from the nanostructures. As described in more detail below, it may be advantageous to not remove the encapsulating material from the nanostructures when, for example, the encapsulating material is used at least in part to support the nanostructures and/or maintain the nanostructures in a certain spatial arrangement (e.g., instead of a positioning the nanostructures on a supportive substrate). Such embodiments may be useful for optical applications where a supportive may otherwise interfere with incoming light. In other embodiments, nanostructures embedded in an encapsulating material can be used to form a composite structure. The encapsulating material may be flexible such that in these and other embodiments, the composite structure can have a curved surface. As shown in FIG. 3H, the pattern of nanostructures formed on a surface may be determined, at least in part, by the pattern of features on substrate 50. However, in some cases, isolated nanostructures may be manipulated to different parts of the surface (e.g., by various methods such as magnetic forces, capillary forces, electrostatic forces, and the like). Additionally and/or alternatively, isolated nanostructures (and/or arrays of nanostructures) may be positioned in association with other components to form a functionally component of a device, as discussed in more detail below.

FIGs. 4A-4O show SEM images of isolated gold nanorings on a substrate fabricated by the method shown in FIG. 3. The diameter of the nanorings of FIGs. 4A and 4B were approximately 3 microns, and the widths and heights of the nanorings were 40 nanometers and 200 nanometers, respectively. FIG. 4B shows a high magnification SEM of the sample shown in FIG. 4A.

FIGs. 4C-4K show high aspect ratio isolated gold nanorings on a silicon substrate after removing the encapsulating material (an epoxy matrix) with oxygen plasma at 0.9 Torr, 70 W for 20 min. As described in more detail below, the aspect ratio is the ratio of minimum lateral dimension of any raised portion of a surface feature (e.g., height) to indentation depth (e.g., thickness of the wall of the ring). Here, the wall thickness and the height of the rings were about 40 nm and 500 nm, respectively; thus, these structures had an aspect ratio of 12.5. FIGs. 4C-4E show circular rings, FIGs. 4F-FH show square nanorings, and FIGs. 4I-4K show double rings. FIGs. 4D, 4G, and 4J show top views of the free-standing nanostructures; FIGs. 4E, 4H, and 4K show top views of the nanostructures lying on a silicon substrate on their sides to indicate the heights of the structures.

FIGs. 4L-4O show SEM images of various nanorings with different aspect ratios. The thickness of the wall of the rings was ~40 nm for all the nanorings; their heights were: (FIG. 4L) 70 nm (aspect ratio = 1.75), (FIG. 4M) 200 nm (aspect ratio = 5), (FIG. 4N) 500 nm (aspect ratio = 12.4), (FIG. 4O) 1 μ m (aspect ratio = 25). The images were taken at angles that show the differences in height of the structures.

In other embodiments, the nanorings can be fabricated to have even higher aspect ratios. For example, a nanoring having a diameter of 2 microns, a width of 10 nm, and a height of 1 micron can have an aspect ratio of 100:1. A plurality of such nanostructures can be formed essentially simultaneously. These nanostructures may useful, for instance, in applications requiring large surface areas.

As shown in the embodiment of FIG. 3, material 70 was deposited on all sides of features 52 of the substrate. The resulting nanostructures formed included nanorings in the shape of these features (e.g., in the shape of the circumferences of the protrusions). In other embodiments, however, material 70 can be deposited on only portions of protrusions 52. For example, material deposited on only half of the surfaces of the protrusions can form structures such as semi-circular rings. Thus, in some embodiments, the shapes of nanostructures can depend not only on the features of the substrate, but also on the method and/or amount of material deposited on the substrate.

In yet another embodiment, after deposition of a first material 70 on all or portions of the substrate that includes features and/or indentations, a second material can be deposited on top of material 70. In such consecutive coating steps, complex multi-layer nanostructures can be formed.

A first material may be coated on at least a portion of the substrate and a second material may be coated on another portion of the substrate. In some cases, the first and second portions overlap such that at least a portion of the second material is on top of the first material. In other cases, the first and second portions do not overlap, e.g., the first material may cover a first side of a cube and the second material may cover a second side of the cube. The first and/or second materials may be conductive, semiconductive, or insulative. In some instances, additional layers may be deposited. For instance, alternating metallic and non-metallic materials may be deposited to form various multi-layer nanostructures. Such structures may be useful for forming functional nano-scaled devices.

As described herein, various types of composite nanostructures can be formed using methods of the invention. In one particular embodiment, a composite structure can be formed by providing a first structure comprising a plurality of first nanostructures positioned in a particular arrangement in association with the first material, at least a portion of each first nanostructure embedded in the first material. For example, as shown in FIG. 3G, nanostructures 82 are positioned in an array within encapsulating material 72. The first structure (cut portion 80) may optionally be positioned on a surface. In some cases, a dielectric material can be positioned adjacent the first structure. For example, a thin film of a dielectric material may be deposited on top of the first structure by various methods such as deposition, or by slicing a thin layer of dielectric material and positioning it on top of the first structure. The film of dielectric material may have various thicknesses such as, for example, less than 1 mm, less than 500 microns, less than 200 microns, less than 100 microns, less than 1 micron, less than 500 nanometers, less than 300 nanometers, less than 200 nanometers, less than 100 nanometers, or less than 50 nanometers. The combined first structure and film of dielectric material can then be used as a substrate for positioning a second structure (e.g., a second cut portion) that may include a plurality of second nanostructures positioned in a particular arrangement in association with a second material, at least a portion of each second nanostructure embedded in the second material. For instance, a second cut portion 80 may be positioned on top of a first cut portion 80 to form stacked nanostructures.

In some embodiments, the second nanostructures are different from the first nanostructures. For example, the first nanostructures may have an open loop or closed

loop structure, and the second set of nanostructures may be in the form of a straight wire or a rod-shaped nanostructure. Other combinations of shapes of nanostructures can also be used. (For example, even within the first structure, the plurality of first nanostructures may be the same or different from one another. The shapes and arrangements of

5 nanostructures can be controlled at least in part by features (e.g., protrusions and/or indentations) on the substrate that are used to form the nanostructures.) The plurality of first and second nanostructures may remain in their respective arrangements, wherein each nanostructure is not in direct physical contact with another nanostructure in the arrangement. In some cases, the nanostructures can remain in their respective

10 arrangements due to the encapsulating material, which is not removed from the nanostructures. However, in other embodiments, the encapsulating material is removed from the nanostructures. E.g., the first material may be removed from the first structure and/or the second material may be removed from the second structure. In some cases a portion of the encapsulating material is removed from the first and/or second structure.

15 In other cases, all of the encapsulating material is removed. In instances where the encapsulating material is removed from the first and second structures, isolated composite structures (e.g., stacked nanostructures) can be formed.

As described in more detail below, in such embodiments the first and/or second nanostructures may have a variety of sizes and/or cross-sectional dimensions. Typically,

20 at least one of the nanostructures has a cross-sectional dimension of less than or equal to 500 nanometers, less than or equal to 300 nanometers, less than or equal to 200 nanometers, less than or equal to 100 nanometers, or less than or equal to 50 nanometers.

As described above, in some cases stacked nanostructures can be separated by a dielectric material. However, in other cases a first nanostructure may be positioned

25 adjacent a second nanostructure and the first and second nanostructures may be in direct physical contact with one another. In yet other embodiments, conductive or semiconductive films can be positioned between first and second nanostructures.

The material positioned between the first and second nanostructures (e.g., a dielectric material, in certain embodiments), may be chosen at least in part by one or

30 more of the following: its optical properties, electron conductivity, permeability, and permittivity. For instance, for optical applications, the intervening material may be chosen such that it is transparent in the wavelength of interest.

The material used to form the first and/or second nanostructures may also be chosen at least in part by one or more of its optical properties, electron conductivity, permeability, and permittivity.

Various composite structures can be made using methods described herein. In one embodiment, a composite structure includes a first nanostructure (e.g., a conductive nanostructure), wherein the first nanostructure has three principle intersecting axes, wherein at least a first dimension of the first nanostructure, along a first axis passing through the first nanostructure, is smaller than 500 nm (or 400 nm, 300 nm, 200 nm, 100 nm, or 50 nm) and at least a second dimension of the first nanostructure, along a second axis perpendicular to the first axis passing through the first nanostructure, is smaller than 500 nm (or 400 nm, 300 nm, 200 nm, 100 nm, or 50 nm). In some cases, the composite structure includes an array of such first nanostructures. The composite may also include a second nanostructure (e.g., a conductive nanostructure) positioned adjacent but not in physical contact with the first nanostructure (e.g., an intervening material such as a dielectric material and/or a conductive material can be positioned between the first and second nanostructures). In some cases, more than one layer of material is positioned between the first and second nanostructures. The second nanostructure may have three principle intersecting axes, wherein at least a first dimension of the second nanostructure, along a first axis passing through the first nanostructure, is smaller than 500 nm (or 400 nm, 300 nm, 200 nm, 100 nm, or 50 nm) and at least a second dimension of the second nanostructure, along a second axis perpendicular to the first axis passing through the second nanostructure, is smaller than 500 nm (or 400 nm, 300 nm, 200 nm, 100 nm, or 50 nm). The first and second nanostructures (or a portion thereof) may be positioned at various distances from one another (e.g., measured by the two closest points between the first and second nanostructures). Such a distance may be, for example, less than 1 mm (e.g., such that the first and second nanostructures are positioned less than 1 mm apart), less than 500 microns, less than 200 microns, less than 100 microns, less than 50 microns, less than 1 micron, less than 500 nm, less than 250 nm, less than 200 nm, less than 100 nm, less than 50 nm, or less than 30 nm. The distance between the structures may depend in part by, for example, the dimensions of the first and second nanostructures. For some applications, the distance may also be chosen such the nanostructures can couple to incident light magnetically.

Composite structures described herein may be flexible. In some cases, the composite structure has a curved surface (e.g., in the shape of cylinder).

In embodiments described above, at least a portion of the first and second nanostructures are aligned such that they share a common principle axis. For example, the structures, if positioned on top of one another, may share the same z-axis. Examples of stacked nanostructures are shown in FIGs. 4P and 4Q. FIGs. 4P and 4Q show first nanostructure 86 and second nanostructure 88 sharing the same z-axis. Although not shown, the nanostructures may be offset from one another relative to the z-axis (e.g., the second nanostructure may not be positioned directly above the first nanostructure in some embodiments). In some cases, arrays of these nanostructures can be formed. The nanostructures of these arrays may be embedded or not embedded in a matrix material.

In other embodiments, alternating layers of first nanostructures and second nanostructures (and, optionally, third, fourth, or fifth layers of nanostructures) can be formed. For example, greater than or equal to 2, greater than or equal to 6, greater than or equal to 10, greater than or equal to 15, greater than or equal to 20, greater than or equal to 50, or greater than or equal to 100 alternating layers can be formed. In a composite structure including multiple alternating layers of nanostructures, a first layer may have negative permittivity and a second layer may have negative permeability. As described in more detail below, such structures may have a negative index of refraction (e.g. in the infrared range).

FIG. 5 shows another method of fabricating isolated nanostructures and/or arrays of nanostructures according to another embodiment of the invention. As shown in embodiment illustrated in FIG. 5A, substrate 90, which is formed in material 92, may include a plurality of indentations 94. Material 100 may be deposited on at least a portion of the surface of substrate 90, including in all, or portions of, indentations 94. A section of substrate 90 may be cut, e.g., with a thickness of z , as shown in FIG. 5C. This process can form one or more cut portions 104 including nanostructures 102 embedded in material 92. Material 92 may be removed (partially or completely) from the cut portion to form isolated nanostructures 102.

Nanostructures of the invention may have a variety of shapes and dimensions. The shapes and/or dimensions of nanostructures may depend, at least in part, on the patterns of features on a substrate (e.g., including the shapes, spacing, and density of the protrusions and/or indentations). Non-limiting examples of nanostructure shapes include

lines (e.g., wires), pillars, disks, squares, triangles, rings, tubes, cylinders, and irregular shapes. Advantageously, nanostructures having curved surfaces (e.g., circles, rings, L-, C-, and U-shapes), which may be difficult to fabricate using conventional nanofabrication techniques, may be fabricated using methods described herein.

5 As described herein, in some embodiments, nanostructures have a “closed-loop” structure; that is, one in which the nanostructure forms a closed loop or perimeter when viewed from above, such as an O- (circular closed-loop), Δ - (triangular closed-loop), or $\square$ - (square closed-loop) shape (e.g., as shown in FIGs. 4A-4K). In other embodiments, nanostructures may have an “open-loop” structure. Open loop structures are curved
10 structures that are not completely closed when viewed from above and have at least two end portions that are not connected. Examples of open loop structures are ones having a U-, L-, or C-shape. Arrays of such structures can also be fabricated.

Nanostructures described herein can have varying cross-sectional dimensions. For instance, a nanostructure may have at least one cross-sectional dimension (e.g., a
15 length, width, height, or diameter) of less than 10 microns, less than 1 micron, less than 0.5 micron, less than 0.1 micron, less than 50 nm, less than 20 nm, or less than 10 nm. In some cases, at least two cross-sectional dimensions of the nanostructure may be less than 10 microns, less than 1 micron, less than 0.5 micron, less than 0.1 micron, less than 50 nm, less than 20 nm, or less than 10 nm. In some cases, a nanostructure has three
20 principle intersecting axes (e.g., axes on the same plane as the length, width, and height of the nanostructure), at least a first dimension of the nanostructure, along a first axis passing through the nanostructure, being smaller than 1 micron (or, alternatively, smaller than 0.1 micron, or smaller than 10 nm) and at least a second dimension of the nanostructure, along a second axis perpendicular to the first axis passing through the
25 nanostructure, being smaller than 1 micron (or, alternatively, smaller than 0.1 micron, or smaller than 10 nm). In some embodiments, nanostructures can be etched to form even smaller structures after they have been formed by methods described herein.

In some cases, the nanostructures described herein may be substantially uniform in size and/or composition. For instance, greater than 70%, greater than 80%, greater
30 than 90%, greater than 95%, or greater than 99% of the nanostructures fabricated may be substantially uniform in size and/or composition (e.g., the dimensions of the nanostructures may be within $\leq 1\%$). In some instances, nanostructures with the above

characteristics can be fabricated essentially simultaneously (e.g., in a single step).

Monodispersed nanostructures have use in a variety of applications.

Any suitable material can be used to form nanostructures of the invention. In one embodiment, a nanostructure of the invention may comprise a metal. In some cases, the metal film includes a transition element. Non-limiting examples of metals include
5 copper (Cu), platinum (Pt), palladium (Pd), gold (Au), nickel (Ni), indium (In), tin (Sn), silver (Ag), lead (Pb), bismuth (Bi), cadmium (Cd), zinc (Zn), antimony (Sb), chromium (Cr), and titanium (Ti). Of course, other metals, such as ones from Groups 3-15 of the Periodic Table of Elements, can be used to form nanostructures. In addition, other
10 materials such as semi-conductors (e.g., elements from Groups 13-16 of the Periodic Table of Elements such as Si, Ga, and As) can also be used.

In other embodiments, organic materials such as polymers (e.g., conductive polymers) and carbon can be used to form nanostructures, such as polymeric or carbon nanowires. (Carbon nanowires of the invention may have different characteristics that
15 carbon nanowires fabricated by chemical synthesis techniques.) Combinations of materials such as the ones listed above can also be used; for example, polymers may be combined with a magnetic material to form magnetically-susceptible nanostructures. Materials used to form nanostructures may be conductive, semi-conductive, or insulating.

20 In some cases, nanostructures are formed from a precursor article (e.g., a cut portion) sectioned from a larger article. The dimensions of a precursor article may depend on the size of the substrate, the thickness of the article from which the precursor article was portioned, and/or the instrument used to section the precursor article. The precursor article may have at least one cross-sectional dimension (e.g., a length, width,
25 height, or diameter) of less than 10 microns, less than 1 micron, less than 0.1 micron, less than 50 nm, less than 20 nm, or less than 10 nm. In some cases, a precursor article has three principle intersecting axes (e.g., axes on the same plane as the length, width, and height of the cut portion), at least a first dimension of the precursor article, along a first axis passing through the precursor article, being smaller than 1 micron (or, alternatively,
30 smaller than 0.1 micron, or smaller than 20 nm) and at least a second dimension of the precursor article, along a second axis perpendicular to the first axis passing through the precursor article, being smaller than 1 micron (or, alternatively, smaller than 0.1 micron, or smaller than 20 nm). In some cases, at least one cross-sectional dimension of the

nanostructure is essentially the same as a cross-sectional dimension of the precursor article. Of course, a plurality of precursor articles may be formed from a single article, and each of these precursor articles may vary in size (e.g., thickness).

Different methods can be used to deposit a material (e.g., a material used to form the nanostructures) on a substrate. An appropriate method may depend on the type of material to be deposited (e.g., a metal compared to an organic material). Examples of methods for depositing conductive or semi-conductive materials (e.g., metals and semi-conductors) include electroplating, vacuum deposition, and thermal evaporation. Examples of methods for depositing organic materials (e.g., polymers and biological and/or chemical materials) include vapor deposition, spin coating, printing, and stamping. In some cases, methods involving solvent evaporation can be used, e.g., coating a surface with a solution of the material dissolved in a solvent and allowing the solvent evaporate. Such methods can coat all, or portions of, a surface with a material. For instance, dipping the substrate in the material may cause the material to cover all of the substrate. Using a microfluidic network to deliver materials to a surface can cause only portions of the substrate to be covered by the material. Those of ordinary skill in the art are aware of many techniques for depositing materials (e.g., films or layers) on a substrate.

Materials deposited on a substrate can cover all or portions of a substrate. The portions of the substrate covered by the material can influence the shape of the nanostructure formed, as discussed above. In some instances, a material is deposited such that it completely covers the substrate, e.g., to form a continuous layer. In other instances, a material may be deposited to form a discontinuous layer. In one embodiment, collimated material (e.g., gold) can be deposited substantially normal to the substrate to ensure a discontinuous film; the sidewalls of the features can intentionally be left free of deposited material. In another embodiment, non-collimated material deposition can be used to form thin films on all surfaces of the substrate. In yet another embodiment, material can be deposited at an angle (e.g., less than or equal to 15°, less than or equal to 30°, less than or equal to 45°, less than or equal to 60°, less than or equal to 75°, or less than or equal to 90°) relative to the substrate such that the film is deposited on only certain portions of the substrate (e.g., on certain portions of the protrusions and/or indentations). Depositing material at an angle may be performed multiple times at different positions on a single substrate to form free standing structures having

different shapes. For example, features in the shape of a cube may be treated with deposition material to selectively coat two sides of the cube to form free-standing structure in the shape of an "L" using methods described herein. Such procedures are described in more detail below.

