



US 20030116531A1

(19) **United States**

(12) **Patent Application Publication**

Kamins et al.

(10) **Pub. No.: US 2003/0116531 A1**

(43) **Pub. Date: Jun. 26, 2003**

(54) **METHOD OF FORMING ONE OR MORE NANOPORES FOR ALIGNING MOLECULES FOR MOLECULAR ELECTRONICS**

(52) **U.S. Cl. 216/41; 216/39**

(76) Inventors: **Theodore I. Kamins**, Palo Alto, CA (US); **Yong Chen**, Redwood City, CA (US); **Patricia A. Beck**, Palo Alto, CA (US)

(57)

ABSTRACT

Correspondence Address:
HEWLETT-PACKARD COMPANY
Intellectual Property Administration
P.O. Box 272400
Fort Collins, CO 80527-2400 (US)

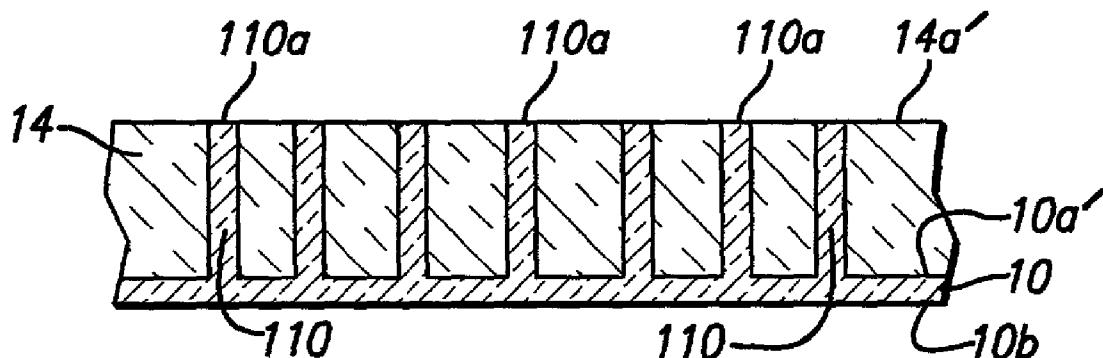
(21) Appl. No.: **10/029,583**

(22) Filed: **Dec. 20, 2001**

Publication Classification

(51) Int. Cl.⁷ **C03C 15/00; C03C 25/68**

A technique is provided for forming a molecule or an array of molecules having a defined orientation relative to the substrate or for forming a mold for deposition of a material therein. The array of molecules is formed by dispersing them in an array of small, aligned holes (nanopores), or mold, in a substrate. Typically, the material in which the nanopores are formed is insulating. The underlying substrate may be either conducting or insulating. For electronic device applications, the substrate is, in general, electrically conducting and may be exposed at the bottom of the pores so that one end of the molecule in the nanopore makes electrical contact to the substrate. A substrate such as a single-crystal silicon wafer is especially convenient because many of the process steps to form the molecular array can use techniques well developed for semiconductor device and integrated-circuit fabrication.



