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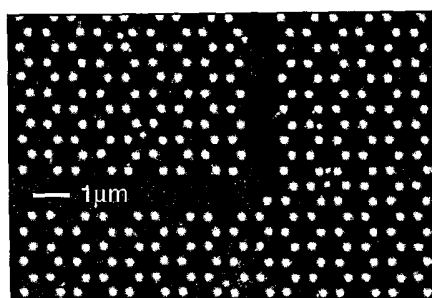
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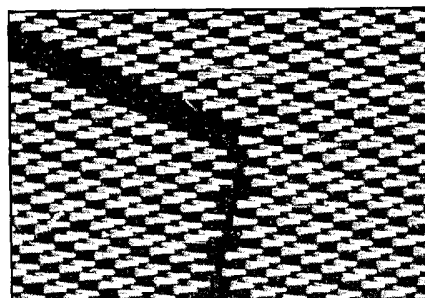
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(54) Title: PRECISELY POSITIONED NANOWHISKERS AND NANOWHISKER ARRAYS AND METHOD FOR PREPARING THEM



a



b

(57) Abstract: A nanoengineered structure comprising an array of more than about 1000 nanowhiskers on a substrate in a predetermined spatial configuration, for use for example as a photonic band gap array, wherein each nanowhisker is sited within a distance from a predetermined site not greater than about 20% of its distance from its nearest neighbour. To produce the array, an array of masses of a catalytic material are positioned on the surface, heat is applied and materials in gaseous form are introduced such as to create a catalytic seed particle from each mass, and to grow, from the catalytic seed particle, epitaxially, a nanowhisker of a predetermined material, and wherein each mass upon melting, retains approximately the same interface with the substrate surface such that forces causing the mass to migrate across said surface are less than a holding force across a wetted interface on the substrate surface. A nanoengineered structure comprising an array of more than about 1000 nanowhiskers on a substrate in a predetermined spatial configuration, for use for example as a photonic band gap array, wherein each nanowhisker is sited within a distance from a predetermined site not greater than about 20% of its distance from its nearest neighbour. To produce the array, an array of masses of a catalytic material are positioned on the surface, heat is applied and materials in gaseous form are introduced such as to create a catalytic seed particle from each mass, and to grow, from the catalytic seed particle, epitaxially, a nanowhisker of a predetermined material, and wherein each mass upon melting, retains approximately the same interface with the substrate surface such that forces causing the mass to migrate across said surface are less than a holding force across a wetted interface on the substrate surface.

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**PRECISELY POSITIONED NANOWHISKERS AND NANOWHISKER
ARRAYS AND METHOD FOR PREPARING THEM**

Cross-Reference to Related Applications

5 This application claims the benefit of the priority of US Provisional Patent Application Nos. 60/459,989 filed April 04, 2003, 60/472,721 filed May 23, 2003, 60/512,771 filed October 21,2003, and 60/524,891 filed November 26, 2003, the entirety of which are incorporated herein by reference.

Background of the Invention

10 **Field of the Invention**

 This invention relates generally to structures and devices produced by techniques of nanotechnology

 More specifically, the invention relates to such structures and devices incorporating at least one element, essentially in one-dimensional form, and that is of
15 nanometer dimensions in its width or diameter, and that is produced by the so-called Vapour-Liquid-Solid (VLS) mechanism. For the purposes of this specification, such element will be termed a "nanowhisiker".

Brief Description of the Prior Art

 Nanotechnology covers various fields, including that of nanoengineering,
20 which may be regarded as the practice of engineering on the nanoscale. This may result in structures ranging in size from small devices of atomic dimensions, to much larger scale structures for example on the microscopic scale. Commonly, such structures include nanostructures. Typically, nanostructures are devices having at least two dimensions less than about 1 μm (i.e., nanometer dimensions). Ordinarily,
25 layered structures or stock materials having one or more layers with a thickness less than 1 μm are not considered to be nanostructures. Thus the term nanostructures includes free-standing or isolated structures having two dimensions less than about 1 μm that have functions and utilities that are different from larger structures and are typically manufactured by methods that are different from conventional procedures
30 for preparing somewhat larger, i.e., microscale, structures. Thus, although the exact boundaries of the class of nanostructures are not defined by a particular numerical size limit, the term has come to signify such a class that is readily recognized by those skilled in the art. In many cases, an upper limit of the size of the at least two dimensions that characterize nanostructures is about 500 nm. In some technical

contexts the term “nanostructure” is construed to cover structures having at least two dimensions of about 100 nm or less. In a given context the skilled practitioner will recognize the range of sizes intended. In this application the term “nanostructure” or “nanowhisker” is intended to refer to an elongated structure having at least two
5 transverse dimensions less than about 1 μm , as indicated above.

Nanostructures include one-dimensional nanoelements, essentially in one-dimensional form, and that are of nanometer dimensions in their width or diameter, and that are commonly known as a nanowhisker, nanorods, nanowires, nanotubes, etc.