5 A material deposited on a substrate can have various thicknesses. In some cases, the thickness of the material deposited may define a cross-sectional dimension of the nanostructure formed in that material. A layer of material may have a thickness of, e.g., equal to or less than 1 micron, equal to or less than 100 nanometers, equal to or less than 50 nanometers, equal to or less than 40 nanometers, equal to or less than 30 nanometers,
10 equal to or less than 20 nanometers, or equal to or less than 10 nanometers.

 In some embodiments, a substrate may include a surface having a variety of features defined therein by protrusions (i.e., raised portions) and/or indentations (i.e., recessed portions). The substrate may include features having a variety of lateral dimensions. For instance, the substrate may include at least one feature with a lateral
15 dimension of less than about 100 microns, less than about 50 microns, less than about 10 microns, less than about 5 microns, less than about 1 micron, or less than 0.25 microns. The substrate may be fabricated using various methods such as e-beam lithography, which can be combined with reactive etching steps to create even smaller features.

 A substrate may include one or more different patterns of features including lines,
20 circles, squares, triangles, pyramids, cylinders, and irregular shapes. The patterns (including the shapes, spacing, and density) of the features on the substrate can control the pattern of nanostructures formed in a cut portion (e.g., embedded nanostructures), and/or the pattern of isolated nanostructures formed on a surface.

 In other embodiments, a substrate can be substantially smooth, i.e., the substrate
25 may not include protrusions or indentations. These types of substrates may be useful, for example, for forming nanostructures in the form of long wires. Substrates without protrusions and/or indentations may also be suitable for certain material deposition techniques (e.g., depositing a material used to form a nanostructure using a microfluidic system). Additionally, a substrate may be planar, or it may be curved.

30 Numerous protrusions and/or indentations may be present on a substrate. For example, a single substrate may include more than 5000 isolated protrusions and/or indentations, more than 10^6 isolated protrusions and/or indentations, or more than 10^9 isolated protrusions and/or indentations. As such, a substantially equivalent number of

nanostructures can be fabricated from one cut portion. For example, one isolated protrusion and/or indentation may be used to form one isolated nanostructure of a cut portion. Of course, the same protrusions and/or indentations of a substrate can be used to form several cut portions, and, therefore, multiple numbers or arrays of nanostructures
5 can be fabricated from one substrate. For instance, a single substrate including 1000 isolated protrusions and/or indentations may be cut 100 times to form 10^5 isolated (or embedded) nanostructures.

Such protrusions and/or indentations may be used form arrays of nanostructures (which may be isolated or embedded in a matrix/encapsulating material). The
10 nanostructures may be positioned at various distances from one another in the array, which may depend on the distances between the protrusions and/or indentations on the substrate. Different types of arrays of nanostructures can be formed. For example, hexagonal arrays, face-centered cubic arrays, and other types of arrays of nanostructures can be fabricated.

15 In some instances, the nearest distance between two nanostructures in an array is, for example, less than 1 mm, less than 500 microns, less than 200 microns, less than 100 microns, less than 50 microns, less than 1 micron, less than 500 nm, less than 250 nm, less than 200 nm, less than 100 nm, less than 50 nm, or less than 30 nm. The distance between structures, as well as the size of the nanostructures themselves, can form unit
20 cells (e.g., a simplest repeating unit) of different sizes. Different sizes of units cells can have different properties. For instance, smaller unit cells can be used to select smaller wavelengths of light for optical applications (e.g., optical filters). The protrusions and/or indentations may form a "patterned area" on the substrate. The patterned area may be larger than 1 mm^2 , larger than 0.5 cm^2 , larger than 1 cm^2 , larger than 2 cm^2 , or
25 larger than 5 cm^2 . In some cases, this patterned area of the substrate can be cut in such a way to form a patterned area of nanostructures within the cut portion. The patterned area of nanostructures within the cut portion may have an area that is substantially equivalent to the patterned area of the substrate. The nanostructures of the cut portion may be
30 transferred to a surface to form isolated nanostructures, e.g., arranged in the form of the pattern.

An individual feature included in the protrusions and/or indentations of a surface can have various aspect ratios in some embodiments of the invention, e.g., depending on the method in which the features are made. The aspect ratio of a feature is the ratio of

minimum lateral dimension of any raised portion of a surface feature to indentation depth. An individual feature may have an aspect ratio of greater than or equal to 2, greater than or equal to 5, greater than or equal to 10, greater than or equal to 20, greater than or equal to 50, or greater than or equal to 100 in some instances. Methods of forming features in a substrate are described in more detail below.

A substrate or article (including a nanostructure material associated with the substrate or article) can be cut or sectioned by a variety of methods. In some cases, a particular method of cutting may depend on the physical properties of the substrate, e.g., the hardness, elasticity, or crystallinity of the surface. For example, for some crystalline surfaces such as silicon, substrates can be cut by fractioning the substrate. In other embodiments, a sharp cutting edge, such as a microtome, can be used. Several different microtomes are known in the art, including those made by Leica. These microtomes can be equipped with different types of cutting edges including diamond knives and trimming blades. Certain microtomes may be suitable for cutting extremely hard and brittle materials such as ceramics (including oxides (e.g., glass, alumina, zirconia), non-oxides (e.g., carbides, borides, nitrides, and silicides) and composites (e.g., particulate reinforced composites, and combinations of oxides and non-oxides)). Semiconductors (e.g., silicon, GaAs, etc.), super conducting oxides, and nanocrystalline ceramics can also be cut. In other cases, microtomes are suitable for cutting polymers (e.g., epoxies, acrylates, and silicones).

Different types of cutting edges may be suitable for different samples, for instance, tungsten carbide knives may be suitable for cutting certain polymers. For very small samples, such as when cutting below 1 micron, glass or diamond knives can be used. In some instances, these instruments can be used at low temperatures, e.g., below -100°C. Such temperatures may be important, e.g., for cutting elastomers and thermoplastics which may not be cut satisfactorily at ambient temperatures. The angle of the cutting edge can also be varied, e.g., to modify a cut portion. Those of ordinary skill in the art are aware of many techniques for cutting different materials.

Portions of a substrate or article can be cut serially or in parallel. As such, by applying methods described herein, a plurality of nanostructures (including isolated nanostructures or embedded nanostructures) may be fabricated essentially simultaneously. For example, greater than 1000, greater than 10^4 , greater than 10^5 ,

greater than 10^6 , or greater than 10^7 nanostructures may be fabricated essentially simultaneously (e.g., in a single cutting step or a single removal step).

A variety of different materials may be used as encapsulating materials. Suitable encapsulating materials may have physical properties (e.g., hardness) that make it
5 appropriate for cutting, e.g., with a microtome or another suitable apparatus. In some cases, it may be desirable for the encapsulating material to provide mechanical support for the nanostructures that are formed upon cutting, and/or to allow the cut portions to be manipulated. Another consideration when choosing a suitable encapsulating material is compatibility with the material used to form the nanostructures. In some cases, for
10 example, an encapsulating material can be easily and quickly removed or separated from the nanostructures, e.g., without destroying or damaging the nanostructures. An encapsulating material may be removed by appropriate methods such as etching in an oxygen plasma or using an appropriate solvent that can dissolve the encapsulating material. In other instances, an encapsulating material may be chosen based on its ability
15 to adhere to the material used to form the nanostructure, e.g., such that additional adhesion layers are not required.

In one embodiment, an encapsulating material is polymeric. Polymeric materials suitable for use in fabrication of the substrate may have linear or branched backbones, and may be crosslinked or noncrosslinked, depending upon the particular polymer and
20 the degree of formability or hardness desired of the substrate. A variety of polymeric materials are suitable for such fabrication, including epoxy polymers (e.g., Araldite 502), acrylate polymers, and silicone polymers. Epoxy polymers are characterized by the presence of a three-member cyclic ether group commonly referred to as an epoxy group, 1, 2-epoxide, or oxirane. For example, diglycidyl ethers of bisphenol A may be used, in
25 addition to compounds based on aromatic amine, triazine, and cycloaliphatic backbones. Another example includes the well-known Novolac polymers. Examples of silicone polymers suitable for use include those formed from precursors including the chlorosilanes such as methylchlorosilanes, ethylchlorosilanes, and phenylchlorosilanes, and the like. Another example of a silicone polymer is poly(dimethylsiloxane) (PDMS).
30 Exemplary polydimethylsiloxane polymers include those sold under the trademark Sylgard by the Dow Chemical Company, Midland Michigan, and particularly Sylgard 182, Sylgard 184, and Sylgard 186.

In another embodiment, an encapsulating material may include a ceramic. Ceramics may include oxides (e.g., glass, alumina, zirconia), non-oxides (e.g., carbides, borides, nitrides, and silicides) and composites (e.g., particulate reinforced composites, and combinations of oxides and non-oxides).

5 A variety of different materials may be used as substrates for depositing materials. In some cases, the material used to form the substrate may be the same as the encapsulating material, such as those listed above. Materials used to form a substrate may be chosen based on its ability to be conformed to form features on the substrate (e.g., by patterning, molding, or other suitable techniques).

10 Features of a substrate may be formed according to a variety of methods. According to one method, the features of a substrate can be micromachined from a material such as a semi-conductor. According to another method, the features can be formed lithographically by providing a surface, depositing a film of material onto the surface, coating an exposed surface of the material with resist, irradiating the resist
15 according to a predetermined pattern, removing irradiated portions of the resist from the material surface, contacting the material surface with a reactant selected to react chemically therewith and selected to be chemically inert with respect to the resist such that portions of the material according to the predetermined pattern are degraded, removing the degraded portions, and removing the resist to uncover portions of the
20 material formed according to the predetermined pattern to form the mold surface. Negative or positive resist may be used, and the procedure can be adjusted accordingly. According to another method of forming features, a surface may be provided, and coated with resist. Then portions of the resist may be irradiated according to a particular predetermined pattern. Irradiated portions of the resist may then be removed from the
25 substrate to expose portions of the substrate surface according to the predetermined pattern, and the substrate may be contacted with a plating reagent such that exposed portions according to the predetermined pattern are plated. Then, the resist may be removed to uncover portions of the exposed substrate according to the predetermined pattern bordered by plated portions of the substrate to form the features.

30 Other methods of forming features (e.g., protrusions or indentations) include etching, stamping, molding, and the like.

A method of fabricating features on a substrate by molding may be as follows. A template consisting of an exposed and developed photoresist pattern on silicon is

prepared (This type of fabrication is described in any conventional photolithography text, such as Introduction to Microelectronic Fabrication, by Richard C. Jaeger, Gerold W. Neudeck and Robert F. Pierret, eds., Addison-Wesley, 1989). Templates such as electron microscopy grids or other corrugated materials may also be used. The template
5 is placed in a container such as a petri dish. A 10:1 (w:w or v:v) mixture of PDMS-Sylgard Silicone Elastomer 184 and Sylgard Curing Agent 184 (Dow Corning Corp., Midland, Michigan) is poured into the petri dish. It is not necessary to put the mixture of PDMS-elastomer and curing agent under vacuum to remove dissolved dioxygen. The PDMS can be cured at room temperature for 30 to 60 min. This cure can
10 be followed by additional curing at 65 °C for approximately 1-2 hours or until the polymer is rigid. After cooling to room temperature, the PDMS-stamp is carefully peeled from the template and can be used as a substrate. Advantageously, multiple substrates can be formed from a single template (or mold).

Those of ordinary skill in the art can select substrates, encapsulating materials,
15 nanostructure materials, etc. based upon general knowledge of the art and available references concerning material properties, preferential adhesion between certain materials, and compatibility of materials, in combination with the description herein.

Another aspect of the invention includes methods for positioning a plurality of nanostructures on a surface. In some cases, positioning includes providing a structure,
20 such as a cut portion of an article, including a plurality of nanostructures positioned in a particular arrangement in the structure. At least a portion of each nanostructure in the structure can be embedded in the structural material (e.g., an encapsulant material). For instance, the sides of the nanostructures may be encapsulated in the structural material, with the tops and bottoms of the nanostructures exposed. In other embodiments, all
25 surfaces of the nanostructures may be embedded in the structural material. The cut portion may be positioned on a surface, e.g., by methods using capillary, magnetic, or electrostatic forces. For example, in one embodiment, the cut portion may float at a fluid/air interface or may be suspended in a fluid, and a surface may be brought underneath the cut portion in the fluid and pulled back carefully to let the cut portion sit
30 on the surface. As such, nanostructures may be directly transferred to the surface. In another embodiment, a hollow loop may be used to position a cut portion on a surface. For instance, the cut portion may float at a fluid/air interface or may be suspended in a fluid, and the cut portion may be picked up in a drop of water using a loop (e.g., 2 mm in

diameter) and positioned on a surface. Using such methods, nanostructures may be indirectly transferred to the surface. Advantageously, methods of positioning nanostructures enable the transfer of nanostructures to various types of surfaces having different compositions (e.g., metallic, semi-conductive, and polymeric surfaces), and/or
5 surfaces having different shapes and/or geometries (e.g., flat surfaces, curved surfaces, surfaces having multiple faces (e.g., a cube), and surfaces already patterned with features).

In some cases, after positioning a cut portion on a surface, the structural material of the portion may be removed from the surface by methods such as plasma oxidation
10 and/or removal using a solvent (e.g., dissolving the structural material in an appropriate solvent that does not dissolve the nanostructures). Heat and/or sonication may also be applied to aid removal. Sometimes, removal of the structural material from a cut portion may occur before positioning the cut portion or the nanostructures on a surface. Sometimes, the nanostructure is at least partially embedded in an interior portion of the
15 cut portion (e.g., a precursor article), and a nanostructure may be removed or separated from the interior portion of the cut portion. In other cases, a nanostructure may be removed or separated from the exterior surface of the cut portion. Those of ordinary skill in the art can determine appropriate methods of removing or separating materials from nanostructures, e.g., based on the compatibility of the structural materials and
20 nanostructure materials with a particular method.

Sometimes, the plurality of nanostructures remain on the surface in the particular arrangement that they were in when embedded in the cut portion. In some embodiments, adjacent nanostructures are not in direct physical contact with one another and nanostructures are separated from one another via the structure material (encapsulating
25 material). When the structure material is removed from the surface, each nanostructure may be physically isolated from another nanostructure in that particular arrangement, e.g., to form isolated nanostructures. In certain embodiments, adjacent nanostructures are not in direct physical contact with one another and the nanostructures are separated from each other via a non-solid substance (e.g., a liquid or air). In other embodiments, a
30 second material different material from the encapsulating material can be used to at least partially embed the nanostructures.

In some embodiments, a first set of nanostructures can be positioned on a surface, and a second set of nanostructures can be positioned relative to the first set of

nanostuctures. For instance, as shown in FIG. 6A, a first set of nanostructures may include a set of parallel nanowires. A second set of nanowires may be positioned substantially perpendicular to the first set of nanowires, as shown in FIG. 6B. In other embodiments, first and second sets of nanostructures can be positioned at different
5 positions relative to one another. E.g., the first and second sets of nanostructures may be positioned at an angle of 30°, 60°, or 75° relative to one another. Additionally, third or more sets of nanostructures can be positioned on the same surface. In some cases, different sets of nanostructures can be layered on top of one another. E.g., a first set may include nanostructures having particular shapes and/or dimensions, and the second set
10 may include nanostructures having shapes and/or dimensions different from that of the first set. As such, complex nanostructures and/or nanostructure networks can be fabricated.

Nanostructures of the invention can be used in a variety of applications. For instance, nanostructures may be used as sensors, tags or probes, electrodes, switches, or
15 transistors. In some cases, nanostructures can be integrated into a functional component of a functional device. The structural, chemical, and/or electronic properties of the nanostructures can be used to create devices of a variety of types. In addition, structural, chemical, and/or electronic changes associated with nanostructures can modulate the properties of the nanostructures.

20 In some cases, enhancements in local fields and strong scatterings of nanostructures can be used in a number of applications, including surface-enhanced Raman scattering, subwavelength optical waveguiding, biolabeling, and biosensing. Nanostructures of noble metals (e.g., Ag or Au) show different colors due to their surface plasmon resonances. These particles interact strongly with visible light through the
25 resonant excitation of the collective oscillations of their conduction electrons. As a result of these oscillations, local electromagnetic fields near the particle can be many orders of magnitude higher than the incident fields; these strong, oscillating fields generate intense scattered light around the wavelength of the resonant peak. The magnitude, peak wavelength, and spectral bandwidth of the plasmon resonance of a
30 nanostructure may depend on the size, shape, composition, and local environment of the nanostructure. As such, the plasmon resonances of nanostructures of the invention can be easily tuned by varying such parameters. The differences in optical properties of such nanostructures are illustrated in Examples 3-5.

In some instances, the differences in surface-enhanced Raman scattering (SERS) of nanostructures can be used in certain applications (e.g., sensing). Since vibrational information is very specific for certain materials (e.g., the size, shape, composition, and local environment of a nanostructure), it can provide a fingerprint by which the nanostructure can be identified. Compared with some metal nanoparticles, nanostructures of the invention, which may have, e.g., sharp corners and/or large surfaces areas, can greatly enhance electric fields and can have increased total SERS efficiency.

In other embodiments, nanostructures in the form of metal nanowires can be used as waveguides to propagate light under subwavelength scales. The ability to engineer plasmon resonances may optimize the nanowire sizes for different colors of light.

In some embodiments, nanostructures may be appropriately functionalized (e.g., with a coating of material) to impart desired characteristics (e.g., surface properties) to the nanostructures. For example, the nanostructure may be functionalized or derivatized to include compounds, functional groups, atoms, or materials that can alter or improve properties of the nanostructure. Nanostructures are particularly suitable for chemical functionalization on their exterior surfaces, as is well known.

In some embodiments, a nanostructure may be functionalized with functional groups which can specifically interact with an analyte. The functional groups may include compounds, atoms, or materials that can alter or improve properties such as compatibility with a suspension medium (e.g., water solubility, water stability, i.e., at certain pH ranges), photo-stability, and biocompatibility.

Nanostructures may be modified using species such as self-assembled monolayers (SAMs). Nanostructures can be modified with any of a variety of SAM-forming materials, such as those described in U.S. Patent No. 5,512,131 of Kumar, et al., published April 30, 1996 and incorporated herein by reference.