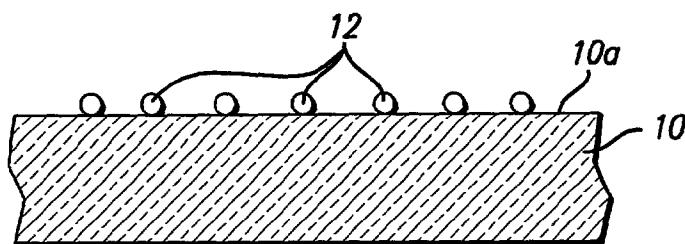


FIG. 1a

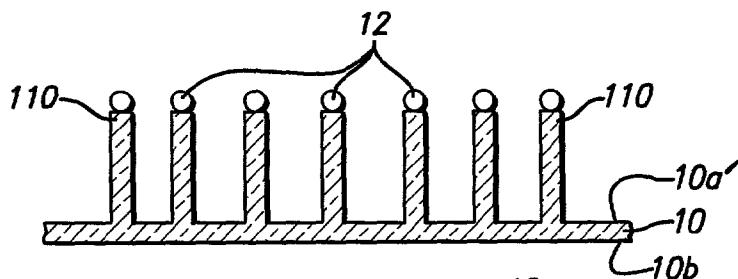


FIG. 1b

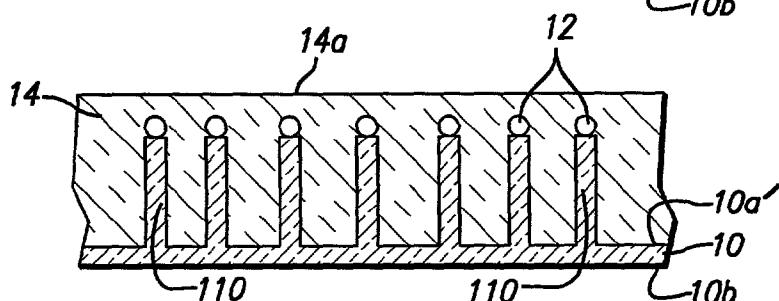


FIG. 1c

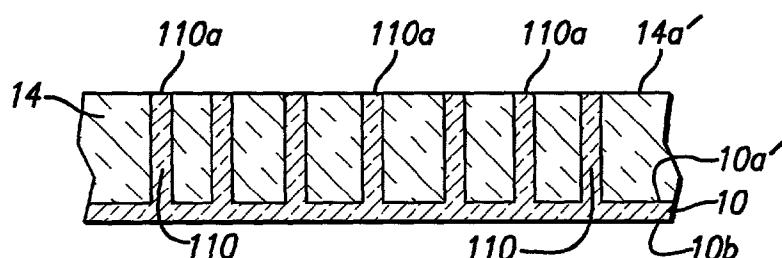


FIG. 1d

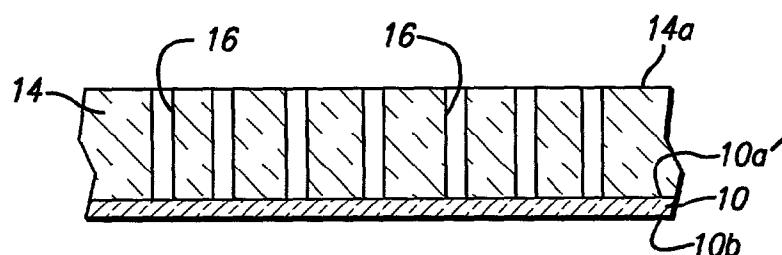


FIG. 1e

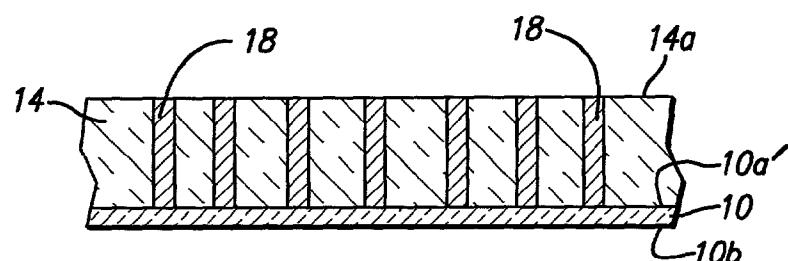


FIG. 1f

METHOD OF FORMING ONE OR MORE NANOPORES FOR ALIGNING MOLECULES FOR MOLECULAR ELECTRONICS

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] The U.S. Government has a paid-up license in this invention and the right in limited circumstances to require the patent owner to license others on reasonable terms as provided for by the terms of Contract No. MDA 97201-3-0005 awarded by the Defense Advanced Research Projects Agency.

TECHNICAL FIELD

[0002] The present invention is related generally to forming nanopores useful for aligning molecules.

BACKGROUND ART

[0003] The field of molecular electronics relies on ordered placement of molecules on a supporting substrate, which is often an electrode of an electronic device. For most applications, the molecules should have a definite orientation or be oriented with respect to the substrate plane, often perpendicular to it. Molecular films are often formed by Langmuir-Blodgett techniques to obtain a uniform monolayer or multilayer film. However, the orientation of the molecules is often difficult to control using Langmuir-Blodgett techniques until carefully refined for each combination of molecule and substrate and even then may be complicated by domains. A more robust method of aligning the molecules is needed using a technique that is less sensitive to the particular molecule being used. In addition, some applications require molecules to be spaced (separated) from each other; this cannot be readily accomplished by Langmuir-Blodgett techniques.