10 As regards nanowhiskers, the basic process of whisker formation on substrates, by the so-called VLS (vapour-liquid-solid) mechanism, is well known. A particle of a catalytic material, usually gold, for example, on a substrate is heated in the presence of certain gases to form a melt. A pillar forms under the melt, and the melt rises up on top of the pillar. The result is a whisker of a desired material with
15 the solidified particle melt positioned on top. (See E.I Givargizov, Current Topics in Materials Science, Vol. 1, pages 79-145, North Holland Publishing Company, 1978.) The dimensions of such whiskers were in the micrometer range.

Although the growth of nanowhiskers catalyzed by the presence of a catalytic particle at the tip of the growing whisker has conventionally been referred to as the
20 VLS (Vapour-Liquid-Solid process), it has come to be recognized that the catalytic particle may not have to be in the liquid state to function as an effective catalyst for whisker growth. At least some evidence suggests that material for forming the whisker can reach the particle-whisker interface and contribute to the growing whisker even if the catalytic particle is at a temperature below its melting point and
25 presumably in the solid state. Under such conditions, the growth material, e.g., atoms that are added to the tip of the whisker as it grows, may be able to diffuse through a the body of a solid catalytic particle or may even diffuse along the surface of the solid catalytic particle to the growing tip of the whisker at the growing temperature. Evidently, the overall effect is the same, i.e., elongation of the whisker catalyzed by
30 the catalytic particle, whatever the exact mechanism may be under particular circumstances of temperature, catalytic particle composition, intended composition of the whisker, or other conditions relevant to whisker growth. For purposes of this application, the term “VLS process”, or VLS mechanism, or equivalent terminology, is intended to include all such catalyzed procedures wherein nanowhisker growth is

catalyzed by a particle, liquid or solid, in contact with the growing tip of the nanowhisker.

International Application Publication No. WO 01/84238 discloses in Figures 15 and 16 a method of forming nanowhiskers wherein nanometer sized particles from an aerosol are deposited on a substrate and these particles are used as seeds to create filaments or nanowhiskers.

For the purposes of this specification the term nanowhiskers is intended to mean one-dimensional nanoelements with a width or diameter (or, generally, a cross-dimension) of nanometer size, the elements having been formed by the so-called VLS mechanism. Nanowhiskers are also referred to in the art as "nanowires" or, in context, simply as "wires", and such terminology, as used in this application, is equivalent to the term "nanowhiskers"

Positioning whiskers at selected positions on a substrate is desirable for an integration of whisker technology with current semiconductor component technology.

Several experimental studies on the growth of nanowhiskers have been made, the most important reported by Hiruma et al. They grew III-V nano-whiskers on III-V substrates in a metal organic chemical vapor deposition (MOCVD) growth system. (See K. Hiruma, et al., J. Appl. Phys. 74, page 3162 (1993); K. Hiruma, et al., J. Appl. Phys. 77, page 447 (1995); K. Hiruma, et al., IEICE Trans. Electron. E77C, page 1420 (1994); K. Hiruma, et al., J. Crystal Growth 163, pages 226 – 231 (1996)) Their approach relied on annealing a thin Au film to form the seed particles. In this way, they achieved a homogeneous whisker width distribution, the mean size of which could be controlled by the thickness of the Au layer and the way this layer transforms to nanoparticles. With this technique, it is difficult to control the size and surface coverage separately.

Sato et al., Appl. Phys. Lett. 66(2), 9 January 1995, disclose an attempt to grow four nanowhiskers, the position or site of each nanowhisker being predetermined by use of four respective windows in an SiO₂ mask. The mask was then removed and growth was initiated. The results were, in general, unsatisfactory for producing a structure with nanowhiskers sufficiently precisely positioned for electronics/photonics components, one reason being that the nanowhisker growth site could not be accurately localised, on account of the use of a thin film for forming the seed particle. Further the structure consisting of four nanowhiskers was not extended

to include a large number of nanowhiskers such as is necessary for many applications.

US Patent No. 5,332,910 discloses a micro-cavity laser comprising a plurality of semiconductor rods arranged at a distance equal to an integer sub-multiple of light emitted from the semiconductor rod. In one embodiment, a focussed ion beam was used to create seeds in a substrate from which nanowhiskers were grown. In another embodiment, nanowhiskers were grown by MOCVD in etched holes in an SiO₂ mask.

A component that is of considerable interest is a photonic bandgap array. This comprises an array of a large number of elements (that may be projections or holes) in a substrate and that provide a different refractive index from the surrounding medium. Selective area MOVPE growth (SA-MOVPE) has been used to develop two-dimensional photonic bandgap structures, but these appear of limited applicability. (See Akabori et al., *Physica* E13, pages 446-450, March 2002).

Work has also been carried out for forming photonic band gap structures from carbon nanotubes, where single-seeded arrays have been synthesized using methods such as self-assembly nanosphere lithography and optical lithography. (See K. Kempa et al., *Letters*, Vol. 3, No. 1, pages 13-18, 19 November 2002). However tubes are not ideal structures for forming areas of different refractive index.

In co-pending US Patent Application Serial No. 10/613,071, filed July 7, 2003, the contents of which are incorporated herein by reference and co-pending International Application PCT/GB2003/002929, a method of producing arrays of nanowhiskers is described suitable for use as photonic bandgap structures.

Summary of the Invention

In general terms, the invention comprises a nanotechnological or nanoengineered structure comprising at least one nanowhisker located at a predetermined site with an accuracy of location that is within a predetermined dimensional tolerance, sufficient for use in an electronics/photronics component.