In some embodiments, nanostructure may be modified with functional groups that interact with an analyte to form a bond with the analyte, such as a covalent bond (e.g., carbon-carbon, carbon-oxygen, oxygen-silicon, sulfur-sulfur, phosphorus-nitrogen, carbon-nitrogen, metal-oxygen or other covalent bonds), an ionic bond, a hydrogen bond (e.g., between hydroxyl, amine, carboxyl, thiol and/or similar functional groups, for example), a dative bond (e.g., complexation or chelation between metal ions and monodentate or multidentate ligands), or the like. The interaction may also comprise

Van der Waals interactions. In one embodiment, the interaction comprises forming a covalent bond with an analyte. The functional group may also interact with an analyte via a binding event between pairs of biological molecules. For example, the functional group may comprise an entity, such as biotin that specifically binds to a complementary
 5 entity, such as avidin or streptavidin, on a target analyte. Such interactions with an analyte may cause the nanostructure to have a detectable change in property (e.g., optical scattering, color, or size) that can allow the detection of the interaction.

In some embodiments, the analyte may be a chemical or biological analyte. The term "analyte," may refer to any chemical, biochemical, or biological entity (e.g., a
 10 molecule) to be analyzed. In some cases, nanostructures of the invention may have high specificity for the analyte, and may be, e.g., a chemical, biological, explosives sensor, or a small organic bioactive agent (e.g., a drug, agent of war, herbicide, pesticide, etc.). In other embodiments, a nanostructure may comprise a functional group that acts as a binding site for an analyte. The binding site may comprise a biological or a chemical
 15 molecule able to bind to another biological or chemical molecule in a medium, e.g., in solution. For example, the binding site may be capable of biologically binding an analyte via an interaction that occurs between pairs of biological molecules including proteins, nucleic acids, glycoproteins, carbohydrates, hormones, and the like. Specific examples include an antibody/peptide pair, an antibody/antigen pair, an antibody
 20 fragment/antigen pair, an antibody/antigen fragment pair, an antibody fragment/antigen fragment pair, an antibody/hapten pair, an enzyme/substrate pair, an enzyme/inhibitor pair, an enzyme/cofactor pair, a protein/substrate pair, a nucleic acid/nucleic acid pair, a protein/nucleic acid pair, a peptide/peptide pair, a protein/protein pair, a small molecule/protein pair, a glutathione/GST pair, an anti-GFP/GFP fusion protein pair, a
 25 Myc/Max pair, a maltose/maltose binding protein pair, a carbohydrate/protein pair, a carbohydrate derivative/protein pair, a metal binding tag/metal/chelate, a peptide tag/metal ion-metal chelate pair, a peptide/NTA pair, a lectin/carbohydrate pair, a receptor/hormone pair, a receptor/effector pair, a complementary nucleic acid/nucleic acid pair, a ligand/cell surface receptor pair, a virus/ligand pair, a Protein A/antibody
 30 pair, a Protein G/antibody pair, a Protein L/antibody pair, an Fc receptor/antibody pair, a biotin/avidin pair, a biotin/streptavidin pair, a drug/target pair, a zinc finger/nucleic acid pair, a small molecule/peptide pair, a small molecule/protein pair, a small molecule/target pair, a carbohydrate/protein pair such as maltose/MBP (maltose binding

protein), a small molecule/target pair, or a metal ion/chelating agent pair. In some cases, the nanostructures may be used in applications such as drug discovery, the isolation or purification of certain compounds, and/or implemented in assays or high-throughput screening techniques (e.g., sensing arrays).

5 In some cases, nanostructures can be positioned in association with a plurality of other components to form a functional component of a functional device. For instance, a nanostructure (e.g., a carbon nanowire or a semi-conductive polymer nanowire) may be functionalized with a biomolecule (e.g., biotin) specific to an analyte to be determined (e.g., streptavidin). The nanostructure may be positioned on a surface proximate a
10 source and a drain to form a field-effect transistor. Detection of the analyte may be measured by the difference in current flowing across the nanostructure when the nanostructure is exposed to the analyte and in the absence of the analyte.

Patterned arrays of nanostructures described herein can also have applications in nanophotonics. For instance, such structures may be used to form negative index of
15 refraction materials (NIMs), frequency-selective surfaces (FSS), infrared optical polarizers, and nanostructures for surface-enhanced Raman spectroscopy.

Frequency-selective surfaces (FSS) are two-dimensional periodic arrays of structure (e.g., metallic structures) that transmit or reflect radiation at specific frequencies. FSS are useful in, for example, beam-splitters, filters, and polarizers. In
20 FSS, the reflection or transmission is strongest when the wavelength of the incident electromagnetic field resonates with the metallic structures comprising the FSS. This resonant frequency is mainly determined by the size and shape of the unit elements of the FSS, while the bandwidth of resonance--as well as total reflectivity or transmittance--depend on density and periodicity of unit elements. For an FSS comprising identical
25 straight metallic wires (an antenna array), the longest wavelength of the resonance is approximated by equation 1; in this equation, λ_r

$$\lambda_r/2 \sim n_{eff}l \quad (1)$$

$$n_{eff} = \left(\frac{n_1^2 + n_2^2}{2} \right)^{1/2} \quad (2)$$

is resonance wavelength, l is the length and perimeter of the wire or shape along which
30 the induced current has a half-wavelength current distribution pattern when the wire is suspended in air or vacuum ($n_{eff} = 1$). The value of n_{eff} is given by eq. 2, where n_1 and n_2 are refractive indices of the media above (e.g., air, $n=1$) and below (e.g., supporting

substrate) the metal structure. At this resonant wavelength, the wire is approximated as a simple electric dipole. For a simple non-straight wire (for example, those having L- or U-shapes), L becomes the tip to tip distance for the half wavelength resonance condition. In addition to this long wavelength resonance, high order or harmonic resonances at
5 shorter wavelength (for example, $\lambda_r/2$) can also be excited in open loop nanostructures even at normal incidence with proper polarization of incident light. Accordingly, harmonic modes in L-shaped and U-shaped structures can be observed.

In one embodiment, nanostructures (e.g., arrays of nanostructures that may be isolated and/or embedded in a material) are used to form a FSS. A FSS can couple to
10 incident light magnetically if it includes, for example, open loop nanostructures such as split-ring and/or U-shaped structures, because the magnetic field perpendicular to the plane of the nanostructures can induce circulating electrical current in them. U-shaped metallic structures may have a magnetic resonance at infrared wavelengths.

In another embodiment, nanostructures described herein are used to form
15 negative index of refraction materials. NIMs can be formed by, for example, assembling a first set of nanostructures having a negative permittivity adjacent a second set of structures having a negative permeability. The first and second sets of nanostructures may be positioned such that they are not in direct physical contact with one another (e.g., such that a current cannot substantially pass from one a nanostructure of the first set to a
20 nanostructure of the second set). In some instances, the first and second sets of nanostructures are separated from each other by a dielectric film. For example, nanostructures (e.g., open loop nanostructures), which may be isolated in some instances, or at least partially embedded in a matrix (encapsulating material) in other instances, may be positioned adjacent thin wire structures to form a composite nanostructure. The open
25 loop nanostructures and thin wire structures may each be conductive (e.g., formed of a conductive material such as gold), and a dielectric material such as a thin film polymer or ceramic may be positioned between the two structures. The dielectric material may be chosen such that it does not interfere with (e.g., absorb) the wavelength of interest. In embodiments in which the encapsulating material is not removed from the first and/or
30 second sets of nanostructures, the particular encapsulating material may also be chosen such that it does not interfere with the wavelength of interest.

In one particular embodiment, U-shaped nanostructures and nanowires are used to form a negative index material. U-shaped nanostructures may be a simplified version

of an initial split-ring structure for the construction of materials with negative index. The fundamental mode of the U-shaped nanostructure can magnetically couple to the incident field, since a magnetic field normal to the U plane will induce the same current pattern shown in FIG. 14D. Accordingly, a composite structure may have a negative index of refraction as it combines split-ring structures (e.g., a U-shaped nanostructure having negative permittivity) with metal wire structures (e.g., a straight-wire shaped nanostructure having negative permeability). Due to the size scale of these nanostructures, this composite structure may be selective towards wavelengths in the infrared region. These structures can be used as, for example, optical filters.

In certain embodiments, as the wavelength of interest enters the mid-infrared (MIR) (4-20 μm) and near-infrared (NIR) regions (0.8-4 μm) or the visible region (0.4-0.7 μm), the sizes of features (of the nanostructures) necessary for functional FSS may be on the order of the wavelength of light (Eq. 1). To fabricate such NIR/MIR FSS having features in this size range and over large (e.g., mm^2) areas, methods of fabricating patterned (e.g., metallic) nanostructures described herein can be used. Accordingly, in some embodiments, a composite structure comprising nanostructures described herein are selective towards wavelengths in the mid-infrared region (MIR) (e.g., 4-20 μm), near-infrared (NIR) region (e.g., 0.8-4 μm), or the visible region (e.g., 0.4-0.7 μm).

In other embodiments, three dimensional FSS and/or NIM can be formed using nanostructures described herein. In some cases, nanostructures are positioned on surfaces having multiple faces, e.g., a cube, as well as curved surfaces, such as a cylinder.

The following examples are intended to illustrate certain embodiments of the present invention, but are not to be construed as limiting and do not exemplify the full scope of the invention.

EXAMPLE 1

Fabrication of Nanowires

This example illustrates a method of fabricating isolated structures such as nanowires according to certain embodiments of the invention.

Nanowires can be fabricated according to the scheme illustrated in FIG. 1. A thin layer (~500 nm) of positive photoresist (Shipley 1805, www.microchem.com) was spin-coated at 4000 rpm for 40 s on a Si/SiO₂ substrate (<100>, N/phosphorus or P/boron doped, 1-10-cm, from Silicon Sense; Nashua, NH) and baked on a hotplate at 115 °C for

5 min. This layer of photoresist was exposed through a chrome mask patterned with 2- μ m lines spaced by 2 μ m in a Karl Suss mask aligner with a UV-light source (365-405 nm) to generate lines of photoresist after development (CD-26, www.microchem.com).

After coating a gold film with thickness between 10 and 40 nm on this patterned
5 substrate using e-beam evaporation, the photoresist was removed by lift-off using acetone. After drying the sample with nitrogen gas, a layer of an Araldite-based epoxy prepolymer (~500 μ m) was coated on this substrate and cured at 60 °C overnight. The epoxy was purchased from Electron Microscope Science (Araldite 502 kit; Fort Washington, PA). The epoxy was prepared by mixing different components included in
10 a kit in the following amounts: 5 mL of diglycidyl ether of bisphenol-A (isopropylidenediphenol) (Araldite 502), 5.5 mL of dodecenyl succinic anhydride (DDSA), and 0.3 mL of benzyldimethylamine (BDMA). The cured epoxy was mechanically peeled from the silicon substrate; the gold film adhered to the cured epoxy substrate, and separated from the silicon substrate. This sample was cut into small strips
15 (~1 cm long, 2 mm wide) with a razor blade and embedded into the same epoxy prepolymer in a polyethylene mold (Electron Microscopy Sciences, Fort Washington, PA). Curing generated an epoxy slab comprising embedded metal.

The epoxy block containing the embedded metal film was trimmed with a razor blade to an area of ~0.5 mm $\times$ 0.5 mm with the aid of microscope; the trimming
20 exposed the metal layer. Thin epoxy film sections were sliced from the sample using a microtome with a diamond knife, with water in the sample-collecting boat (Ultracut microtome, Leica MZ6). The sectioning speed was set at 1 mm/s. The thin, sectioned polymer sections containing embedded metal nanowires floated on the surface of water.

In order to position the polymer film on a substrate, a solid substrate (e.g., a TEM
25 grid or a silicon wafer) was immersed into the water in the boat and pulled back to let the floating polymer film sit on the solid substrate. Alternatively, the film was picked up in a drop of water with a loop (~2 mm in diameter) and deposited on a solid substrate. The epoxy component of a section transferred to a solid substrate was removed with oxygen plasma (250 mTorr, 70 w barrel etcher) by exposing for 300 s. Gold nanowires were left
30 on the substrate, as shown in FIG. 2.

FIG. 2 shows SEM images of typical free-standing gold nanowires viewed in an angle. FIG. 2A shows gold nanowires with dimensions of ~2 μ m (length) by 40 nm (width) by 50 nm (height). FIG. 2B shows gold nanowires with dimensions of ~2 μ m

(length) by 10 nm (width) by 100 nm (height); these nanowires had a high aspect ratio of 10:1. The insets show high magnification images of the same samples. The orientations of FIG. 2A and 2B were at a 45° oblique angle. The SEM images were obtained using a LEO 982 SEM operating at 2 kV.

5 This example illustrates a method of fabricating isolated structures such as nanowires according to certain embodiments of the invention. This example also shows that nanostructures having high aspect ratios (e.g., 10:1) can be fabricated with well-controlled dimensions using such a method.

10 EXAMPLE 2

Fabrication of Nanorings

This example illustrates a method of fabricating isolated structures such as nanorings according to certain embodiments of the invention.

Nanorings can be fabricated according to the scheme illustrated in FIG. 3. A
15 poly(dimethyl siloxane) (PDMS) mold having desired features (e.g., the negative of the structures used to form the nanorings) can be obtained by molding PDMS prepolymer against an SU8 patterned substrate. The SU8 substrate can be patterned with desired features (e.g., the positive of the structures used to form the nanorings) which can be fabricated by conventional photolithography using standard procedures for soft-
20 lithography. For instance, a 2- μ m-thick layer of SU8 photoresist (SU8-5 purchased from MicroChem Corp.; Newton, MA) film can be coated on a silicon wafer (<100>, N/phosphorus or P/boron doped, 1-10 Ω -cm, from Silicon Sense; Nashua, NH) by spin-coating the prepolymer at 3000 rpm for 30s. The films of SU8 can be patterned by photolithography. The patterned surface can be coated with a release layer (e.g., using
25 Tridecafluoro-tetrahydrooctyl-trichlorosilane from United Chem. Tech; Bristol, PA), and molded with PDMS (Dow Corning's Sylgard 184 kit, mixing catalyst and prepolymer in a ratio of 1:10).

The PDMS mold can be replicated into an Araldite-based epoxy by molding the epoxy precursor against the PDMS master on a 15 nm thick silver coated silicon
30 substrate. This silver layer was used to facilitate the lift-off of the epoxy from the silicon substrate due to its poor adhesion with silicon substrate. The epoxy was cured at 60 °C for 12 h. The epoxy, which was composed of a diglycidyl ether of bisphenol-A (isopropylidenediphenol), was purchased from Electron Microscope Science (Araldite

502 kit; Fort Washington, PA). The epoxy was prepared by the mixing different components included in a kit in the following amounts: 5 mL of diglycidyl ether of bisphenol-A (isopropylidenediphenol) (Araldite 502), 5.5 mL of dodecenyl succinic anhydride (DDSA), and 0.3 mL of benzyldimethylamine (BDMA).

5 The epoxy was coated directly with a gold film by sputtering. A second layer of epoxy was used to cover this substrate (e.g., to embed the gold film). After curing the second layer of epoxy, the epoxy was peeled from the silicon substrate together with the silver. The silver was subsequently etched with nitric acid (V:V=1:1).

10 The epoxy slab comprising the gold film was trimmed with a razor blade to an area of $\sim 0.2 \text{ mm} \times 0.2 \text{ mm}$. The patterned plane was aligned parallel to the edge of a diamond knife with the aid of microscopy so that the sample could be cut uniformly. Thin epoxy film sections of the sample were sliced using a microtome (Ultra microtome, Leica RM2165) with water filling in the sample-collecting boat of the diamond knife (DiatomeTM, Ultra 35°). The sectioning speed was set at $1 \text{ } \mu\text{m/s}$ with a selected section
15 thickness, which can be precisely controlled by the instrument. The thin, sectioned polymer sections containing the embedded metal nanostructures floated on the surface of water.

20 In order to position the polymer film on a substrate, a solid substrate (e.g., a TEM grid or silicon wafer) can be directly immersed into the water and pulled back carefully to let the floating polymer film sit on the solid substrate. Alternatively, the polymer film can be picked up in a drop of water with a loop ($\sim 2 \text{ mm}$ in diameter) and deposited onto the substrate. The epoxy sections that were transferred onto a solid substrate were removed with oxygen plasma (250 mTorr, 70 w barrel etcher) for 300 s. Gold nanorings were left on the substrate, as shown in FIG. 4.

25 FIGS. 4A and 4B show SEM images of patterned isolated gold nanorings on a silicon substrate after removing the epoxy with oxygen plasma. The diameter of the ring is $\sim 3 \text{ } \mu\text{m}$. The width and the height of the ring are about 40 nm and 200 nm respectively. FIG. 4B shows a high magnification SEM image of the structures shown in FIG. 4A. SEM images were obtained using a LEO 982 SEM operating at 2 kV.

30 This example illustrates a method of fabricating isolated structures such as nanorings according to certain embodiments of the invention. This example also shows that nanostructures having different geometries can be fabricated with well-controlled dimensions using such a method.

EXAMPLE 3

Characterization of Gold Nanowires by Optical Scattering

This example shows that gold nanowires fabricated using methods of the invention can be characterized by optical scattering.

FIG. 7A outlines an apparatus that can be used to record the scattering spectra of individual nanowires (e.g., nanowires shown in FIG. 2 fabricated using the method discussed in Example 1). Nanowires were illuminated with unpolarized, focused, white light from a high-intensity fiber light-source (Fiber Illuminator, OSL1). The incident beam of light was perpendicular to the long axis of the nanowire at an angle of about 60° with respect to the normal to the silicon substrate. Scattered light from the nanowire was collected selectively using a microscopic objective with a long working distance (Mitutoyo SL50, NA = 0.55). This dark-field illumination maximized the scattering from the nanoparticles, and minimized the background scattering from the substrate. The collected light then passed through a polarizer parallel to the short axis of the nanowire (y direction) and focused on the plane of the entrance slit of a single-grating monograph (Triax 550, Jobin Yvon Horiba); this apparatus enabled video imaging of the nanowires and measurements of their spectrum. The polarizer enabled selection of surface plasmon resonances with polarization traverse to the long axis of the wire. An individual nanowire, or a small group of wires, could be selected for analysis by adjusting the width and height of the slit.