[0004] One approach to providing spaced holes in a substrate (silicon nitride-coated silicon) is disclosed by M. Park et al, "Block Copolymer Lithography: Periodic Arrays of ~10⁶ Holes in 1 Square Centimeter", *Science*, Vol. 276, pp. 1401-1404 (30 May 1997). However, the block copolymer mask is easily ablated during reactive ion etching, thus limiting this approach in the depth of the holes that can be formed. Further, the block copolymers that are used are not commercially available, and must be synthesized for each use, which is inconvenient for use outside the laboratory.

DISCLOSURE OF INVENTION

[0005] In accordance with the present invention, a method is provided for forming one molecule or an array of molecules aligned at a defined orientation to the substrate. The method is also useful for forming a mold for deposition of other materials therein and for spacing or separating molecules.

[0006] The array of molecules is formed by dispersing them in a small single hole (nanopore) or in an array of small, aligned holes (nanopores) in a substrate. Typically, the material in which the pores are formed is electrically insulating. The underlying substrate may be either electrically conducting or insulating. For electronic device applications, the substrate is, in general, electrically conducting and may be exposed and accessible at the bottom of the

pores so that one end of the molecule in the nanopore makes electrical contact to the substrate.

[0007] The method for forming a nanopore array for aligning molecules for molecular electronic devices comprises:

[0008] (a) providing a substrate having a first major surface and a second major surface, substantially parallel to the first major surface;

[0009] (b) forming an etch mask on the first major surface, the etch mask comprising one or a plurality of nanoparticles;

[0010] (c) directionally etching the substrate from the first major surface toward the second major surface, using the etch mask to protect underlying portions of the substrate against the etching, thereby forming a plurality of pillars underneath the etch mask;

[0011] (d) forming a layer of insulating material on the surface of the etched substrate, including between the pillars and either partially covering or embedding the pillars; and

[0012] (e) removing the pillars to leave a plurality of nanopores in the insulating layer.

[0013] If the pillars are embedded, then between steps (d) and (e), a process step is added to expose the ends of the pillars.

[0014] During the directional etching, the substrate may be maintained normal to the etching source to thereby provide nanopores that are substantially perpendicular to the substrate. Alternatively, the substrate and the etching source may be maintained at a pre-selected angle relative to each other to provide nanopores that are in a defined orientation relative to the substrate.

[0015] The method of the present invention aligns the molecules in a fixed direction, using a technique that is less sensitive to the particular molecule being used.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] FIGS. 1a-1f are cross-sectional views, illustrating the method steps according to an embodiment of the present invention.

BEST MODES FOR CARRYING OUT THE INVENTION

[0017] The discussion which follows is primarily directed to forming an array of nanopores. However, it will be appreciated that the same approach can be used to form a single nanopore.

[0018] In accordance with the present invention, a technique is provided for forming an array of molecules aligned in a pre-selected defined orientation relative to the substrate. In one embodiment, that orientation is preferably substantially perpendicular. The array of molecules is formed by dispersing them in an array of small, aligned holes (nanopores) in a substrate. Typically, the material in which the pores are formed is electrically insulating. The underlying substrate may be either electrically conducting or insulating. For electronic device applications, the substrate is generally electrically conducting and may be exposed and accessible

at the bottom of the pores so that one end of the molecule in the nanopore makes electrical contact to the substrate. A substrate such as a single-crystal silicon wafer is especially convenient because many of the process steps to form the molecular array can use techniques already well developed for integrated-circuit fabrication. For example, heavily doped silicon has sufficient electrical conductivity to serve as one electrode for the molecules. Alternatively, a metal layer can be formed over the silicon or over an oxide on silicon if lower resistivity or electrical isolation is needed.

[0019] The following steps are used to form the array:

[0020] Turning to **FIG. 1a**, a substrate **10** is shown. The substrate, if insulating, may be an oxide, such as silicon dioxide or aluminum oxide, or a nitride, such as silicon nitride, or an oxynitride, such as silicon oxynitride or a carbide, such as silicon carbide. If conducting, the substrate may be heavily doped single crystalline or polycrystalline silicon or a metal or a metal layer over silicon or silicon dioxide.