The invention further comprises a nanoengineered structure comprising a multiplicity of nanowhiskers in a predetermined spatial configuration, the nanowhiskers being disposed within the configuration at predetermined sites to within a predetermined dimensional tolerance.

The invention further comprises a nanoengineered structure comprising an array of a large number of nanowhiskers in a predetermined spatial configuration, the nanowhiskers being disposed within the configuration at predetermined sites to

within a predetermined dimensional tolerance. For the purposes of this specification, "array" is intended to mean an assembly of about 1000 one-dimensional nanoelements; in all circumstances, the array comprises more than 500 such elements, and may commonly comprise more than about 10^6 such elements.

5 Such structures in accordance with the invention have many applications, for example photonic band gap structures, displays such as Field Emitting Displays, electromedical devices with a large number of probes/sensors, or electronic/photronics components such as memory circuits where a large number of elements are included at predetermined positions. In the situation where one or more nanowhiskers are
10 employed for example in a photonics/electronics circuit, where the nanowhisker has to be positioned extremely accurately with respect to adjoining parts of the circuit, the invention provides a mechanism for such positioning.

The invention also comprises methods of producing such structures.

At least in a preferred embodiment, the invention comprises a method for
15 producing a structure including at least one nanowhisker on a substrate, the method comprising:

providing at least one mass of a catalytic material on a surface of a substrate that is of a predetermined material at a predetermined position on the surface,

20 annealing the substrate to remove surface oxide and to form from each said mass a respective catalytic seed particle,

applying heat and introducing at least one material in gaseous form such as to grow epitaxially, from each catalytic seed particle by the VLS process (as defined above), a nanowhisker of a predetermined material,

25 and wherein annealing and nanowhisker growth conditions are regulated, such as to maintain the nanowhisker within a predetermined tolerance of position from said predetermined position.

The annealing step removes surface oxide. This oxide layer gives a different wetting behavior for the mass than a perfect crystalline surface with free atomic bonds. A perfect crystal surface wets the mass much better, so it sticks. If the native
30 oxide is removed inhomogeneously, due to dirt or other variations this may interfere in an unpredictable manner with nanowhisker growth. In accordance with the invention, it has been found that the annealing step plays a significant part in accurate positioning of the nanowhisker. It has been found that an obstacle to precise positioning of the nanowhiskers in the array is that the catalytic mass may move from

its predetermined site. An issue in preventing movement is formation of a catalytic seed particle from the catalytic mass. During the annealing step, the catalytic mass melts and forms an interface with the substrate, through which atoms of the substrate material are absorbed, to alloy with the catalytic material, thus forming a catalytic seed particle. The more material is absorbed, and the closer the alloy becomes to a eutectic composition, the faster supersaturation conditions can be achieved for subsequent nanowhisker growth. As the catalytic mass melts, it is important that the interface formed, essentially determined by surface tension "wetting" considerations, provides a surface area that is such as to hold the mass in its initial position and to permit adequate diffusion of atoms across the interface. If the wetting is insufficient, the mass may tend to form a ball with only a small interface, with a high risk that the ball may migrate rapidly across the surface. Alternatively if the wetting effect is excessive, the mass may spread out across the surface, with a high risk of fragmentation and growth of a nanowhisker at an unpredictable position.

A number of process parameters play a role in this issue. For example while the temperature should be high enough to remove oxide and provide a clean substrate surface, it should not be so high as to cause the mass to absorb excessive substrate material, and to "eat" into the surface. Particularly in the case of semiconductor III-V or II-VI materials, there may occur evaporation from the substrate of group V or VI element, creating a large number of free atomic bonds that may contribute to migration of the mass. To counteract evaporation, annealing may take place in an atmosphere containing appropriate group V or VI material.

A further important consideration is the initial shape and material constitution of the catalytic mass. The mass may include, in its initial constitution, separate regions of catalytic material, e.g. gold, and a material that will alloy with the catalytic material, e.g. indium, and assist in establishing supersaturation conditions for nanowhisker growth. This reduces the requirement for the mass to alloy with the substrate material in forming a seed particle, and hence increases the stability of the mass and its resistance to migration forces. As preferred, a sandwich of layers of catalytic/alloying/catalytic material is employed.

As regards the shape of the mass, it has been found that an optimal shape is one that upon melting retains approximately the same interface, in position and area, with the substrate. In this way, the mass, as it changes to a catalytic seed particle, tends to "stick" to its original position, and does not spread out, nor reduce its area of

contact that may cause migration across the substrate surface. A preferred shape for a mass of pure catalytic material is a disc with a diameter: height ratio of 3:1; this provides the same interfacial area when it melts into a theoretically perfect semi-sphere. In practice it has been found that a ratio between 10:1 and 2:1 is acceptable.

5 However for a catalytic mass containing a region of alloying material, it has been found that a much higher ratio, e.g. 50:1, is acceptable, since there is a reduced need for the catalytic mass to interact with the substrate surface. In general terms, during the formation of a catalytic seed particle from the catalytic mass, the holding force of the wetted interface with the substrate surface should resist forces causing migration

10 of the mass across the surface.