The as-obtained spectra depended on the spectrum of the incident white light, the focusing and collecting optics, and the response of the spectrometer. In order to remove these effects and isolate the plasmon resonance spectrum of the nanowires, the nanowire sample was replaced with a broad-band white-light target (which has a constant scattering response over wide range of frequencies) and its scattering spectrum was obtained using the same procedure. The as-obtained spectrum of the nanowires was then normalized to the reference spectrum of the broad-band target.

FIG. 7B shows the normalized scattering spectra of four randomly selected nanowires in a single sample. The scattering spectra of the four nanowires were displaced vertically to show reproducibility. The nanowires measured were 2 μm long, 20 nm wide, and 50 nm high. This plot shows that the variation in position of the resonance peak among the nanowires was negligible. The spectral variation between

nanowires from separate cut portions of the same thickness was also negligible. These observations established the optical homogeneity of the nanowires generated by the methods described herein. The optical homogeneity of the nanowires implies that the nanowires were uniform in composition and dimension.

5 This example shows that gold nanowires fabricated using methods of the invention can be characterized by optical scattering. This example also illustrates that nanowires having uniform composition and dimensions can be fabricated according to certain embodiments of the invention.

10 EXAMPLE 4

Surface Plasmon Resonances of Gold Nanowires with Different Cross-Sectional Dimensions

This example shows that nanowires with different cross-sectional dimensions can have different optical properties.

15 The nanowires shown in FIG. 8 were fabricated using the method described in Example 1. Nanowires with different cross-sectional dimensions were fabricated by changing the thicknesses of the metal film deposited on the articles (e.g., to change the heights of the nanowires) and by changing the thickness of the cut portions (e.g., to change the widths of the nanowires). The nanowires were all 2 μm long (x). The dimensions of the cross-sections are marked in each figure by y and z (the thickness of gold film and the thickness of the cut portion, respectively). The sizes of nanowires appear larger than their actual dimensions, due to optical diffraction.

20 FIGS. 8A-8C show color, dark-field, optical images of nanowires with different cross-sections, obtained using a standard optical microscopic system with dark-field illumination (Nikon 43300-522 with CCD camera). All optical images were taken under the same conditions with polarization perpendicular to the long axis of the nanowires. For each set of wires with the same width (y), the color shows a red-shift with increasing height (z).

25 FIGS. 8D-8F show the scattering spectra of gold nanowires corresponding to those in FIGS. 8A-8C. Emission spectra were collected simultaneously from four nanowires during each measurement in order to increase the signal-to-noise ratio, and to average the small spectral variation from wire to wire. As shown in these figures, the

spectrum shifts to longer wavelengths with increasing height (z) for the same set of wires with fixed width (y). This spectral observation agrees well with the optical color images.

This example shows that gold nanowires with different cross-sectional dimensions fabricated using methods of the invention can have different optical properties. Such nanowires may be useful for a number of applications, including surface-enhanced Raman scattering, subwavelength optical waveguiding, biolabeling, and biosensing.

EXAMPLE 5

10 Finite-Difference Time-Domain Simulations of Scattering Spectra of Gold Nanowires

This example shows that Finite-Difference Time Domain (FDTD) simulations performed on nanowires are in good agreement with the experimental measurements of scattering spectra described Example 4.

The configuration of the simulation was similar to that of the experiment (e.g., as shown in FIG. 2A), except that in the simulation, the nanowire was suspended in air rather than supported on a substrate. For each simulation, an incident exciting plane wave was launched at the same angle (60°). The scattering amplitude at individual wavelengths was calculated, and the far-field scattered field was obtained. The scattering spectrum was then calculated by integrating the scattered field over angles set by the numerical aperture of the collecting objective (NA=0.55). The frequency-dependent dielectric constant of gold was obtained from literature.

FIGS. 9A-9C shows the results of these FDTD simulations. For each set of fixed widths (10 nm, 20 nm, or 40 nm) of the nanowires, the resonance peak shifted to a longer wavelength as the height increased. The dimensions of the cross-section are marked in each figure by y and z. Simulations and experiments showed the same trend in the red shift of the spectra as the z/y ratio increased. Since the polarization of the incident field was at 60° with respect to z axis in the z-y plane, it excited two modes of surface plasmons, polarized along the z direction and the y direction, respectively. The total scattering spectrum arose from the plasmons excited by the z and y components of the incident electric field. Analysis of data from the simulations shows that the scattered field was almost the superposition of fields generated by two dipoles oscillating along the z and y directions. In this particular experimental configuration, the light-collection efficiency for y-polarized emission was eight times larger than for z-polarized, and their

contributions to the recorded intensity were about equal when the z/y aspect ratio was 1.5. For wires with aspect ratios larger than 1.5, the spectra were dominated by the scattering generated by z polarized plasmons, especially near the resonance wavelength.

FIG. 9D plots the dependence of the wavelength of maximum plasmon scattering against the z/y aspect ratio of the nanowires for the experimental measurements and simulations. Both the experimental data and the FDTD simulation showed a similar red shift when the aspect ratio of the cross-section of the nanowire increased. The resonance peaks of the experimental data were, however, uniformly at longer wavelengths than those of the simulations. This discrepancy likely reflects the fact that the simulations assumed that the nanowires were suspended in air, rather than supported on a silicon substrate. Similar effects have been reported in the literature.

This example shows that Finite-Difference Time Domain (FDTD) simulations performed on nanowires are in good agreement with the experimental measurements of scattering spectra described Example 4.

EXAMPLE 6

Fabrication and Characterization of Square Closed-Loop Shaped Nanostructures Over a Large Area

This example describes a procedure for fabricating closed-loop structures over large areas.

FIG. 10 shows an example of a scheme 200 for the fabrication of square closed-loop shaped nanostructures extending over large areas (e.g., $\sim 9 \text{ mm}^2$). Briefly, epoxy substrates 210 patterned with $\sim 2 \times 2 \text{ }\mu\text{m}$ square post features 216 were fabricated by casting epoxy prepolymer on a PDMS mold 218 using soft-lithographic procedures on a layer 220 (e.g., a 15-nm-thick film of gold) supported on a substrate 222 (e.g., test-grade silicon wafer with a top layer 224 of SiO_2). The gold layer facilitates separation of epoxy from the Si/ SiO_2 : gold adheres poorly to Si/ SiO_2 in the absence of an adhesion-promoting layer such as Ti or Cr. A gold film 226 (e.g., 40-nm thick) was deposited on selected sides of these square posts on the epoxy substrate using line of sight or shadow (angle) deposition by electron beam evaporation. Embedding the metal-coated epoxy substrate in more epoxy of the same kind generated an epoxy article 228 including the topographically structured thin gold film. At step 230, the epoxy article was peeled off from the silicon surface. The epoxy article was trimmed into a smaller article 232 with

an area of 2 mm by 1.5 mm with a razor blade, and this article was cut/sectioned in a plane parallel to the patterned surface (in the direction of arrows 236) using an ultramicrotome (Leica UCT) equipped with a diamond knife (Diatome, 45° knife angle). The edge of the knife and face of the epoxy article must be carefully aligned in order to obtain articles of uniform thickness over a large area ($\sim 3 \text{ mm}^2$). Alignment requires several steps; a detailed procedure for microtome alignment is described in more detail below.

Cut/sectioned epoxy articles 240 were collected on the surface of water contained in the sample trough mounted to the backside of the diamond knife. These thin epoxy sectioned articles were transferred onto a solid substrate 244 (e.g., TEM grid or single crystal CaF_2) by submerging small sections of the substrate in the trough, and pulling it toward the surface in a way that allowed the floating polymer film containing the gold nanostructures to settle on it. Epoxy matrix 246, which was used as an encapsulating material, was removed by etching in an oxygen plasma; this process left an array of gold nanostructures 248 supported on solid substrate 244. The adhesion between the gold nanostructures and the substrate was not very robust and in some cases, the nanostructures separated from the substrate on rinsing the surface with laboratory solvents. The nanostructures can be stabilized on the surface by coating a thin film (e.g., $\sim 50 \text{ nm}$) of, for example, silicon dioxide or silicon nitride on the silicon substrate prior to transferring the sectioned article onto the substrate.

As the epoxy sectioned articles are generated by the action of the diamond knife, they are transferred to the surface of the water. There, capillary forces cause them to form ordered aggregates; this self-assembly enables the generation of large-area patterns by stacking. FIG. 11A is a digital image of the square loop-shaped nanostructures 248 formed by the method described above on a silicon ($\text{Si}(100)$) substrate patterned over a $\sim 9 \text{ mm}^2$ area; this area 250 reflects the self-assembly of three individual epoxy slabs 252, 254, and 256 (each 3 mm^2) into an ordered rectangle. FIG. 11B is a dark field optical microscopy image of the square-loop shaped nanostructures. The SEM images in FIG. 11C show nanostructures 248 with a wall thickness of $\sim 50\text{-nm}$, and with 100-nm height. These two dimensions correspond to the thickness of the gold film deposited by e-beam evaporation, and of the thickness of the sectioned epoxy article generated by the microtome.

The following materials were used to fabricate the nanostructures described above. Araldite 502 epoxy was purchased from Electron Microscope Science (Fort Washington, PA). The epoxy was prepared by mixing different components included in the kit in the following amounts: 5 mL of diglycidyl ether of bisphenol-A (isopropylidenediphenol) (Araldite 502), 5.5 mL of dodecenyl succinic anhydride (DDSA), and 0.3 mL of benzyldimethylamine (BDMA). A number of substrates transparent in the mid-infrared were used to support arrays of both L-shaped and closed loop nanostructure arrays. The infrared permissive substrates were submerged in water during the sample (sectioned epoxy article) collection process and therefore was chosen based in part by its resistance to attack or dissolution by water. Calcium fluoride (CaF_2 , Harrick Scientific, 19-mm diameter single-crystal disc, 2-mm thick) is slightly soluble in water and transmits light from 1.5 to 9 μm . Zinc selenide (ZnSe , International Crystal Laboratories, Garfield, NJ) is insoluble in water and transmits light from 0.6 to 16 μm . For polarization experiments, a KRS-5 polarizer (Reflex Analytical Corporation, Ridgewood, NJ) was placed in the path of the incident beam. KRS-5 (thallium bromide iodide) is optically transparent from 0.6-40 μm with an index of refraction of 2.37 at 11 μm .

The nanostructures were observed by SEM measurements using a LEO 982 SEM operating at 2 kV.

The following are a set of instructions that can be used to align an edge of a knife to a face of an epoxy article to obtain articles of uniform thickness over a large area ($\sim 3 \text{ mm}^2$). Correct alignment may be critical for obtaining high uniformity across a mm^2 area section. The alignment of the microtome can require several steps.

Check alignment of knife and block.

- a) Press fiber optics light button (lower button on upper left panel of microtome to turn on fiber optics light.
- b) Increase magnification of binoculars to highest magnification.
- c) Adjust position of binoculars if necessary.
- d) Move knife toward block until it is close to block and reflection of knife is present on block face.
- e) To align block face with knife edge along length of block:

- i) This adjustment should not be necessary if you have removed 1-2 sections from face of block with trimming knife before placing the sectioning knife in holder.
- 5 ii) Observe reflection while slowing moving block past knife edge by turning handwheel.
- iii) Shadow should maintain same height from bottom to top of block of block face.
- iv) If shadow decreases in height, top of block face is closer to knife than the bottom of block face.
- 10 v) If the shadow increases in height from the bottom to the top of the block, the bottom of the block face is closer to the knife than the top of the block face.
- vi) To adjust, increase the distance between the block face and knife.
 - 1. Loosen the arc segment mount with mount locking screw and rotate holder so that arc is in the up-down position.
 - 15 2. Rotate specimen holder 90° so that parallel top and bottom edges of block are horizontal to knife edge.
 - 3. Rotate arc with specimen slide adjustment screw on arc segment mount until the shadow remains even in height along length of block.
- f) To align knife so that knife edge is parallel to block face across width of block:
 - 20 i) Observe height of reflection across width block.
 - ii) Shadow should be uniform in height across width of block face.
 - iii) If shadow is higher at one side than the other, the block face is farther away from knife on the side with the higher shadow.
 - 25 iv) To adjust, carefully rotate knife holder toward this side of block with stage rotation micrometer knob until shadow is uniform in thickness across width of block. Be careful not to hit block face with the knife when loosening and rotating the holder.
 - v) You may wish to increase the distance between the block face and the knife a small amount.
 - 30 vi) To align block so that bottom edge of block face is parallel with knife edge:
 - 1. Move block slowly past knife with handwheel and observe shadow as it appears on bottom of block face and disappears at top of block.
 - 2. If top and bottom edges of the block are parallel to each other and to the knife edge, the shadow will appear across the entire width of the block at the lower edge and leave the top edge at the same time.
 - 35

3. If the shadow appears on the lower edge at one side of the block before the other side, the edge of the block is not parallel to the knife.

To adjust, rotate holder with specimen rotation adjustment screw until shadow of knife appears on lower edge of block evenly across the block width. Be careful not to hit block face with the knife when loosening and rotating the holder. You may wish to increase the distance between the block face and the knife a small amount.

EXAMPLE 7

Optical Properties of Square Closed-Loop Shaped Nanostructures Over a Large Area

This example shows that closed-loop nanostructures can be used to form frequency selective surfaces (FSS) that have resonances that are anisotropic with respect to polarization of an electric field.

Square closed looped nanostructures we fabricated using the method described in Example 6 except the nanostructures were positioned on a ZnSe substrate ($n_{\text{eff}}=1.8$ with $n_{\text{ZnSe}}=2.4$ at $11\ \mu\text{m}$ and $n_{\text{air}}=1$) instead of a silicon substrate. FIG. 11D is an IR transmission spectrum of the closed loop nanostructures (shown by line 260). A single major resonant peak at $11\ \mu\text{m}$ independent of the polarization of the incident infrared light, and with a transmittance at a wavelength of maximum scattering of 45%, was observed.

In some cases involving FSS work, $\lambda_r \sim n_{\text{eff}} \cdot C$ (eq. 3) can be used to estimate the resonant wavelength, where C is the circumference of the loop. Here, another procedure based on Eq. (1) can be used to estimate wavelength. Without wishing to be bound by theory, for simplicity, it is assumed that the incident light is polarized along the y-axis as shown in the inset of FIG. 11D. The arrows 260 and 262 show the pattern of the induced current. There are two oscillating currents with mirror symmetry and with the mirror plane parallel to the polarization of the electric field. In this geometry, the electric field induces two identical dipoles, each with a length $l = C/2$. According to Eq. (1), the resonance wavelength is $\lambda \sim 2n_{\text{eff}}l = n_{\text{eff}} \cdot c$ which is consistent with the result from Eq.(3). Even in the case when the polarizer is not along y-axis (FIG. 11D inset), each induced dipole also has an effective length l equal to $C/2$, which results the same resonance wavelength, $\sim 11\ \mu\text{m}$. In any case, two dipoles are induced by the electrical field; each dipole involves half of the total length of the loop; this equality explains why only a single resonance peak is observed, whose position is independent of the polarization of

the incident light. In this explanation, the interaction between the two dipoles is neglected. This argument is applicable to FSS of a simple closed structures. Line 262 of FIG. 11D (open symbols) is the calculated scattering spectrum from a single square (side length = 2 μm) simulated using FDTD methods. The position of the FDTD-derived
5 resonance peak position and its width are in good qualitative agreement with the experimental observations described above.

For optical measurements, a Nicolet Fourier-transform infrared spectrometer in transmission mode was used to characterize the sample optically. A piece of aluminum foil (~200 μm thick) with a punched hole directly in front of the sample was used to
10 support the sample. The small hole enabled the incident beam (~1 mm^2 diameter) to transmit through the substrate area with the nanostructure array thereby increasing the signal to noise ratio. For all transmittance measurements, 128 scans with a resolution of 4 cm^{-1} were averaged. A separate spectrum of the clean substrate was collected and subtracted from the spectrum of the FSS surface.

15 For FDTD simulations, a commercial Finite-Difference Time-Domain (FDTD) software (xfdtd, from remcom.com) was used to calculate the back-scattering (reflectance, R) spectra from an individual element nanostructure (closed loop, L-shaped or U-shaped nanostructures) in air. To calculate back scattering spectra, an incident Gaussian pulse excites the structure, and the back scattered electrical field in time
20 domain was calculated. The ratio of the power spectrum of scattered field to the power spectrum of the incident field yielded the scattering spectrum in frequency domain. The reflectance spectrum for an FSS array is linearly proportional to a single unit with the constant of proportionality dependent on the density of unit structure, if the weak interaction between the units is neglected. Transmittance (T) through the sample was
25 related to reflectance (R) by the relationship, $T=1-R$. The reflectance spectra were plotted with y-axis values reversed and rescaled to match the experimentally measured transmittance spectra. The objective of the simulation was not to provide absolute transmittance, but to confirm the main features of transmission spectrum, such as its resonance position, and its linewidth. In the simulation, gold nanostructures were
30 approximated by a wire with cross-section 50-nm wide $\times$ 100-nm height, as determined during fabrication. The structures were approximated as an ideal rectangle, L or U (angle set to 90° for adjoining arms). The dimensions for these structures in the simulation were set according to SEM measurements. The Debye mode was used to

model the dielectric property of gold; the parameters for the Debye model were infinite dielectric constant = 1.001, static dielectric constant = -7499, conductivity = 8.84×10^6 S/m, and relaxation time = 7.5×10^{-15} s. These parameters gave the best fit to the index of gold for light with a wavelength of 2-10 μm . The n_{eff} is calculated from eq. 2; the n_{eff} for ZnSe substrate is 1.8, the n_{eff} for CaF_2 is 1.2, and $n_{\text{eff}} \sim 1.2$ for polymer.

EXAMPLE 7

Optical Properties of Open-Loop L-Shaped Nanostructures Over a Large Area and Their Optical Properties

This example shows that open-loop nanostructures can be used to form frequency selective surfaces (FSS) that have resonances that are dependant upon the polarization of an electric field. The nanostructures may be supported by a substrate.

L-shaped open loop nanostructures were fabricated by modifying the metal deposition procedure of Example 6. Shadow evaporation from a single direction was used to coat two sides of a template of square epoxy posts selectively. In such a procedure, a single shadow evaporation with the sample mounted 60° from the plane for line-of-sight evaporation onto a single corner was used to generate L-shaped nanostructures. The U-shaped nanostructures were supported on CaF_2 substrate.