[0021] Next, an etch mask of nanoscopic dimensions is applied to the substrate **10**, for example, using nanoparticles **12**. Nanoparticles of well controlled dimensions are readily available. For example, suspensions containing nanoparticles may be commercially obtained. One such source, Ted Pella, Inc. (Redding, Calif.), provides gold nanoparticles in a sol, with gold particles available in specific sizes ranging from about 2 nm to 250 nm. These nanoparticles are usually composed of an inorganic crystalline core, typically a metal, that is coated with an organic species to keep the nanoparticles from agglomerating. These nanoparticles **12** can be dispersed on the surface **10a** of the substrate **10** from the liquid phase. Alternatively, the nanoparticles **12** can be formed by depositing a material of one lattice constant on a substrate having a different lattice constant and using the forces from the lattice mismatch to form nanoparticulate islands of the depositing material. As shown in **FIG. 1a**, the nanoparticles **12** are distributed on a major surface **10a** of the substrate **10** to a coverage less than a single layer. That is, the nanoparticles are separated from each other by a space and there are no multiple layers of the nanoparticles.

[0022] In either case, the nanoparticles **12** are then used as an etch mask, and the substrate **10** is directionally etched, for example using reactive ion etching (RIE) to a controlled depth. The etch chemistry and nanoparticulate material **12** are selected so that the material comprising the substrate **10** is etched much faster than the nanoparticulate material. This etch process produces an array of pillars **110** on the new surface **10a'** of the substrate **10**. The nanoparticulates **12** may be removed before further processing or may be left on the pillars **110** (and typically removed during subsequent processing). As shown in **FIG. 1b**, the nanoparticles **12** serve as an etch mask for directional RIE, leaving pillars **110** on an etched surface **12b**.

[0023] Because the nanoparticles **12** comprise a metallic core, they are better able to withstand the rigors of RIE, and are not readily ablated, as are organic polymers. The ability to survive longer during RIE means that taller pillars, and hence deeper nanopores, can be fabricated.

[0024] It will be appreciated that the cross-section of a pillar need not be perfectly uniform over its entire height, but may evidence some taper, as a consequence of the etching process.

[0025] The length of the pillars **110** can be tailored to have a specific relation to the length of the molecules to be inserted in the formed nanopores. The remaining thickness of the substrate **10** (the distance between back surface **10b** and the new front surface **10a'**) must be sufficient to provide suitable mechanical strength to the substrate **10**.

[0026] Next, the array of pillars **110** must be transformed into a corresponding array of holes **16**, in which the molecules **18** can be placed. This is accomplished in the following manner: An insulating material **14** is formed on the surface **10a'** of the substrate **10**, surrounding and covering the pillars **110**. Examples of suitable insulating materials include oxides, such as silicon dioxide and aluminum oxide, nitrides, such as silicon nitride, oxynitrides, such as silicon oxynitride, carbides, such as silicon carbide, and diamond-like carbon (DLC). Silicon dioxide may be formed by any number of well known techniques, including, but not limited to, thermal deposition and spin-on-glass (SOG). Thin aluminum oxide, for example, on the order of 12 to 25 Å thick, is formed by totally reacting aluminum in oxygen during deposition or depositing Al and oxidizing afterwards. Still further examples of suitable insulating materials include polymers that have the requisite chemical and electrical properties, i.e., a slower differential etch rate than the pillars **110** and electrically insulating attributes. Such insulating polymers are well known; an example includes poly-fluoroalkylenes, which may be produced in a carbon-hydrogen-fluorine plasma.

[0027] The insulating material **14** may be formed by chemical vapor deposition or by liquid-phase techniques commonly used in semiconductor device processing. Good filling of the space between the pillars **110** is critical. The surrounding material **14** will typically extend above the top of the pillars **110** so that the pillars are completely covered, but this is not essential. Depending on the subsequent processing, a resultant flat (planar) top surface **14a** may or may not be important. As shown in **FIG. 1c**, a layer **14** of an oxide, e.g., silicon dioxide (SiO_2), is blanket-deposited, employing well-known deposition techniques, to completely or partially cover the pillars **110**. Examples of suitable deposition methods include chemical vapor deposition (CVD) (e.g., high density plasma CVD or thermal CVD or ozone-assisted CVD or plasma-enhanced CVD) and spin-coating, all of which are well-known in the art of semiconductor device fabrication.