In a first aspect therefore, the invention provides a method for producing a structure including at least one nanowhisker on a substrate, the method comprising:

providing a substrate of a predetermined material, and providing at least one mass of a catalytic material on a surface of the substrate at a predetermined position

15 on the surface,

applying heat and introducing at least one material in gaseous form such as to create a respective catalytic seed particle from each said mass, and to grow, from the catalytic seed particle, epitaxially, by the VLS process (as defined above), a nanowhisker of a predetermined material,

20 and wherein each said mass is such that during the formation of the catalytic seed particle, forces causing the mass to migrate across said surface are less than a holding force across a wetted interface on the substrate surface.

In a further aspect, the invention provides a nanoengineered structure comprising a substrate of a predetermined material, and at least one mass of a catalytic material formed on the substrate surface in a predetermined position,

25 wherein each said mass is such that, upon heating and melting to form a catalytic seed particle for subsequent nanowhisker growth, a wetted interface with the substrate is formed such that forces causing the mass to migrate across the surface are less than the force provided by the wetted interface holding the mass in its predetermined

30 position.

As regards the initial formation of the masses of catalytic material, this may be carried out by an electron beam lithography lift off process, or, as preferred from cost considerations, a nanoimprint lithography method wherein a stamp is used to define the masses in their predetermined positions.

In accordance with the invention, it has been found that a factor in determining accurate positioning is the time in which nucleation of a nanowhisker takes place. By "nucleation" is meant the initiation of the process for epitaxial growth by the VLS method wherein upon the application of heat, atoms of the nanowhisker material are absorbed in the catalytic material to form an alloy, and when supersaturation conditions are achieved, the nanowhisker begins to form between the catalytic seed particle and the substrate at the growth site. Once this nucleation stage has been achieved, the possibility that the nanowhisker may move from its growth site is greatly reduced. In accordance with the invention, it has been found that this nucleation time should be less than a characteristic time for mobility. As regards the "characteristic time" for mobility of a catalytic mass on the surface, this naturally depends on the material compositions of the mass and the substrate surface. Further it will depend on the temperature, since the higher the temperature, the more active will be the catalytic mass, the substrate surface, and gases and vapours surrounding the growth site: this will increase the tendency for movement. The mobility will also depend on the amounts of material introduced in gaseous form at the growth site, since movement may occur if there is insufficient such material, or if there is an imbalance between two gaseous material (e.g., group III-containing material and group V-containing material). Further the mobility will depend on the state of the substrate surface, and the amount of substrate material that can easily take part in the growth process. The "characteristic time" may be expressed as the time for the catalytic mass to move a certain distance. For example this distance may be the maximum desired tolerance for movement from the predetermined growth site. This may be in terms of the mass dimensions, for example the time taken for the mass to move by a distance equal to its own diameter. Alternatively the distance may be a fraction of the distance between nearest neighbours growth sites, say 10%, representing the desired accuracy of positioning.

The invention further provides a method for producing a structure including at least one nanowhisker on a substrate, the method comprising:

- providing a substrate of a predetermined material,
- providing at least one mass of a catalytic material on a surface of the substrate at a predetermined position on the surface,

applying heat and introducing at least one material in gaseous form such as to grow epitaxially, from each catalytic mass by the VLS process, a nanowhisker of a predetermined material,

5 and wherein nanowhisker growth conditions are regulated such that the time for growth nucleation of a nanowhisker at a said predetermined position is less than a characteristic time for the mobility of the respective mass on the substrate surface such as to maintain the nanowhisker within a predetermined tolerance of position from said predetermined position.

10 Commonly, the nanowhisker is a III-V compound, grown on a substrate containing a group III metal such as indium, gallium etc. However the invention is not limited to growth of III-V compounds, but includes any compound, such as II-VI (CdSe for example) and group IV semiconductors (Si, Ge).

15 As regards the substrate material, and the material of the nanowhiskers, these are not commonly the same, but nevertheless there may be some relationship between the materials in order to achieve satisfactory growth. Thus for example where the substrate is a group IV material such as silicon or germanium then the nanowhisker may also be a group IV material. Where the nanowhisker is of a III-V material or a II-VI material, the substrate may be of a material which also contains or comprises a group III or a group II metal. Thus for example where the nanowhiskers are of
20 indium phosphide, the substrate may be of a material that includes indium or gallium.

Further it has been found desirable to regulate activity of one or more elements of nanowhisker material in gaseous form around each site, so as to regulate growth of the nanowhisker. Where for example a III V semiconductor compound is being grown, it is preferred to regulate the activity of the group V element such as
25 phosphorous, arsenic etc. If this further element is present in gaseous form around the nanowhisker site and has excess activity, then in order to provide more group III material to balance the reaction, this may force the catalytic mass to "search" for group III material by migration on the substrate surface. Likewise, if the activity of the group V material is too weak, then proper nanowhisker growth may not occur.
30 For an MOVPE process, where cracking of the organometallic molecules takes place in the vicinity of the growth sites, this implies close control over reaction temperature, and gas volumes. For CBE however, the cracking of the group V

molecules takes place in cracking cells, remote from the growth site, and there is more freedom in selecting a growth temperature and gaseous flow rates.