FIG. 12A is a dark-field optical microscopic image of L-shaped nanostructures patterned over a $\sim 3 \text{ mm}^2$ area after removal of the epoxy matrix, used as an encapsulating material, with an oxygen plasma. These nanostructures have a wall thickness of $\sim 50\text{-nm}$, and 100-nm height. FIG. 12B is a transmission spectrum of an array of these L-shaped nanostructures supported on a CaF_2 substrate ($n_{\text{eff}}=1.2$, with $n_{\text{CaF}_2}=1.36$ at $7 \mu\text{m}$, and $n_{\text{air}}=1$) after normalization for transmission of the substrate (as measured using a clean substrate). The spectrum exhibits two dominant transmission stop-bands 272 and 274 in the mid-infrared region centered at $8.4 \mu\text{m}$ and $4.8 \mu\text{m}$, respectively, with maximum transmissions of 67% and 82%. The L-shaped structure is less isotropic than a square structure with respect to excitations produced by polarized incident light. In order to study the polarization dependence of both resonances, linearly polarized light was used by inserting a broadband wire polarizer in the path of the incident beam. The $8.4 \mu\text{m}$ long wavelength resonance is observed when the polarization of incident light is parallel to the line connecting the two ends of the L-structure, as shown in FIG. 12C (line 276). FIG. 12D shows a single resonant peak at

4.8 μm (line 280) when the polarizer is rotated by 90° such that the polarization is now perpendicular to the diagonal line connecting the two ends of the L.

As shown in the insets of FIGs. 12 C and 12D, there are two different current patterns in the L-shaped structure responsible for these resonances. The inset diagram illustrates the polarization direction (arrows 284) and induced current flow (arrows 286) in the L-shaped nanostructure 288 for the two polarizations of the incident light.

The inset of FIG. 12C shows the first current pattern (fundamental mode, half wavelength resonance) oscillating between the two tips of the L when the E field points from one tip of the L to the other tip. In this case, l in eq. (1) is the sum of the lengths of both arms of the L-shaped nanostructure. This current distribution is responsible for the 8.4- μm resonance. When the polarization of the incident light is perpendicular to the line connecting the two ends of the “L” (FIG. 12D), a relatively symmetric current pattern is induced, in which the “L” is effectively split into two antenna (two dipoles) oscillating in phase. The length for each dipole is about half of the total length. This current pattern is responsible for the 4.8 μm resonance. This 4.8 μm resonance is the harmonic mode of 8.4 μm mode. With this polarization, only the 4.8 μm mode is excited, and the fundamental mode at 8.4 μm is suppressed. At any other arbitrary polarization, both modes will be excited. (FIG. 13 shows transmission spectra of the L shaped nanostructure with polarization parallel to either of the two arms.) Due to the interaction between two harmonic dipoles, the actual resonant wavelength (4.8 μm) is not exactly at half of the fundamental wavelength (8.4 μm). FDTD simulations of the scattering spectra at both polarization conditions in FIG. 12C and 12D (open symbols, lines 278 and 282, respectively) demonstrate the calculated resonance position and bandwidth agree well with experimental measurements.

EXAMPLE 8

Optical Properties of Open-Loop U-Shaped Nanostructures Over a Large Area and Their Optical Properties

This example shows that open-loop nanostructures can be used to form frequency selective surfaces (FSS) that have resonances that are dependant upon the polarization of an electric field. The nanostructures may be supported by the encapsulating (matrix) material used to embed the nanostructures, instead of a substrate.

U-shaped open loop nanostructures were fabricated by modifying the metal deposition procedure of Example 6. Shadow evaporation from multiple directions was used to coat three sides of a template of square epoxy posts selectively. In such a procedure, three consecutive shadow evaporations from three edges of the square
5 template were used to generate U-shaped nanostructures. The nanostructures were not positioned on a substrate after sectioning. Instead, the nanostructures were supported by the epoxy material between the nanostructures (i.e., epoxy matrix was not removed with an oxygen plasma after sectioning to form the article).

The ability to manipulate the free-standing epoxy article containing the U-shaped
10 nanostructure array allows measurements of the optical properties of this array without a supporting substrate (but with the nanostructure remaining embedded in the epoxy film). FIG. 14A is a bright field optical image of an epoxy article 289 (100 nm thick) including U-shaped nanostructures sitting on a hole (~ 1 mm diameter) in a copper sheet (~ 100 μ m thick). FIG. 14B is a dark field optical image of the array of U shaped nanostructures
15 290 of FIG. 14A in the epoxy matrix. The inset is a high-magnification SEM image of a single U-shaped nanostructure with a wall thickness of ~ 50 -nm, and 100-nm height. The transmission spectra of this sample was measured directly (see FIG. 15) using a piece of epoxy film with same thickness as a reference to subtract out absorption features due to the epoxy. As shown in FIG. 14C, three distinct resonant peaks from this sample
20 was observed in the mid-IR region at 5.15 μ m, 6.5 μ m, and 14.75 μ m, respectively.

FIGs. 14D and 14E are transmission spectra of the U-shaped nanostructures with the polarization of the incident light parallel (FIG. 14D) or perpendicular (FIG. 14E) to the line connecting the two ends of the U. The inset diagrams illustrate the polarization direction (arrows 292) and induced current flow (arrows 294) in the U-shaped
25 nanostructure 296 for the two polarizations of the incident light. The U-shaped nanostructure was not isotropic with respect to the polarization of incident light, and the observed number and location of the resonance was dependent on the polarization of the incident light. The right inset of FIG. 14D shows the current distribution for the given polarization. In this pattern, the induced current oscillates between the ends of the U-shaped nanostructure. The length (used in eq. 1) for this dipole oscillation is the total
30 length of the U. The left inset of FIG. 14D is the current pattern responsible for the harmonic mode. There are three dipole oscillators excited along the wire. The length of each oscillator is about the third of the total length; the resonant frequency is

approximately three times higher than the resonant frequency of the fundamental dipole mode (i.e. half wavelength resonance). The inset of FIG. 14E shows the current pattern when the E-field vector of the light is perpendicular to the open side. In this case, two symmetric dipoles are induced, and the length is half of the total length for each dipole.

5 FIGs. 16A and 16B show the effect of choosing an unsuitable substrate for supporting certain nanostructures. FIG. 16A shows an array of U-shaped nanostructures supported on a CaF_2 substrate. FIG. 16B is a transmission spectrum of the nanostructures of FIG. 16A. As shown in FIG. 16B, two strong resonant peaks from 2-10 μm (5.25 μm and 6.75 μm , respectively). Eq. 1 indicates that one should observe the
10 fundamental mode (longest wavelength resonance) at $\lambda > 10 \mu\text{m}$ when l is defined as the total length of U ($\sim 6 \mu\text{m}$). Since CaF_2 substrates are not transparent at wavelengths above ~ 10 micron and ZnSe substrates have a high refractive index, these materials may not be ideal for transmission characterization of U shaped nanostructures having a total length $\sim 6 \mu\text{m}$. Accordingly, as described above, these particular nanostructures may be
15 prepared in the absence of a substrate by maintaining the matrix between the nanostructures.

EXAMPLE 9

Fabrication of a Composite Material Comprising Stacked Nanostructures

20 This example shows the fabrication of a composite material comprising stacked nanostructures. Such materials may be useful for forming NIMs that are selective towards wavelengths in the infrared region.

 The procedure described in Example 8 was used to fabricate an array of U-shaped nanostructures embedded in an epoxy. The U-shaped nanostructures had a wall
25 thickness of $\sim 50\text{-nm}$, and a 100-nm height. A block of epoxy that did not contain nanostructures was then sectioned to a thickness of 150 nm . This sectioned epoxy article was positioned on top of the array of U-shaped nanostructures, and this combined article was used as a substrate for depositing an array of metal nanowires. The metal nanowires were formed using the procedure described in Example 1, except the wires were
30 continuous along one axis.

 The resulting composite structure 320 is shown in FIGs. 17A and 17B. FIG. 17A shows the nanostructures fabricated over a large area (greater than 1 mm^2). FIG. 17B shows a magnified view of the structure of FIG. 17A. The composite structures includes

U-shaped nanostructures 324 embedded in epoxy. Positioned on top of the U-shaped nanostructures are parallel gold nanowires 328, having a width of 40 nm and a height of 50 nm.

5 While several embodiments of the present invention have been described and illustrated herein, those of ordinary skill in the art will readily envision a variety of other means and/or structures for performing the functions and/or obtaining the results and/or one or more of the advantages described herein, and each of such variations and/or modifications is deemed to be within the scope of the present invention. More generally,
10 those skilled in the art will readily appreciate that all parameters, dimensions, materials, and configurations described herein are meant to be exemplary and that the actual parameters, dimensions, materials, and/or configurations will depend upon the specific application or applications for which the teachings of the present invention is/are used. Those skilled in the art will recognize, or be able to ascertain using no more than routine
15 experimentation, many equivalents to the specific embodiments of the invention described herein. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described and claimed. The present invention is directed to each individual feature,
20 system, article, material, kit, and/or method described herein. In addition, any combination of two or more such features, systems, articles, materials, kits, and/or methods, if such features, systems, articles, materials, kits, and/or methods are not mutually inconsistent, is included within the scope of the present invention.

 All definitions, as defined and used herein, should be understood to control over
25 dictionary definitions, definitions in documents incorporated by reference, and/or ordinary meanings of the defined terms.

 The indefinite articles “a” and “an,” as used herein in the specification and in the claims, unless clearly indicated to the contrary, should be understood to mean “at least one.”

30 The phrase “and/or,” as used herein in the specification and in the claims, should be understood to mean “either or both” of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases. Multiple elements listed with “and/or” should be construed in the same fashion, i.e., “one

or more” of the elements so conjoined. Other elements may optionally be present other than the elements specifically identified by the “and/or” clause, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, a reference to “A and/or B”, when used in conjunction with open-ended language such as “comprising” can refer, in one embodiment, to A only (optionally including elements other than B); in another embodiment, to B only (optionally including elements other than A); in yet another embodiment, to both A and B (optionally including other elements); etc.

As used herein in the specification and in the claims, “or” should be understood to have the same meaning as “and/or” as defined above. For example, when separating items in a list, “or” or “and/or” shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also including more than one, of a number or list of elements, and, optionally, additional unlisted items. Only terms clearly indicated to the contrary, such as “only one of” or “exactly one of,” or, when used in the claims, “consisting of,” will refer to the inclusion of exactly one element of a number or list of elements. In general, the term “or” as used herein shall only be interpreted as indicating exclusive alternatives (i.e. “one or the other but not both”) when preceded by terms of exclusivity, such as “either,” “one of,” “only one of,” or “exactly one of.” “Consisting essentially of”, when used in the claims, shall have its ordinary meaning as used in the field of patent law.

As used herein in the specification and in the claims, the phrase “at least one,” in reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the elements specifically identified within the list of elements to which the phrase “at least one” refers, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, “at least one of A and B” (or, equivalently, “at least one of A or B,” or, equivalently “at least one of A and/or B”) can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and optionally including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A); in yet another embodiment, to at least one, optionally including more than one,

A, and at least one, optionally including more than one, B (and optionally including other elements); etc.

It should also be understood that, unless clearly indicated to the contrary, in any methods claimed herein that include more than one step or act, the order of the steps or
5 acts of the method is not necessarily limited to the order in which the steps or acts of the method are recited.

In the claims, as well as in the specification above, all transitional phrases such as “comprising,” “including,” “carrying,” “having,” “containing,” “involving,” “holding,” “composed of,” and the like are to be understood to be open-ended, i.e., to mean
10 including but not limited to. Only the transitional phrases “consisting of” and “consisting essentially of” shall be closed or semi-closed transitional phrases, respectively, as set forth in the United States Patent Office Manual of Patent Examining Procedures, Section 2111.03.

What is claimed is:

CLAIMS

1. A method of fabricating a nanostructure, comprising:
5 providing an article having a surface;
depositing a first material on at least a portion of the surface of the article;
encapsulating at least a portion of the first material in an encapsulating material;
cutting the encapsulating material in a direction that intersects at least a portion of
the first material, thereby forming a cut portion; and
10 removing the encapsulating material from the cut portion, thereby forming an
isolated nanostructure comprising the first material.
2. A method as in claim 1, wherein the surface comprises a plurality of protrusions
and/or indentations.
- 15 3. A method as in claim 2, wherein the distance between two consecutive
protrusions defines a cross-sectional dimension of the nanostructure.
4. A method as in claim 1, wherein the thickness of the cut portion defines a cross-
20 sectional dimension of the nanostructure.
5. A method as in claim 1, wherein the thickness of the first material deposited defines a
cross-sectional dimension of the nanostructure.
- 25 6. A method as in claim 1, wherein the nanostructure has at least one cross-sectional
dimension of less than 20 nm.
7. A method as in claim 1, wherein the cut portion is a precursor article for a
plurality of isolated nanostructures.
- 30 8. A method as in claim 1, further comprising forming a plurality of isolated
nanostructures in a single step.

9. A method as in claim 8, wherein greater than 95% of the plurality of nanostructures are substantially uniform in size.
10. A method as in claim 1, wherein the nanostructure has an aspect ratio of at least 5:1.
11. A method as in claim 1, wherein the nanostructure comprises a curved surface.
12. A method as in claim 1, wherein the first material comprises a metal.
13. A method as in claim 1, wherein the first material comprises an organic material.
14. A method as in claim 1, wherein the first material comprises a polymer.
15. A method as in claim 1, wherein the first material is semi-conductive.
16. A method as in claim 1, further comprising positioning the nanostructure in association with a component to form a functional component of a device.
17. A method of fabricating a nanostructure, comprising:
providing a substrate formed in an article material having a surface defining a plurality of indentations;
depositing a first material on at least a portion of the surface of the substrate;
cutting the substrate in a direction that intersects at least a portion of the first material, thereby forming a cut portion;
removing any substrate from the cut portion; and
forming an isolated nanostructure comprising the first material.
18. A method of positioning a plurality of isolated nanostructures on a surface, comprising:
providing a structure comprising a plurality of nanostructures positioned in a particular arrangement in association with a first material, at least a portion of each nanostructure embedded in the first material;
positioning the structure on a surface;

removing the first material from the surface; and
allowing the plurality of nanostructures to remain on the surface in the particular arrangement, wherein each nanostructure is physically isolated from another nanostructure in the particular arrangement.

5

19. A method as in claim 18, wherein the nanostructures are positioned in association with a component to form a functional component of a device.

10

20. A method of making a device comprising a nanostructure, comprising:
providing a precursor article having three principle intersecting axes, wherein at least a first dimension of the precursor article, along a first axis passing through the precursor article, is smaller than 1 micron and at least a second dimension of the precursor article, along a second axis perpendicular to the first axis passing through the precursor article, is larger than 100 microns;

15

separating, from the precursor article, a nanostructure, wherein the nanostructure has three principle intersecting axes, wherein at least a first dimension of the nanostructure, along a first axis passing through the nanostructure, is smaller than 1 micron and at least a second dimension of the nanostructure, along a second axis perpendicular to the first axis passing through the nanostructure, is smaller than 1 micron; and

20

positioning the nanostructure in association with a plurality of other components to form a functional component of a functional device.

25

21. A method as in claim 20, comprising separating the nanostructure from an interior portion of the precursor article.

30

22. A method as in claim 20, wherein at least one cross-sectional dimension of the nanostructure is essentially the same as a cross-sectional dimension of the precursor article.

23. A method as in claim 20, comprising forming a plurality of nanostructures essentially simultaneously in the same separating step.

24. A method of fabricating a nanostructure, comprising:

providing a supporting article;
positioning a precursor article in supported relationship with the supporting
article; and

separating, from the precursor article, a nanostructure, wherein the nanostructure
5 has three principle intersecting axes, wherein at least a first dimension of the
nanostructure, along a first axis passing through the nanostructure, is smaller than 1
micron and at least a second dimension of the nanostructure, along a second axis
perpendicular to the first axis passing through the nanostructure, is smaller than 1
micron.

10

25. An article made by a process of any preceding claim.

26. A composite structure comprising:

an array of first conductive nanostructures, wherein each first nanostructure has
15 three principle intersecting axes, wherein at least a first dimension of the first
nanostructure, along a first axis passing through the first nanostructure, is smaller than
500 nm and at least a second dimension of the first nanostructure, along a second axis
perpendicular to the first axis passing through the first nanostructure, is smaller than 500
nm;

20

an array of second conductive nanostructures positioned adjacent but not in
physical contact with the first nanostructures, wherein each second nanostructure has
three principle intersecting axes, wherein at least a first dimension of the second
nanostructure, along a first axis passing through the first nanostructure, is smaller than
500 nm and at least a second dimension of the second nanostructure, along a second axis
25 perpendicular to the first axis passing through the second nanostructure, is smaller than
500 nm; and

a dielectric material positioned between the first and second nanostructures,
wherein the first and second nanostructures are positioned less than 1 micron
apart.

30

27. A composite structure as in claim 26, wherein the first and second nanostructures
are positioned less than 500 nm apart.

28. A composite structure as in claim 26, wherein the first and second nanostructures are positioned less than 200 nm apart.
29. A composite structure as in claim 26, wherein the first and second nanostructures
5 are aligned vertically such that they share a common principle axis.
30. A composite structure as in claim 26, comprising a plurality of first nanostructures forming a first layer of nanostructures.
- 10 31. A composite structure as in claim 30, comprising a plurality of second nanostructures forming a second layer of nanostructures.
32. A composite structure as in claim 31, comprising alternating first and second layers.
15
33. A composite structure as in claim 32, comprising at least 10 alternating first and second layers.
34. A composite structure as in claim 26, wherein the first nanostructure is an open-
20 loop nanostructure.
35. A composite structure as in claim 34, wherein the second nanostructure is a straight-wire or rod-shaped nanostructure.
- 25 36. A composite structure as in claim 26, wherein the first nanostructure has a negative permittivity.
37. A composite structure as in claim 34, wherein the second nanostructure has a negative permeability.
30
38. A composite structure as in claim 26 having a curved surface.
39. A composite structure as in claim 26 having a negative index of refraction.

40. An optical filter comprising the composite structure of claim 26, wherein the optical filter is selective towards wavelengths in the infrared range.

- 5 41. A method of forming a composite structure, comprising:
providing a first structure comprising a plurality of first nanostructures positioned in a particular arrangement in association with a first material, at least a portion of each first nanostructure embedded in the first material;
positioning a dielectric material adjacent the first structure;
10 positioning a second structure adjacent the dielectric material such that the dielectric material is positioned between the first and second structures, wherein the second structure comprises a plurality of second nanostructures positioned in a particular arrangement in association with a second material, at least a portion of each second nanostructure embedded in the second material; and
15 allowing the plurality of first and second nanostructures to remain in their respective arrangements, wherein each nanostructure is not in direct physical contact with another nanostructure in the arrangements.