[0028] If the pillars **110** are not already exposed, the insulating material **14** surrounding and covering the pillars is then reduced in thickness so that the tops **110a** of the pillars are exposed. This material removal may be accomplished by chemical-mechanical polishing (CMP), a technique commonly used in integrated-circuit fabrication. In this case, having a flat top surface **14a** before polishing is not critical. At the end of this step, the surface **14a'** is flat; the surface is composed of both the exposed ends of the pillars **110a** and the surrounding insulating material **14**. **FIG. 1d** shows the resulting structure after polishing, leaving a flat surface **14a'** in the insulating layer **14**.

[0029] Alternatively, the material removal may be accomplished by an unmasked single- or multi-step plasma/reactive-ion etch technique. In this case, the top surface **14a** must be flat before the start of the etch process. The selectivity of the plasma/reactive-ion etch can be adjusted during different

portions of the etch process to produce either a flat surface **14a'** (same etch rate) or a surface with the ends **110a** of the pillars **110** either recessed or protruding (different etch rates), as desired. Both CMP and plasma/reactive-ion etching are processes well known in integrated-circuit processing.

[0030] If the layer **14** is deposited in such a manner as to form thinner regions over the pillars **110**, then the unmasked etch step above does not require that the top surface **14a** be flat, as the etching will expose the top of the pillar **110** before the surrounding area is exposed.

[0031] As the final step, the pillars **110** are removed, leaving nanopores **16** extending a specified distance into (or beyond) the insulating material **14**, by employing a selective etch. Because of their extremely small size, the pillars **110** are best removed by gas-phase etching. For example, a selective chemical or plasma etch can remove the pillar material **110** without significantly attacking the surrounding insulating material **14**. If a plasma is used, its composition is selected to be chemically selective, rather than relying on high-energy/high-density ion bombardment. **FIG. 1e** shows the resulting structure, after etching away the pillars **110**, leaving nanopores **16** where the pillars were originally located.

[0032] The nanopores **16** are intended, at least in some applications, to be approximately the size of molecules that are to be placed in them. For example, many long-chain molecules are about 10 nm long and about 1 nm in diameter. The size (diameter) of the nanopores **16**, of course, depends on the size of the pillars **110**. Broadly, however, the nanopores **16** may be formed having a length within the range of about 5 to 100 nm and a diameter within the range of about 1 to 10 nm. It is expected that the aspect ratio (length:diameter) is likely to be less than about 100:1 and, for practical considerations, less than about 25:1.

[0033] At this point, the array of nanopores **16** is essentially complete. The molecules **18** can then be dispersed over the surface. Many of the molecules fill the nanopores **16** and become aligned preferentially in the direction of the nanopores. The degree of alignment depends on the relative diameters and lengths of the nanopores **16** and molecules **18**. **FIG. 1f** illustrates the filling of the nanopores **16** with molecules or other material **18**.

[0034] By proper processing techniques before applying the molecules **18**, the bottom of the nanopores **16** may be made electrically conducting, either by separate deposition of an electrically-conducting film as a buried layer in the substrate **10** or by use of an electrically conductive substrate **10**. Alternatively, the bottom of the nanopores **16** may be covered by a thin tunnel barrier so that a controlled electrical connection between the molecules and the underlying substrate can be made for advantageous use of the molecules in an electronic device. In other cases, a thick insulator may remain if the molecule needs to be electrically isolated.

[0035] The array of nanopores **16** that is formed can find a variety of uses. For example, it may be desirable to characterize a molecule. Such nanopores **16** can isolate individual molecules from each other and permit probing, such as by scanning tunneling microscopy (STM). Alternatively, it may be desirable to form molecular electronic devices. The nanopores **16** not only isolate, or separate, the

individual molecules from each other, but, in the case of long-chain molecules, prevent bending or kinking of the molecules.

[0036] Molecular electronic devices may employ molecules that are capable of switching in the presence of an electric field. Examples of such molecules include the rotaxanes, pseudo-rotaxanes, catenanes, and spirobifluorans. For such devices, the substrate **10** forms one electrode, and it is easily within the ability of one skilled in this art, based on the teachings that are emerging, to form a suitable second electrode for applying the electric field.