In accordance with the invention, a structure, produced by the aforesaid process, consists of an array of a large number of nanowhiskers in a predetermined spatial configuration, the nanowhiskers being disposed within the configuration at 5 predetermined sites to within a predetermined dimensional tolerance. It has been found that a very high accuracy can be achieved, as illustrated particularly in Example 7 below. Typically, the accuracy is such that the deviation of an actual position of a nanowhisker from a target site in an array of nanowhiskers positioned on 10 a substrate is not greater than about 3.6% of the distance between adjacent target sites of nanowhiskers in the array. Preferably such deviation in actual position is not greater than about 1% of the distance between adjacent target sites of nanowhiskers in the array.

From another point of view, the positional deviation of an individual 15 nanowhisker from its target position can, in accordance with the invention, be no more than a diameter of the whisker, preferably less than half the diameter, more preferably less than 20% of the diameter, still more preferably less than 1% of the diameter, and still even more preferably no more than 0.5% of the diameter.

It has been found that arrays of nanowhiskers in accordance with the 20 invention are produced in extremely accurate geometric structures, wherein each nanowhisker is sited extremely closely to its target or allotted position. This permits use of the array in structures where a large number of nanowhiskers have to be employed and positioned very accurately. Such structures may include, for example, 25 a complex electrical circuit, a display system, or a photonic bandgap array. Examples of these structures are disclosed in our co-pending US Patent Application No. 10/613,071 filed 7 July 2003, the contents of which are incorporated herein by reference.

For the specific application of photonic bandgap (PBG) arrays, what is 30 required is a regular geometric structure of nanowhiskers at predefined locations, i.e., a lattice of points having a defined periodicity. The periodicity depends on the wavelength of radiation to be received by the PBG, but typically the nanowhiskers may be arranged with their axes ideally located on the lattice points with a nearest neighbour distance of about 1 micrometer. The diameter of the nanowhiskers in such

a photonic bandgap array should generally be in the range of about 10%-20% of the period of the PBG lattice. Accordingly, the diameter of the nanowhiskers in such an array should generally be of the order of 100 nanometers, e.g., in a range of about 100-200 nanometers. The tolerance or tolerable deviation of the position of an individual nanowhisker in the array from its lattice point should be on the scale of about 5% of the period of the PBG lattice, i.e., about 50 nanometers for a 1 micrometer lattice.

The invention is applicable to any method of epitaxial growth of nanowhiskers by the VLS process. One particularly preferred epitaxial growth process is MOVPE (MOCVD). Another preferred epitaxial growth technique is Chemical Beam Epitaxy (CBE), where organometallic molecules are introduced into a reaction chamber that is at such a low pressure, that the molecules form beams that are directed towards the growth substrate. Such a technique is described in detail in our co-pending US Patent Application No. 10/613,071, filed July 7, 2003, the contents of which are incorporated herein by reference. With CBE, the difficulties in achieving appropriate growth conditions for accurately positioned nanowhiskers are increased.

It is preferred, as a measure for controlling migration of catalytic masses over the substrate surface during growth, to provide a mask of suitable inert material. The mask may be applied as a layer completely covering the substrate and catalytic masses; when heat is applied the catalytic mass permeates the mask material, to permit growth of nanowhiskers. Alternatively the mask may be apertured, each aperture containing a catalytic mass. This can be performed by a lithographic technique for example.

In a further aspect, the invention provides a method for producing a structure comprising at least one nanowhisker on a substrate, the method comprising:

- providing a substrate,
- providing at least one mass of catalytic material on a surface of the substrate, each mass being located at a respective predetermined position on the surface,
- providing a mask on the substrate surface,
- applying heat and introducing at least one material in vapour form such as to grow by Chemical Beam Epitaxy and the VLS process (as defined above), a nanowhisker by way of each catalytic mass, of controlled height, diameter and

position, and wherein said mask inhibits both growth on the substrate surface and lateral movement of the catalytic masses.

In the case where an apertured mask is employed, it is desirable that the apertures be defined with sufficiently small dimensions that the catalytic mass formed within the aperture is constrained from migration or movement from its predefined position. Commonly, during production of the mask, an apertured mask is formed and then the catalytic material is deposited within the apertures. It is desirable that the mass be of sufficient thickness (usually a height: diameter ratio of 1:3 is desirable), that in an initial process step wherein the catalytic masses are heated to produce seed particles, that the seed particle that is normally in molten form is within a distance less than its own diameter from the edge of the mask. The edge of the mask forms a mechanical barrier to the seed particle, and since the catalytic material does not "wet" the mask, on account of the surface tension properties, this effectively constrains the catalytic mass to its predetermined position. With this constraint, clearly the mobility of the catalytic mass on the substrate surface is decreased significantly as compared to the situation without a mask.

In a further aspect, the present invention provides a nanoengineered structure including at least one nanowhisker on a substrate, a substrate of a predetermined material, a mask of a further material on the substrate surface and being apertured with at least one aperture in a predetermined site and of predetermined diameter, and a nanowhisker projecting from the or each aperture, the base of each nanowhisker at the substrate surface being of a distance from the edge of the mask defining the respective aperture by an amount which is less than about the diameter of the nanowhisker.