20 42. A method of claim 41, comprising removing the first material from the first structure and/or removing the second material from the second structure.

43. A method as in claim 41, wherein the first and second nanostructures are different.

25 44. A method as in claim 41, wherein the first nanostructure is an open loop nanostructure.

45. A method as in claim 41, wherein the second nanostructure is a nanowire.

30 46. A method as in claim 41, wherein the first and/or second nanostructures has at least one cross-sectional dimension of less than or equal to 200 nm.

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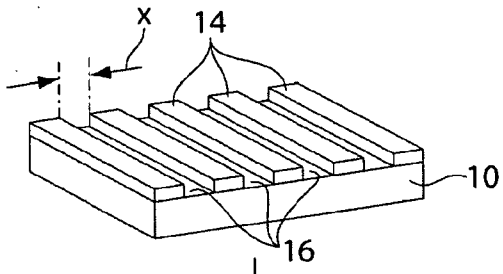


Fig. 1A

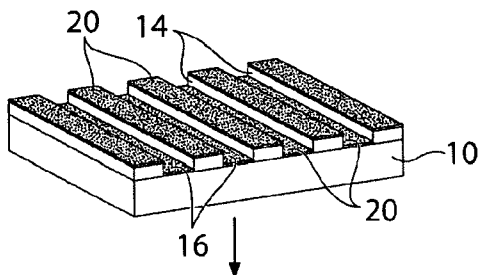


Fig. 1B

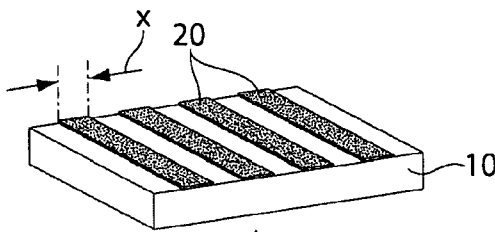


Fig. 1C

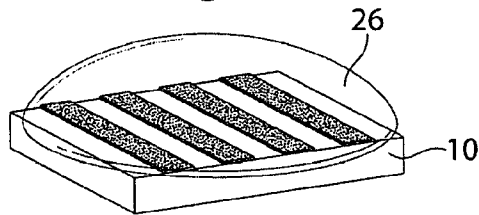


Fig. 1D

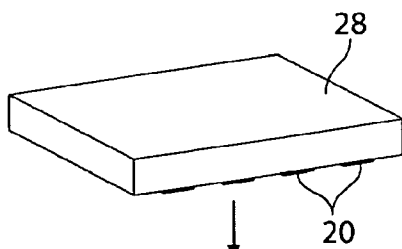


Fig. 1E

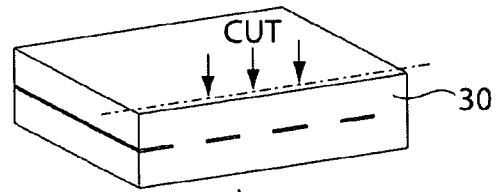


Fig. 1F

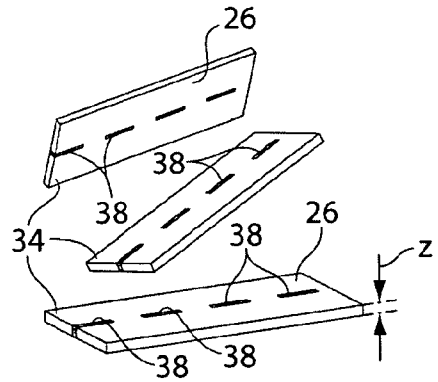


Fig. 1G

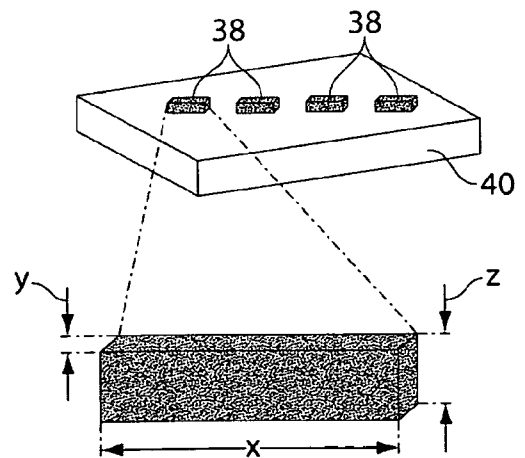


Fig. 1H

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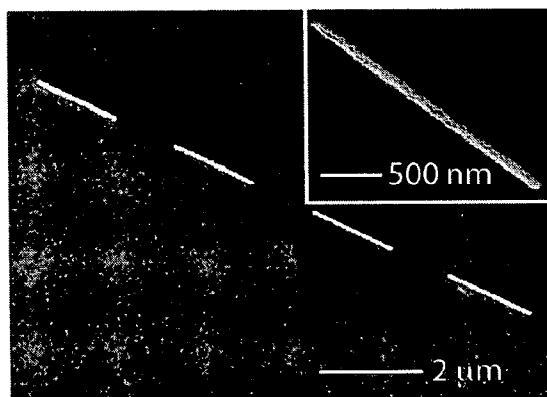


Fig. 2A

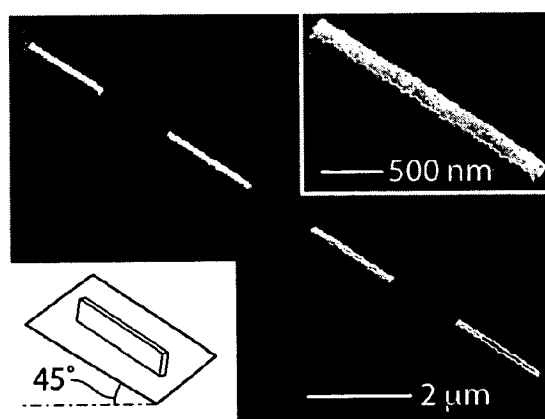


Fig. 2B

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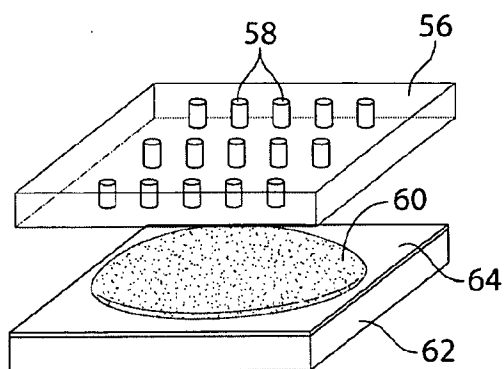


Fig. 3A

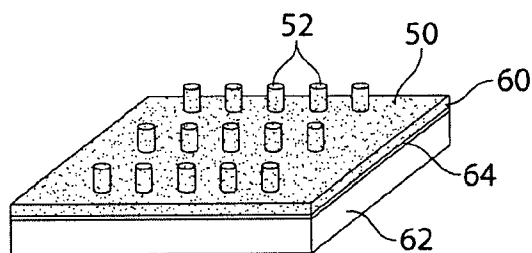


Fig. 3B

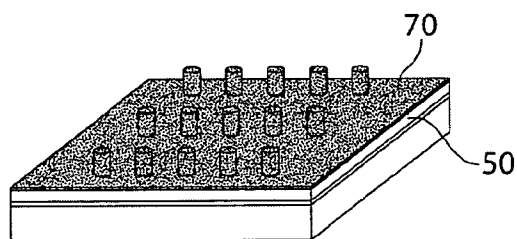


Fig. 3C

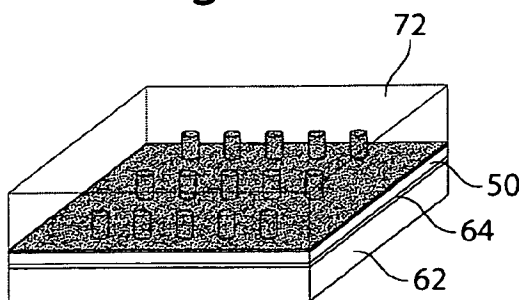


Fig. 3D

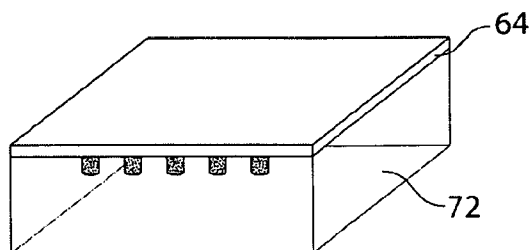


Fig. 3E

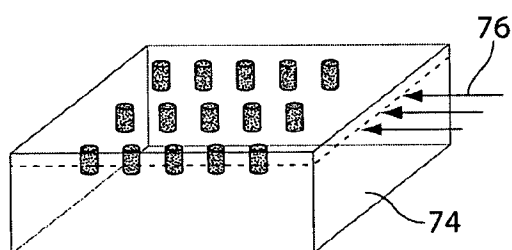


Fig. 3F

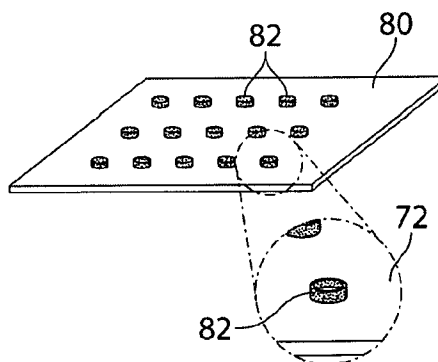


Fig. 3G

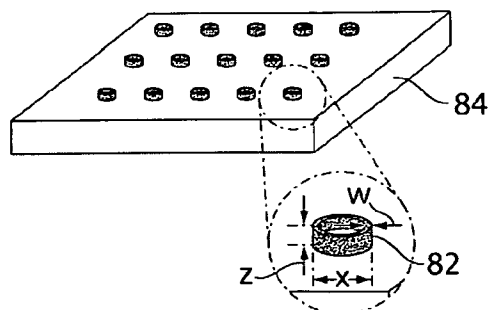


Fig. 3H

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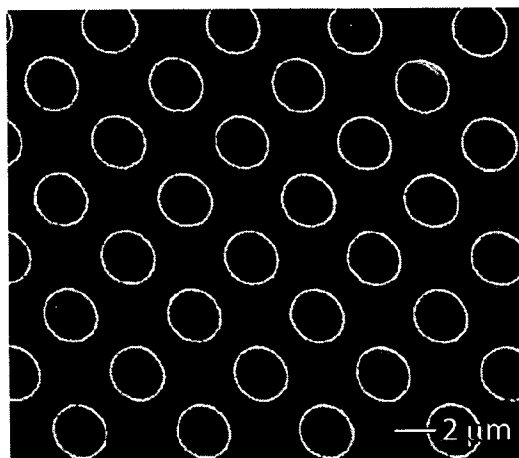


Fig. 4A

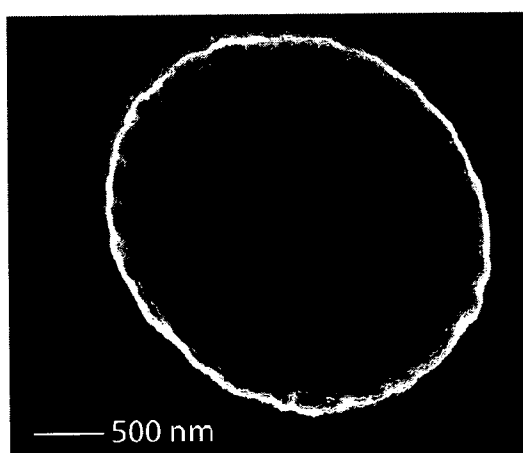


Fig. 4B

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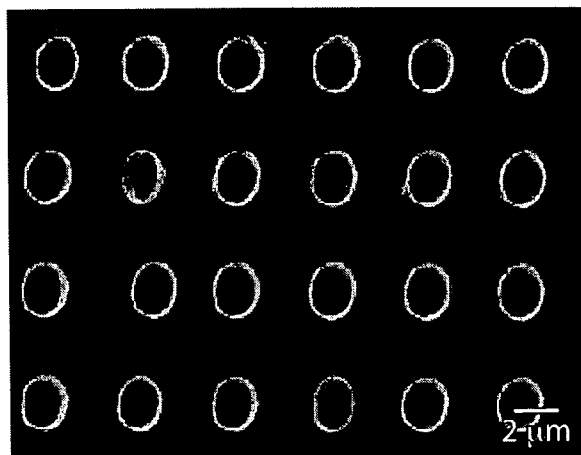


Fig. 4C

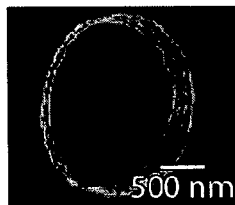


Fig. 4D

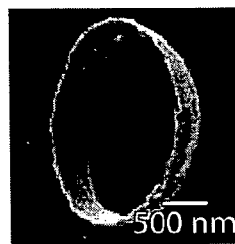


Fig. 4E

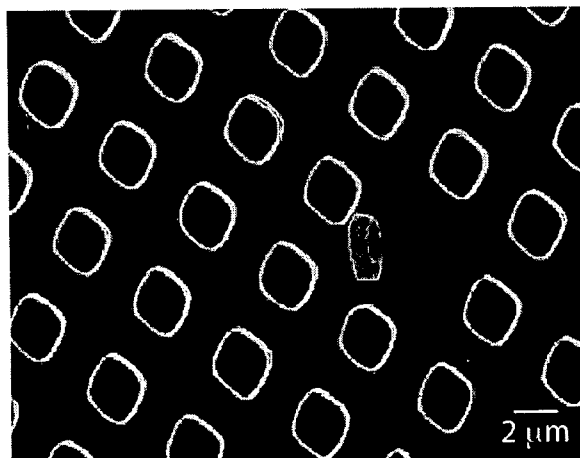


Fig. 4F

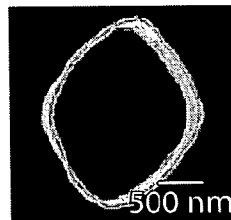


Fig. 4G

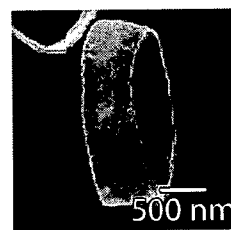


Fig. 4H

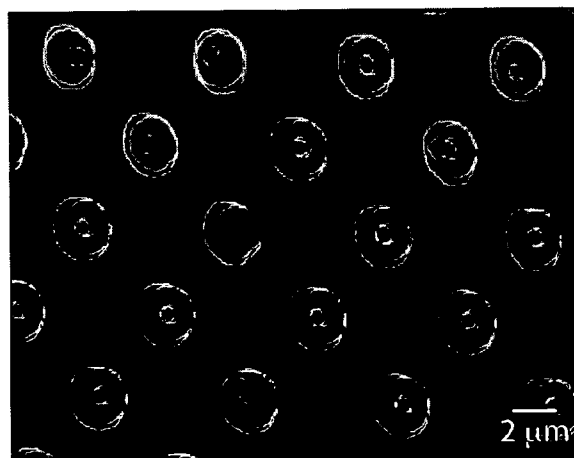


Fig. 4I

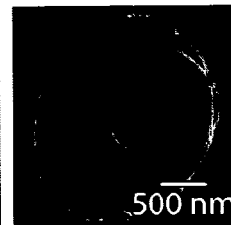


Fig. 4J

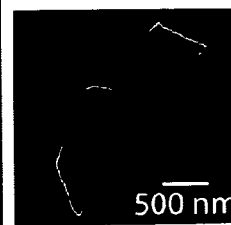


Fig. 4K

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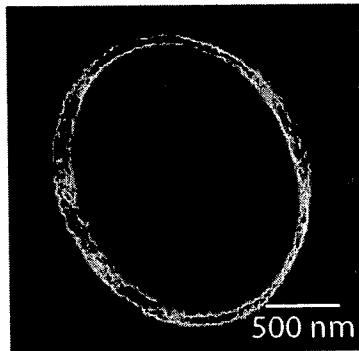


Fig. 4L

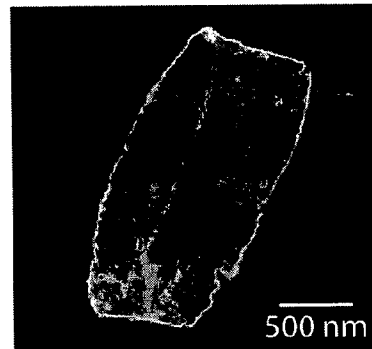


Fig. 4N

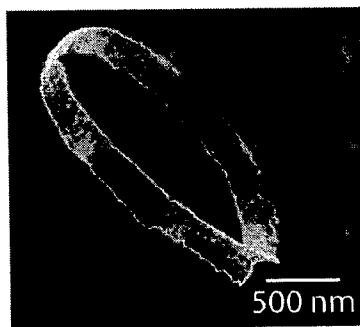


Fig. 4M

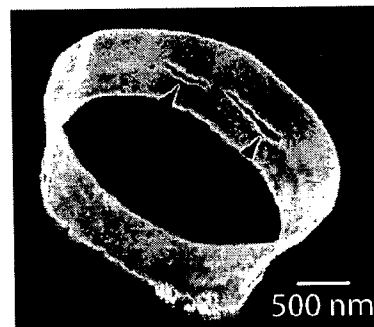


Fig. 4O

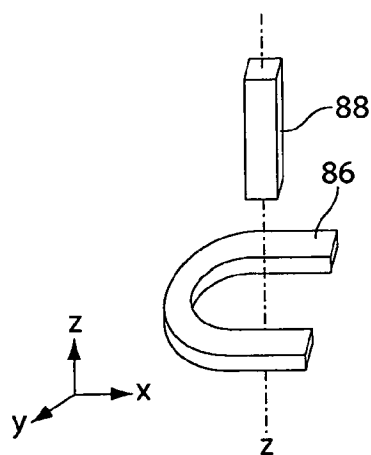


Fig. 4P

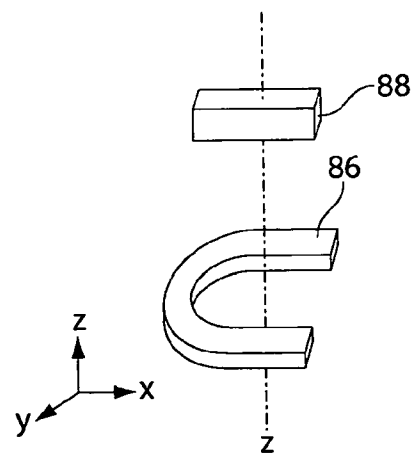


Fig. 4Q

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Fig. 5A

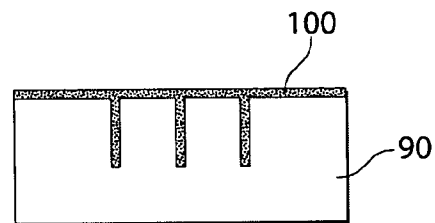


Fig. 5B

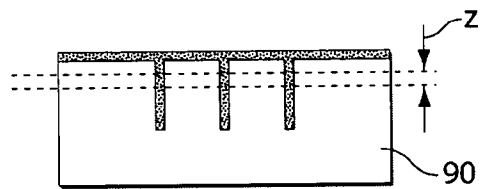


Fig. 5C

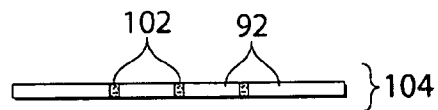


Fig. 5D

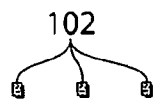


Fig. 5E

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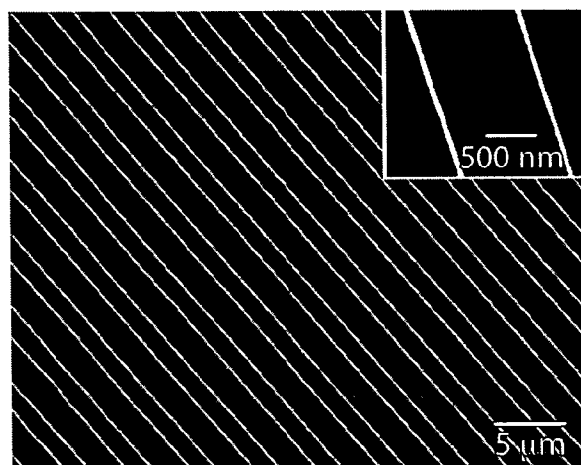