[0037] Filling the nanopores **16** with a material **18** such as a semiconductor or a magnetic material can be used to produce electronic or magnetic devices. The nanopores can be filled by a selective chemical vapor deposition process or possibly by electrochemical deposition. In either case, the nanopore is filled from the bottom toward the top. More conventional processes that nucleate material on the walls of the pore will be difficult to implement because of the small diameter and high aspect ratio of the nanopores **16**.

[0038] The foregoing discussion is directed primarily to the preferred orientation of the nanopores **16** relative to the substrate **10**, namely, substantially perpendicular. Other orientations may also be obtained, less than 90 degrees, such as by changing the angle of the etch source to the substrate or tilting the substrate during directional etching.

INDUSTRIAL APPLICABILITY

[0039] The method of forming a nanopore array is expected to find use in the fabrication of molecular electronic devices and for the physical and electrical characterization of molecules.

What is claimed is:

1. A method for forming at least one nanopore for aligning at least one molecule for molecular electronic devices or for forming a mold for deposition of a material, comprising:
 - (a) providing a substrate having a first major surface and a second major surface, substantially parallel to said first major surface;
 - (b) forming an etch mask on said first major surface, said etch mask comprising at least one nanoparticle;
 - (c) directionally etching said substrate from said first major surface toward said second major surface, using said etch mask to protect underlying portions of said substrate against said etching, thereby forming at least one pillar underneath said etch mask;
 - (d) forming a layer of insulating material on said etched substrate, including around said at least one pillar and at least partially covering said at least one pillar; and
 - (e) removing said at least one pillar to leave at least one said nanopore in said insulating layer.
2. The method of claim 1 for forming a nanopore array for either aligning or spacing molecules for electronic devices or for forming said mold, wherein: in step (b), said etch mask comprises a plurality of said nanoparticles; in step (c), a plurality of said pillars is formed by said directional etching; in step (d) said layer of insulating material is formed between said pillars and at least partially covering said

pillars; and in step (e), said plurality of pillars is removed to leave said array of nanopores.

3. The method of claim 1 wherein said at least one nanoparticle has an average particle size within a range of about 1 to 10 nm.

4. The method of claim 1 wherein said at least one nanoparticle comprises an inorganic crystalline core covered with an organic layer.

5. The method of claim 1 wherein said at least one nanoparticle is formed by depositing a material of a first lattice constant on said substrate wherein said substrate has a second and different lattice constant to create a lattice mismatch and using forces from said lattice mismatch to form at least one nanoparticulate island of said deposited material.

6. The method of claim 1 wherein said directional etching is carried out using reactive ion etching.

7. The method of claim 1 wherein said insulating material is selected from the group consisting of oxides, nitrides, oxynitrides, diamond-like carbon, and insulating polymers.

8. The method of claim 7 wherein said insulating material is selected from the group consisting of silicon dioxide, aluminum oxide, silicon nitride, and silicon oxynitride.

9. The method of claim 7 wherein said insulating material is formed by chemical vapor deposition or by liquid-phase techniques.

10. The method of claim 1 wherein said etch mask comprising said at least one nanoparticle is removed prior to forming said insulating material.

11. The method of claim 1 wherein in step (d), said layer of said insulating material is formed to completely cover said at least one pillar and following step (d), said layer of insulating material is reduced in thickness to expose a top of said at least one pillar.

12. The method of claim 1 wherein said layer of insulating material is reduced in thickness by chemical-mechanical polishing or by an unmasked single-step or multi-step plasma/reactive-ion etch technique.

13. The method of claim 1 wherein said at least one pillar is removed by selective etching.

14. The method of claim 1 further comprising filling said at least one nanopore with said material.

15. The method of claim 14 wherein said material comprises a molecular species.

16. The method of claim 14 wherein the bottom of said at least one nanopore is electrically conducting.

17. The method of claim 16 wherein said bottom of said at least one nanopore is made electrically conducting by using as said substrate a material that is electrically conducting.

18. The method of claim 17 wherein said substrate comprises doped single crystal silicon or a doped polycrystalline silicon layer on said substrate.

19. The method of claim 14 wherein prior to filling said nanopores, the bottom of said nanopores is covered with a thin tunnel barrier.

20. The method of claim 14 wherein said material comprises a material selected from the group consisting of semiconductor and magnetic materials.