As regards photonic band gap arrays, or photonic crystals produced in accordance with the invention, in a further embodiment, where the CBE process is employed, as described in detail in our co-pending US Patent Application No. 10/613,071, filed July 7, 2003, 3-dimensional photonic band gap array structures are provided wherein each nanowhisker of the array is formed as a series of alternating segments of two materials with different refractive indices, as described below.

In a further embodiment, each nanowhisker of the photonic crystal is formed with segments of different materials, with sharp heterojunctions therebetween, to provide a quantum dot within the nanowhisker operable as an LED. At least one of the LED structures is activated by connection to suitable contacts, to provide a light

source for transmission of light through the remainder of the photonic crystal structure.

Brief Description of the Drawings

5 Preferred embodiments of the invention will now be described with reference to the accompanying drawings wherein:

Figure 1 (a) is an SEM micrograph of a first example of the invention, of a single hexagonal cell prior to growth for formation of a photonic bandgap array. Gold dots of approximately 125 nm diameter and 45 nm thickness can be seen on the substrate surface. (b) The same structure as in (a) but after growth. The wires have a top diameter of 140 nm and base diameter of 200 nm. The length is approximately 10 1 μm (45° viewing angle);

Figure 2 is a tilted view SEM micrograph of an NIL stamp used in a second example of the invention. The stamp was fabricated from a one-inch Si wafer using Cr as mask for dry etching in SF_6/O_2 . Each column has a height 300 nm and a top diameter of approximately 200 nm. The columns are arranged in a hexagonal pattern with a nearest neighbor distance of 1 μm ;

Figure 3 is an SEM image of a high-density array of thin wires in accordance with a first embodiment of the invention, produced by the first example of the invention. The wires have a length of 3 μm and a top diameter of 50 nm while the base is thicker. The images are taken at 45° and 20° tilt for the main image and inset, respectively;

Figure 4 comprises top (a) and 45° tilted (b) views of a nanowire honeycomb lattice structure. The possibility of defect engineering has been used to create a wave-guiding-like structure;

Figure 5 shows nanowires grown from gold dots with different thickness-to-height ratios, where the thickness was fixed at 17 nm. Starting from the left the diameters of the original dots were 50, 100, 200, 400 and 800 nm;

Figures 6a and 6b are schematic diagrams of a mass of catalytic material before and after melting to form a catalytic seed particle, in accordance with the invention;

Figures 7a-e illustrate the steps in the formation of catalytic particles on a substrate within apertures in a mask, and subsequent growth of nanowiskers by a CBE process, in accordance with a second embodiment of the invention;

Figure 7f is a schematic illustration of a CBE chamber;

Figure 8 is an SEM of a third example of the invention, taken from above and tilted to one side, showing use of a mask for locating the catalytic seed particles;

Figure 9 shows SEMs of a fourth example of the invention: Figure 9a: GaAs (111)B with 45 nm Au coated with a 7 nm layer of SiO_x. Heated at 450° for 15 min.
5 Figure 9b: GaAs(111)B with 45 nm Au. Heated at 450° for 15 min;

Figure 10 shows SEMs of a fifth example of the invention. Figure 10a: InAs (80) with a 45 nm Au-In-Au sandwich. Heated to 450° for 20 min. Original metal disk size was 540 nm. Figure 10b: Same as the left sample but with pure gold;

10 **Figure 11** shows SEMs of a sixth example of the invention. . Figure 11a: GaAs (91)B with a 45 nm Au-In-larger Au sandwich. Heated to 450° for 15 min. Figure 11b: Close-up of one of the larger features. Original disk diameter 2 μm, meaning a shape of $d=48t$;

Figure 12 shows a third embodiment of the invention for providing a three-
15 dimensional photonic bandgap structure;

Figure 13 shows a fourth embodiment of the invention for providing LED sources of light in a photonic band gap structure;

Figure 14 shows a sixth embodiment of the invention for use as an NIL stamp; and

20 **Figure 15** shows a plan view of an array of nanowhiskers prepared according to the invention illustrating the precise positioning of nanowhiskers to form a large array thereof.

Figure 16 shows an enlarged plan view of the array of Figure 15 with the actual locations of the nanowhiskers indicated as well as the locations of the lattice
25 points.

Figure 17 is a histogram of the deviations of the actual locations of the nanowhiskers from the lattice points for the view of Figure 16.

Description of the Preferred Embodiments

As indicated above, the invention provides a method for producing a structure
30 including at least one nanowhisiker on a substrate, wherein a nanowhisiker is grown by the VLS method. In order to achieve the requisite precision in positioning the nanowhiskers, the catalytic seed particles must be precisely located on the substrate and must not move any significant distance before the nanowhisiker begins to grow at the position on the substrate occupied by the catalytic particle. In certain

embodiments of the invention, the catalytic seed particles are formed in openings on a mask formed on the surface of the substrate and confined within the mask openings as whisker growth begins. In other embodiments, the catalytic seed particles are arranged in predetermined positions on the surface of the substrate, and the particles
5 are melted under conditions such that precursor materials for forming the nanowhiskers, supplied as gases, will form a molten alloy with the catalytic particle and crystallize at the substrate surface to provide a nucleus for growth of the nanowhisker. The conditions of nucleation and growth, including temperature, composition of the catalytic particle, surface coverage with oxide, and the like are
10 adjusted such that during the formation of the catalytic seed particle, forces causing the molten particle mass to migrate across the substrate surface are smaller than a holding force provided by a wetted interface between the catalytic particle and the substrate surface.