Fig. 6A

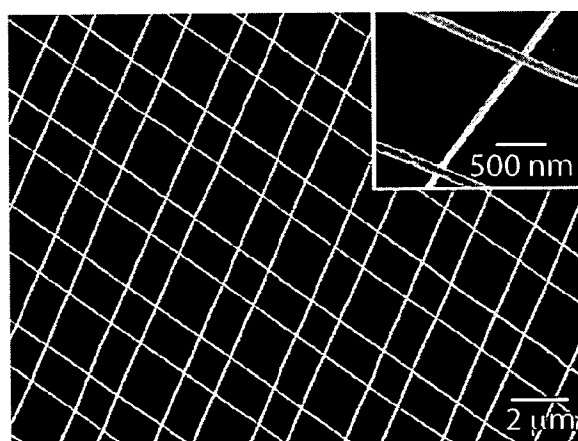


Fig. 6B

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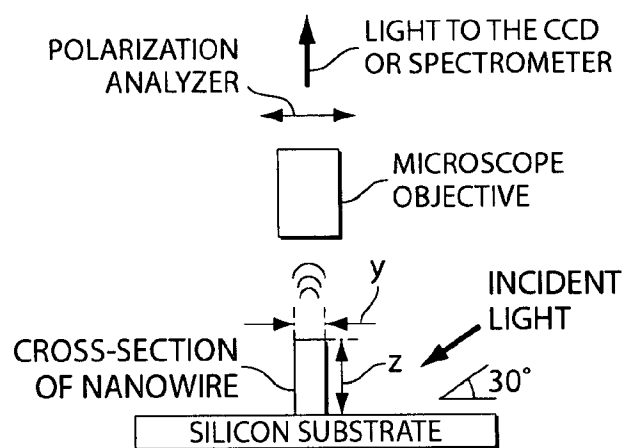


Fig. 7A

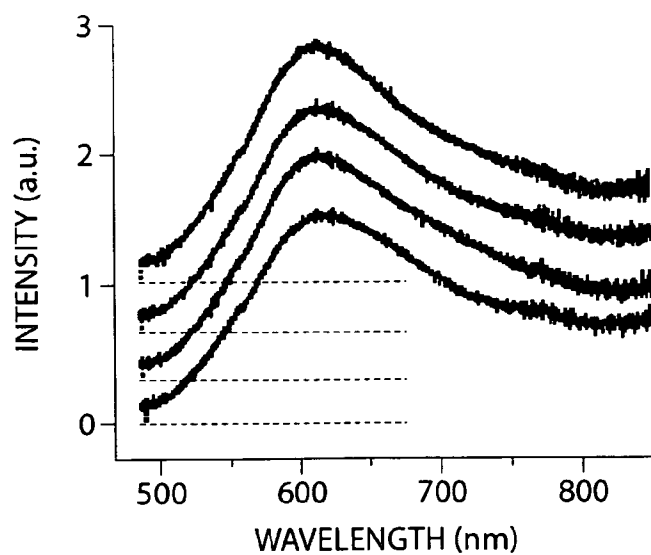


Fig. 7B

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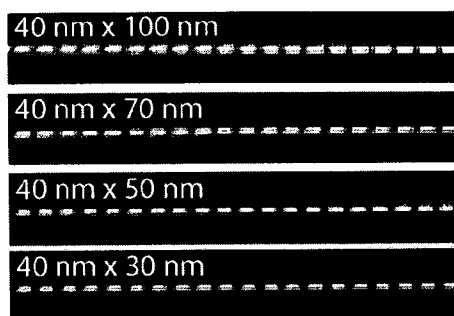
20 μ m

Fig. 8A

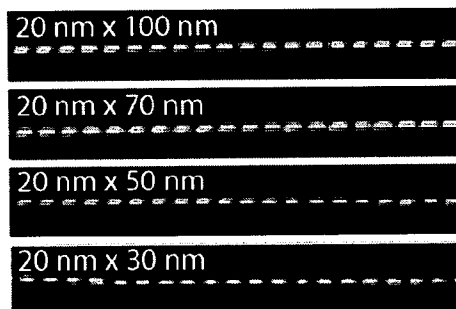
20 μ m

Fig. 8B

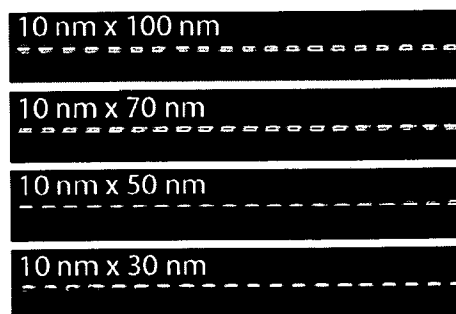
20 μ m

Fig. 8C

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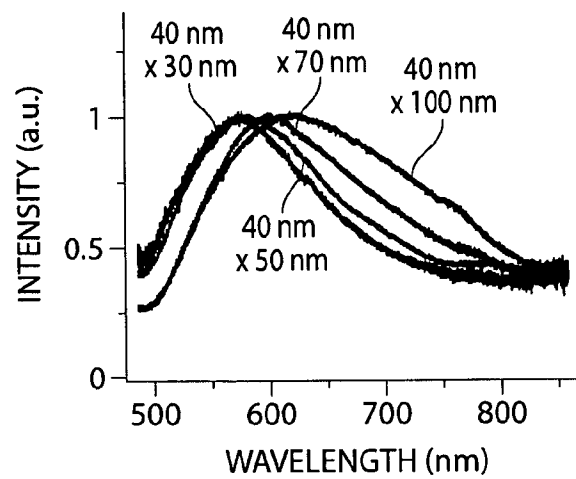


Fig. 8D

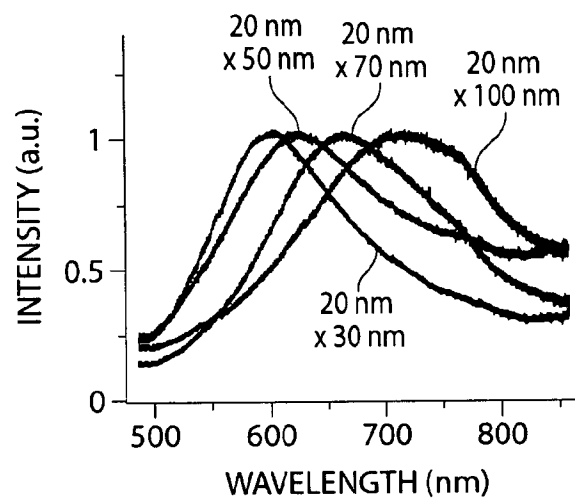


Fig. 8E

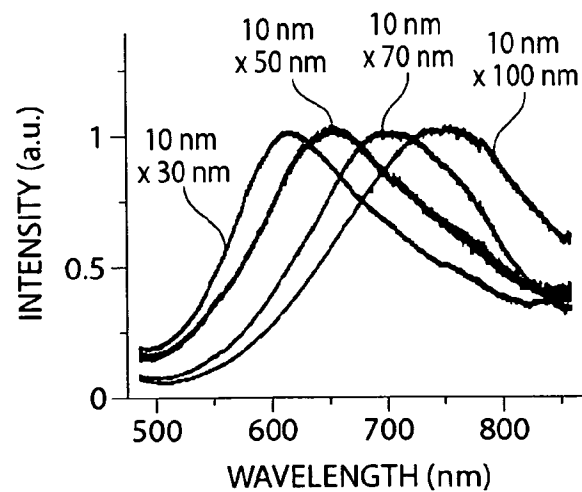


Fig. 8F

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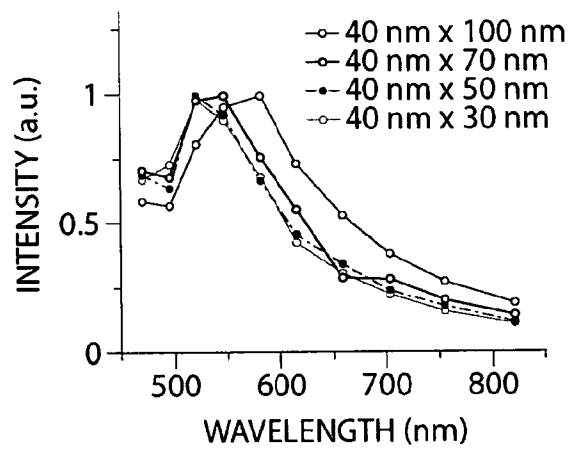


Fig. 9A

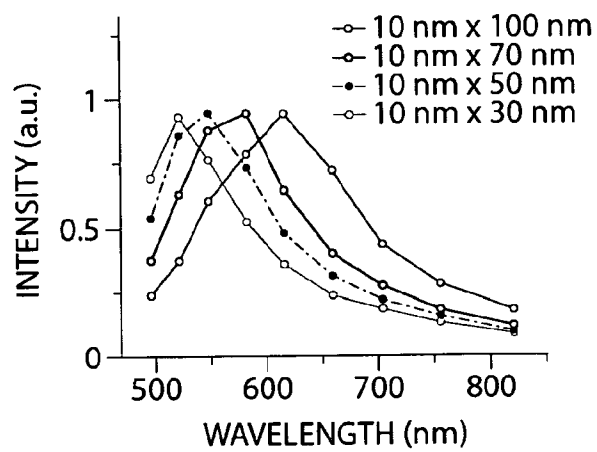


Fig. 9B

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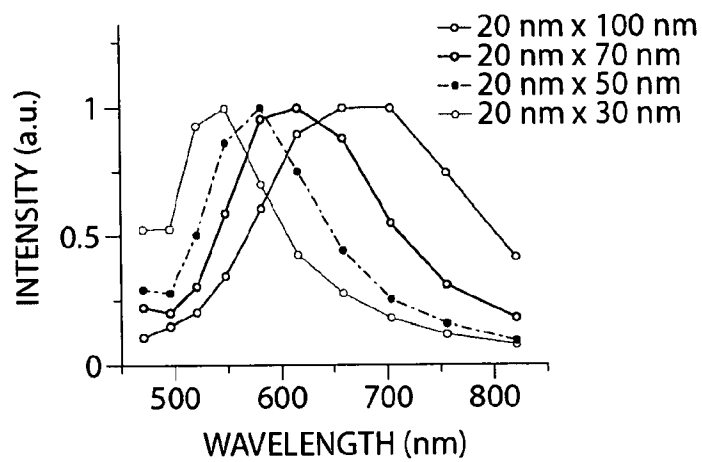


Fig. 9C

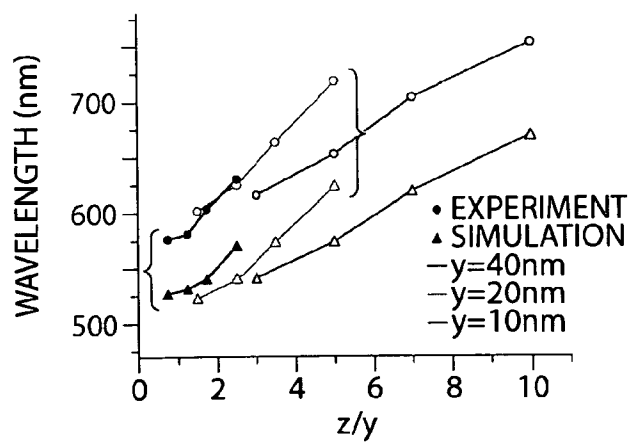


Fig. 9D

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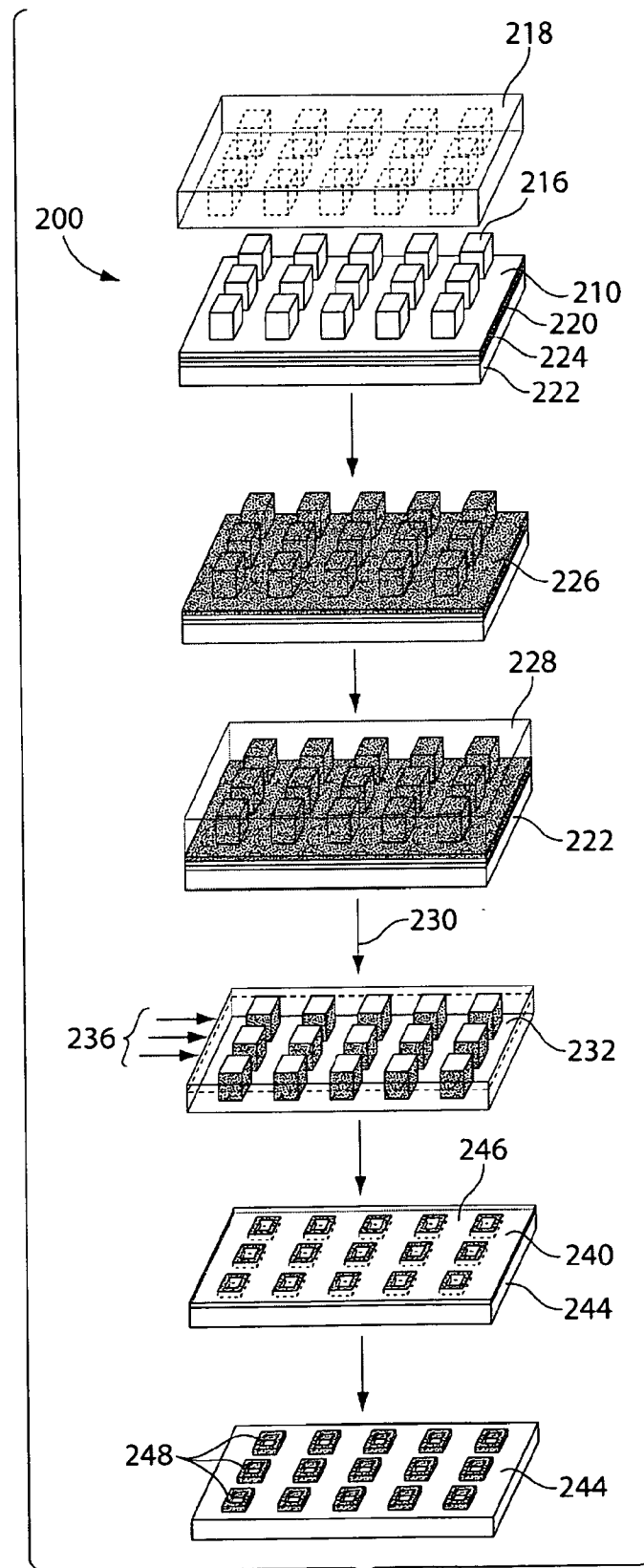


Fig. 10

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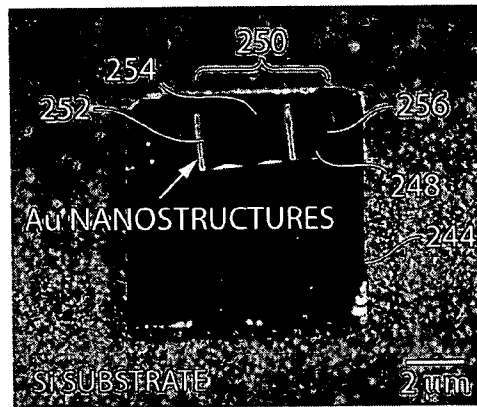