21. The method of claim 1 wherein said at least one nanopore has a length of about 5 to 100 nm and a diameter of about 1 to 10 nm.

22. The method of claim 21 wherein said at least one nanopore has a length of about 10 nm and a diameter of about 1 nm.

23. The method of claim 1 wherein said substrate is selected from the group consisting of oxides, nitrides, oxynitrides, and carbides.

24. A method for forming at least one molecule in a pre-selected orientation relative to a substrate, said method comprising:

(a) forming at least one nanopore by:

(1) providing said substrate having a first major surface and a second major surface, substantially parallel to said first major surface,

(2) forming an etch mask on said first major surface, said etch mask comprising at least one nanoparticle,

(3) directionally etching said substrate from said first major surface toward said second major surface, using said etch mask to protect underlying portions of said substrate against said etching, thereby forming at least one pillar underneath said etch mask,

(4) forming a layer of insulating material on said etched substrate, including around said at least one pillar and at least partially covering said at least one pillar, and

(5) removing said at least one pillar to leave at least one said nanopore in said insulating layer; and

(b) dispersing said at least one molecule in said at least one nanopore.

25. The method of claim 24 for forming a molecular array, wherein: in step (2), said etch mask comprises a plurality of said nanoparticles; in step (3), a plurality of said pillars is formed by said directional etching; in step (4) said layer of insulating material is formed between said pillars and at least partially covering said pillars; and in step (5), said plurality of pillars is removed to leave said array of nanopores and further wherein in step (b), a plurality of said molecules is dispersed, one in each said nanopore.

26. The method of claim 24 wherein said at least one nanoparticle has an average particle size within a range of about 1 to 10 nm.

27. The method of claim 24 wherein said at least one nanoparticle comprises an inorganic crystalline core covered with an organic layer.

28. The method of claim 24 wherein said at least one nanoparticle is formed by depositing a material of a first lattice constant on said substrate wherein said substrate has a second and different lattice constant to create a lattice mismatch and using forces from said lattice mismatch to form at least one nanoparticulate island of said deposited material.

29. The method of claim 24 wherein said directional etching is carried out using reactive ion etching.

30. The method of claim 24 wherein said insulating material is selected from the group consisting of oxides, nitrides, oxynitrides, diamond-like carbon, and insulating polymers.

31. The method of claim 30 wherein said insulating material is selected from the group consisting of silicon dioxide, aluminum oxide, silicon nitride, and silicon oxynitride.

32. The method of claim 30 wherein said insulating material is formed by chemical vapor deposition or by liquid-phase techniques.

33. The method of claim 24 wherein said etch mask comprising said at least one nanoparticle is removed prior to forming said insulating material.

34. The method of claim 24 wherein in step (4), said layer of said insulating material is formed to completely cover said at least one pillar and following step (4), said layer of insulating material is reduced in thickness to expose a top of said at least one pillar.

35. The method of claim 24 wherein said layer of insulating material is reduced in thickness by chemical-mechanical polishing or by an unmasked single-step or multi-step plasma/reactive-ion etch technique.

36. The method of claim 24 wherein said at least one pillar is removed by selective etching.

37. The method of claim 24 further comprising filling said at least one nanopore with said material.

38. The method of claim 37 wherein said material comprises a molecular species.

39. The method of claim 37 wherein the bottom of said at least one nanopore is electrically conducting.

40. The method of claim 39 wherein said bottom of said at least one nanopore is made electrically conducting by using as said substrate a material that is electrically conducting.

41. The method of claim 40 wherein said substrate comprises doped single crystal silicon or a doped polycrystalline silicon layer on said substrate.

42. The method of claim 37 wherein prior to filling said nanopores, the bottom of said nanopores is covered with a thin tunnel barrier.

43. The method of claim 37 wherein said material comprises a material selected from the group consisting of semiconductor and magnetic materials.

44. The method of claim 24 wherein said at least one nanopore has a length of about 5 to 100 nm and a diameter of about 1 to 10 nm.

45. The method of claim 44 wherein said at least one nanopore has a length of about 10 nm and a diameter of about 1 nm.

46. The method of claim 24 wherein said substrate is selected from the group consisting of oxides, nitrides, oxynitrides, and carbides.

* * * * *