Accordingly, as indicated above, in one embodiment of the process of the
15 invention an annealing step is conducted that removes surface oxide. The surface oxide layer has different surface properties as to wettability by the molten catalytic metal mass than a perfect crystalline surface with free atomic bonds. A perfect crystal surface wets the catalytic mass much better, providing a surface force that tends to hold the catalytic particle at a fixed position on the substrate surface. If the
20 native oxide is removed inhomogeneously, due to dirt or other variations, this may interfere in an unpredictable manner with nanowhisker position and growth. In accordance with at least one embodiment of the invention, it has been found that the annealing step plays a significant part in accurate positioning of the nanowhisker. It has been found that an obstacle to precise positioning of the nanowhiskers in the
25 array is that the catalytic mass may move from its predetermined site. An issue in preventing movement is formation of a catalytic seed particle from the catalytic mass. During the annealing step, the catalytic mass melts and forms an interface with the substrate, through which atoms of the substrate material are absorbed, to alloy with the catalytic material, thus forming a catalytic seed particle. The more material is
30 absorbed, and the closer the composition of the alloy becomes to a eutectic composition, the faster supersaturation conditions can be achieved for subsequent nanowhisker growth. As the catalytic mass melts, it is preferable that the interface formed, essentially determined by surface tension "wetting" considerations, provides a surface area that is such as to hold the mass in its initial position and to permit

adequate diffusion of atoms across the substrate-catalytic particle interface. If the wetting is insufficient, the mass may tend to form a ball with only a small interface, with a high risk that the ball may migrate rapidly across the surface. Alternatively, if the wetting effect is excessive, the mass may spread out across the surface, with a high risk of fragmentation and growth of a nanowhisker at an unpredictable position.

A number of process parameters play a role in this issue. For example while the temperature should be high enough to remove oxide and provide a clean substrate surface, it should not be so high as to cause the mass to absorb excessive substrate material, and to “eat” into the surface. Particularly in the case of semiconductor III-V or II-VI materials, there may occur evaporation from the substrate of group V or VI element, creating a large number of free atomic bonds that may contribute to migration of the mass. To counteract evaporation, annealing may take place in an atmosphere containing appropriate group V or VI material.

A further important consideration is the initial shape and material constitution of the catalytic mass. The mass may include, in its initial constitution, separate regions of catalytic material, e.g. gold, and a material that will alloy with the catalytic material, e.g. indium, and assist in establishing supersaturation conditions for nanowhisker growth. This reduces the requirement for the mass to alloy with the substrate material in forming a seed particle, and hence increases the stability of the mass and its resistance to migration forces. As preferred a sandwich of layers of catalytic/alloying/catalytic material is employed.

As regards the shape of the mass, it has been found that an optimal shape is one that upon melting retains approximately the same interface, in position and area, with the substrate. In this way, the mass, as it changes to a catalytic seed particle, tends to “stick” to its original position, and does not spread out, nor reduce its area of contact that may cause migration across the substrate surface. A preferred shape for a mass of pure catalytic material is a disc with a diameter: height ratio of 3:1; this provides the same interfacial area when it melts into a theoretically perfect semi-sphere. In practice it has been found that a ratio between 10:1 and 2:1 is acceptable. However for a catalytic mass containing a region of alloying material, it has been found that a much higher ratio, e.g. 50:1, is acceptable, since there is a reduced need for the catalytic mass to interact with the substrate surface. In general terms, during the formation of a catalytic seed particle from the catalytic mass, the holding force of

the wetted interface with the substrate surface should resist forces causing migration of the mass across the surface.

In particular, in view of the various effects of the growth conditions on the possibility of migration of the catalytic particles, the nanowhisker growth conditions are preferably regulated such that the time for growth nucleation of a nanowhisker at a predetermined position is less than a characteristic time for the mobility of the respective mass on the substrate surface such as to maintain the nanowhisker within a predetermined tolerance of position from said predetermined position.

In view of the above discussion, the skilled practitioner will recognize that a number of experimental parameters or factors are involved in selecting conditions that minimize the tendency of the catalytic particles to migrate across the substrate surface. However, taught by the above disclosure, the practitioner will be able to select the conditions appropriate for achieving the desired stability of position of the catalytic particles on the substrate surface. Such conditions will include the conditions assuring that forces causing the catalytic particle or mass to migrate across the surface are less than a holding force across a wetted interface on the substrate surface, and that the time required for growth nucleation is less than a characteristic time for the mobility of a catalytic particle or mass on the surface of the substrate.

As mentioned summarily above, the method of the invention is capable of providing one or more nanowhiskers precisely positioned at predetermined points on a substrate surface. Such precision may be extended to the formation of arrays ("nanonengineered structures") comprising very many nanowhiskers, even up to an array of 10^6 or more nanowhiskers, precisely positioned in relation to one another and/or a predetermined reference point on the surface.