Fig. 11A

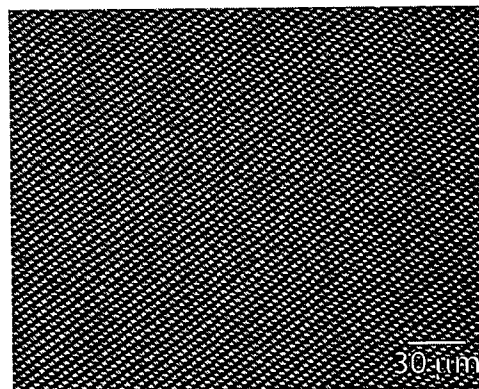


Fig. 11B

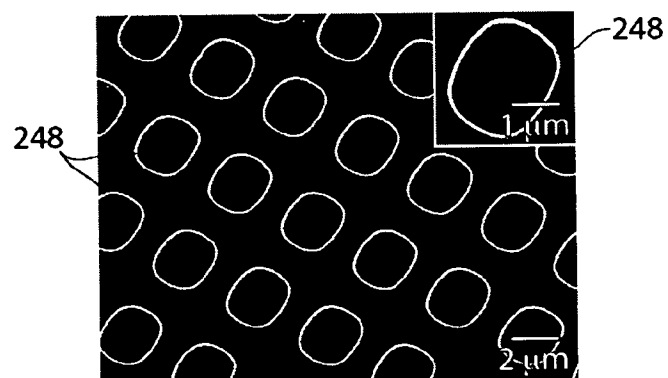


Fig. 11C

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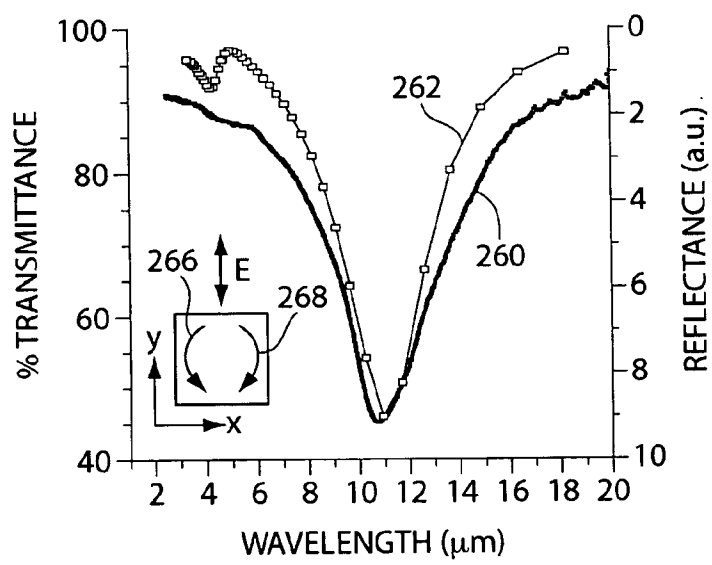


Fig. 11D

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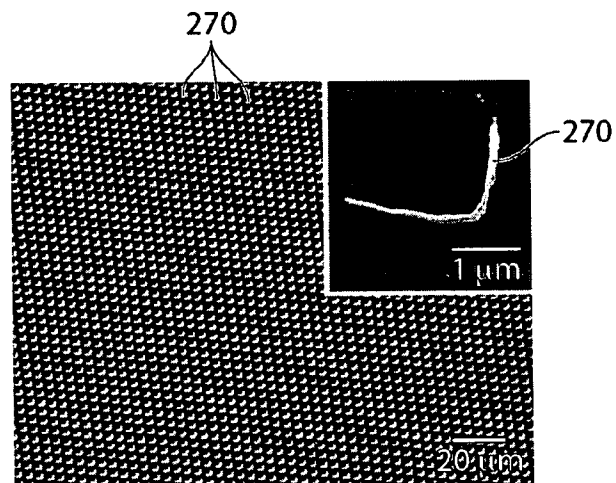


Fig. 12A

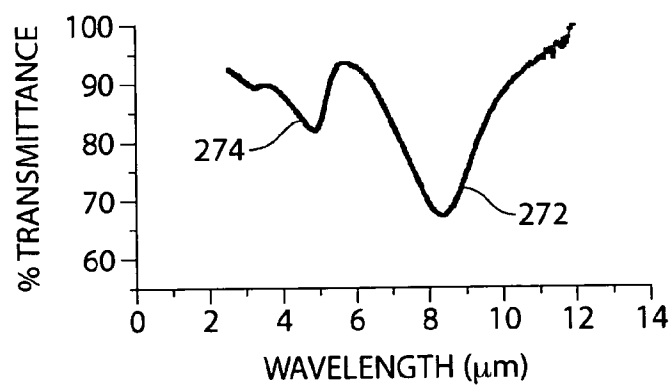


Fig. 12B

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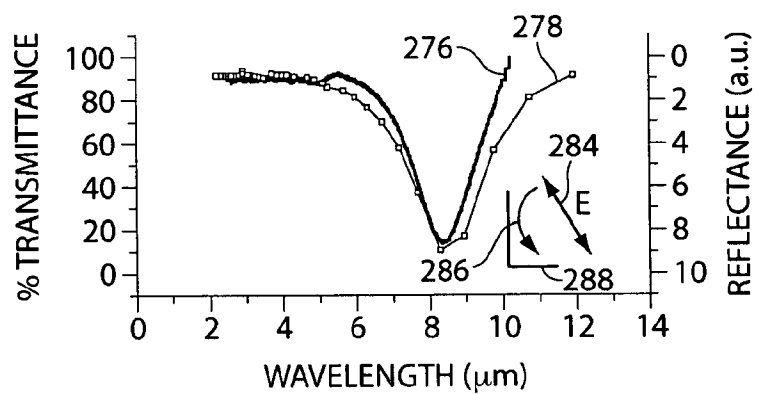


Fig. 12C

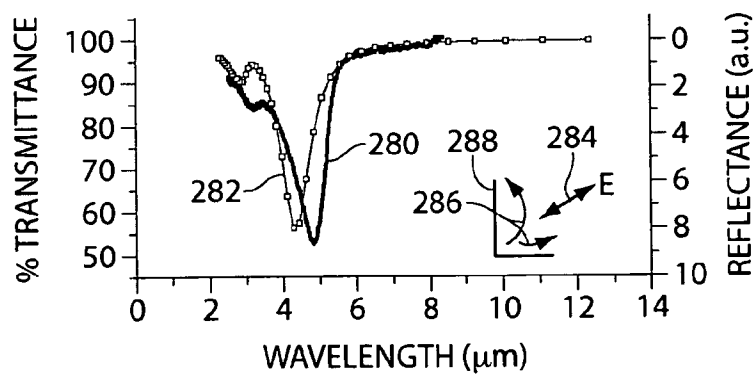


Fig. 12D

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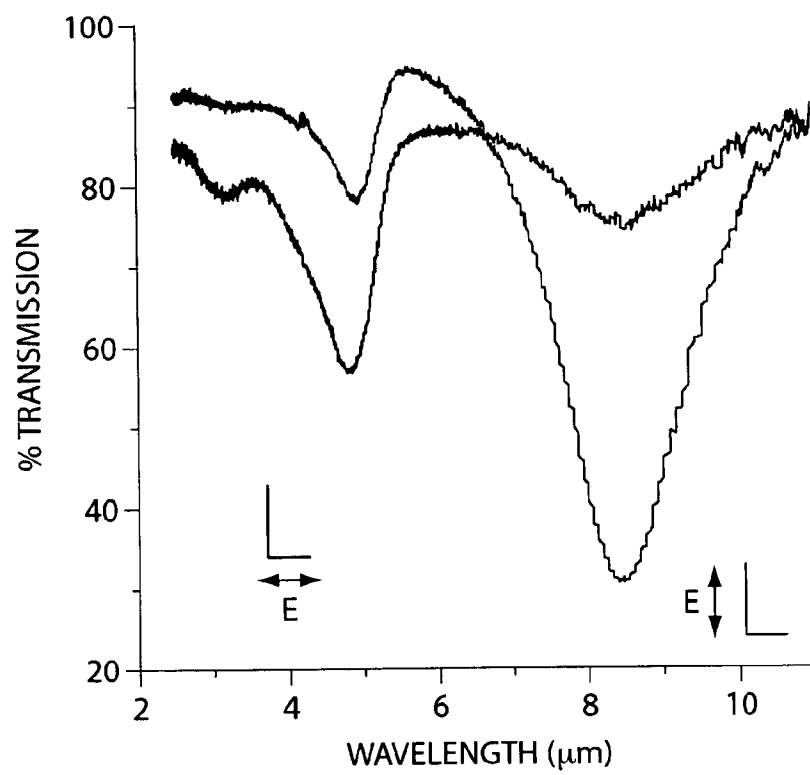


Fig. 13

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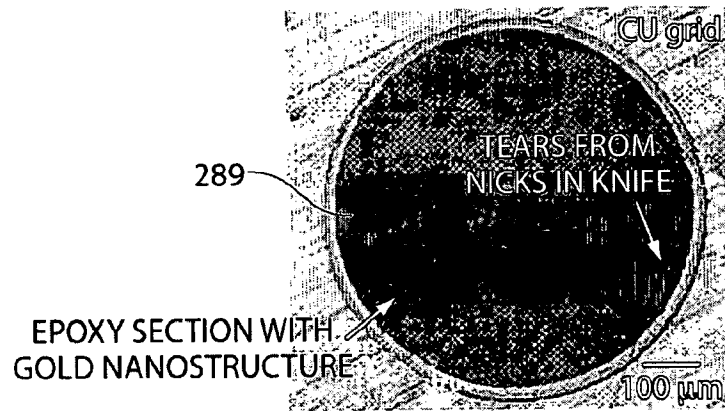


Fig. 14A

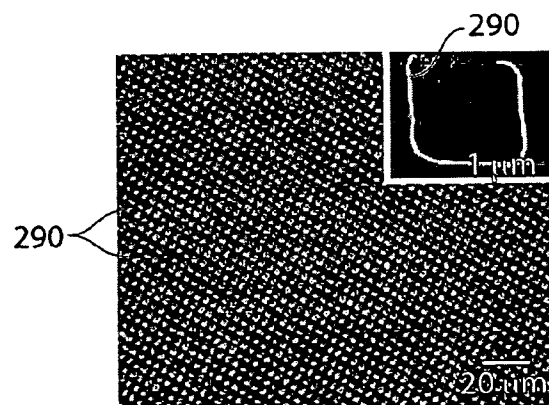


Fig. 14B

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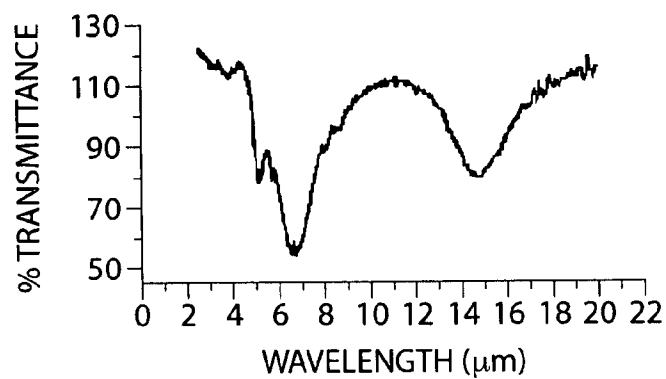


Fig. 14C

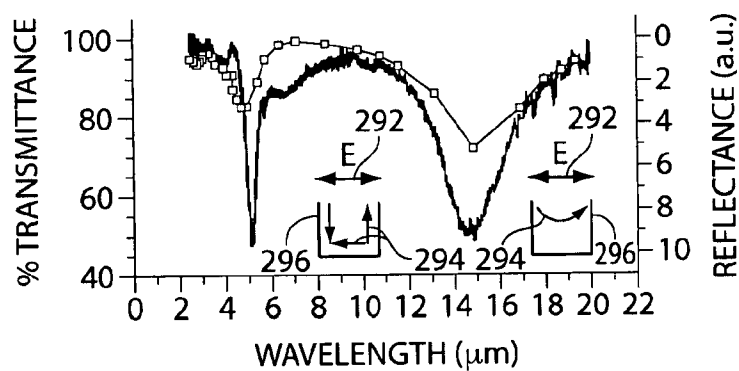


Fig. 14D

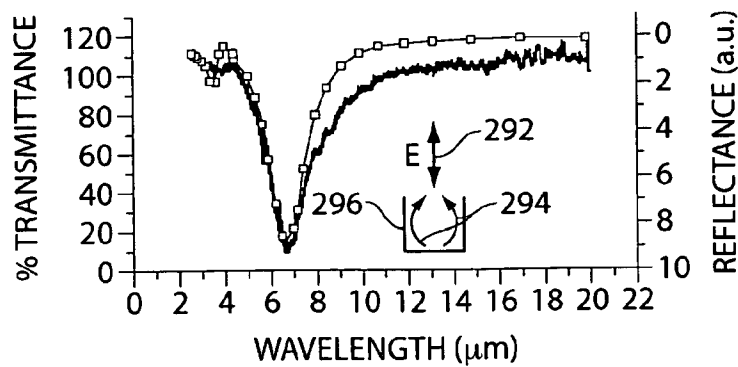


Fig. 14E

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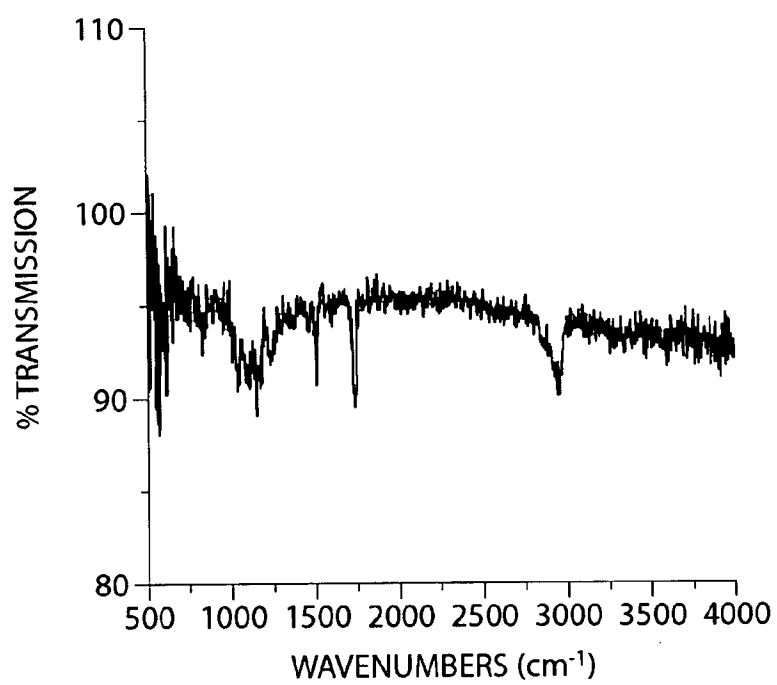


Fig. 15

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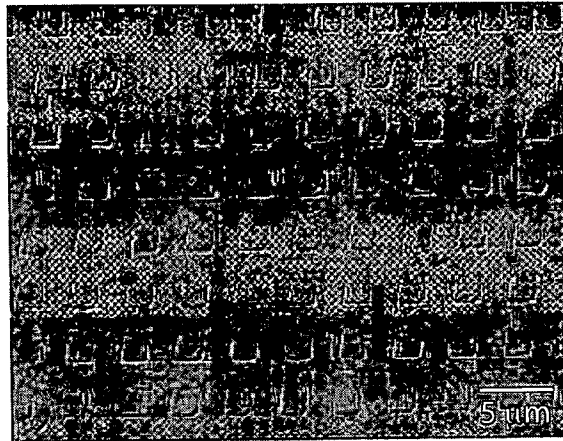


Fig. 16A

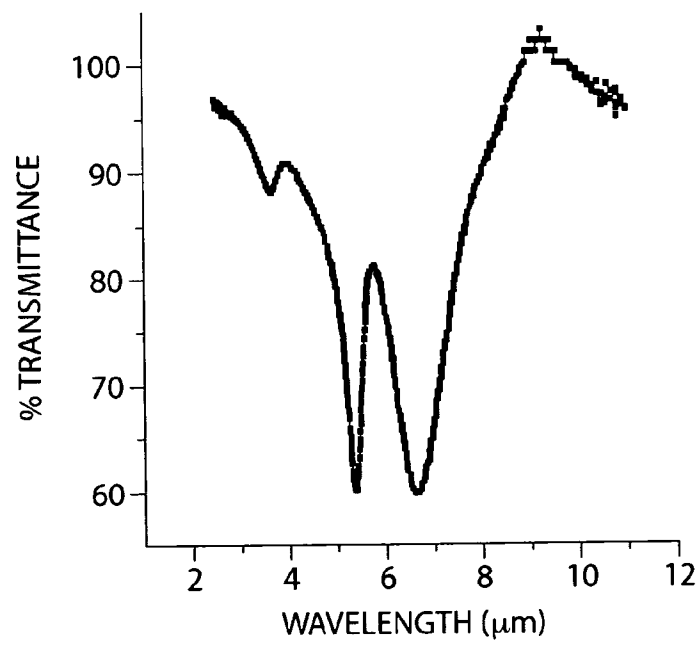


Fig. 16B

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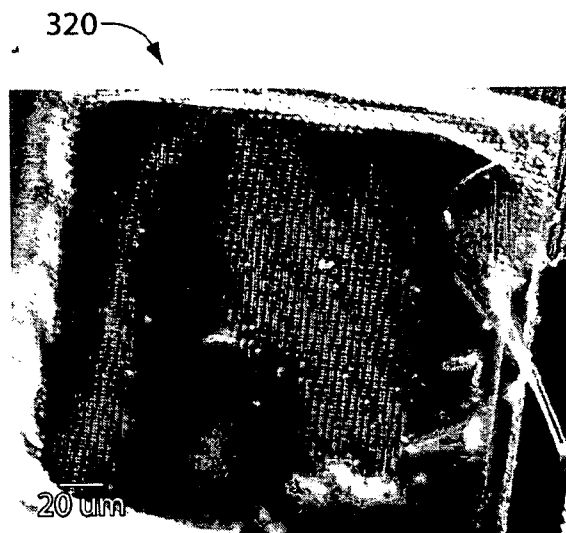


Fig. 17A

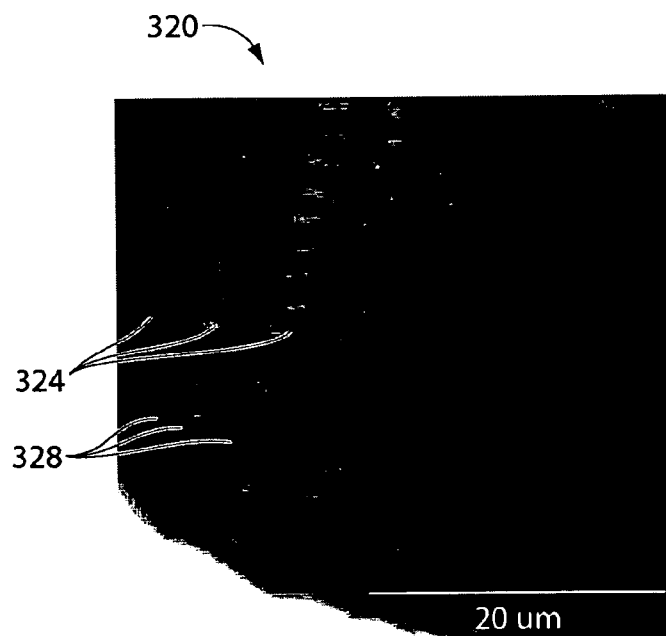


Fig. 17B