The precision required in a given practical embodiment will vary depending on the particular requirements of the application and on the size of the nanowhiskers or array of nanowhiskers that is used. Those skilled in the art will also recognize that initial positioning of nanomasses of material that become the catalytic particles is subject to limitations arising from difficulties in forming and manipulating such small objects. Thus, the precision attainable by lithographic techniques such as are conventional in the art, and used in the examples described herein, is subject to well-known limitations imposed by the physics and chemistry of the resist layers, the resolution of a particular pattern exposure apparatus, and the like. For example, patterns having features with dimensions of the order of 500 nm can be produced

relatively easily; but features with dimensions of the order of 20 nm are very difficult to produce and position precisely on a surface.

Analysis of a particular structure produced at a nanoscale may also be difficult and can be limited by the resolution of available observation equipment, e.g., scanning electron microscopes (SEMs).
5

However, according to the invention, the position on the surface of a substrate of a nanowhisker formed by the process of the invention may be precisely controlled to achieve the precision required in a given application. For example, if nanowhiskers of relatively large diameter, e.g., 200 nm – 500 nm (or more) are prepared, variations in the size of the nanowhiskers themselves may be greater than
10 the precision with which they are positioned on the surface. However, for small nanowhiskers, e.g., 20 nm or the like, the positional accuracy may be limited by the accuracy with which the catalytic particles can be positioned (e.g., by lithographic techniques) on the substrate surface.

In any case, according to the method of the invention, the precision with
15 which the nanowhiskers are positioned on the substrate surface can be achieved by precise positioning of the catalytic masses and will not be significantly degraded by the growth process.

The precision with which a nanowhisker is positioned on a substrate surface
20 may also be defined in terms of the diameter of the nanowhisker itself. Such a definition may be more useful where, among a plurality of nanowhiskers, the spacing is relatively close, i.e., the spacing between adjacent nanowhiskers is a few diameters thereof. Under such a criterion, it is according to the invention to position nanowhiskers such that the distance between neighboring nanowhiskers does not
25 deviate from the predetermined distance by more than about 20% of the diameter of the nanowhisker. Preferably such deviation will be less than about 10% of the diameter of the nanowhisker and more preferably not more than about 5% of the diameter of the nanowhisker.

The precision with which the nanowhiskers and arrays thereof are defined is
30 discussed above in terms of percentage deviation from a predetermined dimension because such a definition is generally useful in a particular practical application. Furthermore, such a definition in terms of percentage deviation from a predetermined dimension may take account of a lack of precision in positioning the catalytic particles, e.g., by lithography, or in the techniques used to measure the positions of

the particles and analyze the deviations of those positions from a predetermined reference point. Consequently, in a particular embodiment the precision defined in linear dimensions might vary from that defined in another embodiment. In any case, deviations in the position of a nanowhisker from a predetermined reference point can
5 be less than several nanometers, e.g., less than about 20 nm, preferably less than about 10 nm and most preferably about 5 nm or less.

As mentioned above, the catalytic seed particle may incorporate the elements of to be supplied to the growing nanowhisker, thus to form an alloy with the catalytic metal. For example the catalytic particle may be an alloy incorporating a proportion
10 of a Group III element and a Group V element in a gold catalytic particle. If the catalytic mass deposited on the surface of the substrate is a pure material, e.g., pure gold, or is an incompletely saturated alloy of the catalytic metal and the growth materials, the catalytic particle may initially attack the substrate and dissolve some of the growth materials therefrom to form a fully saturated alloy. Inasmuch as such
15 dissolution of material from the substrate may not proceed isotropically, it is possible that the catalytic particle may shift somewhat from its initial position before catalytic growth of the nanowhisker commences. Such a shift evidently would degrade the precision with which the nanowhisker is positioned on the substrate. Accordingly, it is preferred to incorporate at least some of the growth materials into the catalytic
20 mass that is deposited on the surface of the substrate before the heated growth phase of the process is initiated. This can be accomplished, for example, by depositing a layered catalytic mass incorporating at least one layer of the catalytic metal, e.g., gold, and a layer of the growth material that is to form the nanowhisker, e.g., a III-V compound. When the growth step of the process is initiated, the catalytic metal and
25 the growth material will form an alloy immediately, thus minimizing the tendency of the catalytic particle to attack the substrate. Evidently, incorporation of any amount of the growth material will tend to reduce the tendency of the catalytic particle to attack the substrate. However, although it is not excluded that some local dissolution of the substrate might be desired, e.g., to provide a more perfect interface for the base
30 of the nanowhisker, it is generally preferred to incorporate a sufficient amount of the growth material into the catalytic mass as deposited to at least form a fully saturated alloy.

A preferred embodiment of the invention will be described of a lithographic fabrication method for synthesizing arrays of vertical nanowires with single-wire control. Electron beam lithography (EBL) and metal lift-off were used to define a pattern of gold discs, transformed by annealing into growth catalysing nanoparticles.

5 Nanowires were then grown using metal-organic vapour phase epitaxy (MOVPE)

Example 1

Samples were prepared from an n-type InP (111)B wafer. The (111)B substrate orientation was chosen since it is well known that the preferred wire growth direction is (111) B. The samples were cleaned on a spinner with acetone and isopropanol (IPA). They were then coated with poly(methylmethacrylate) (PMMA)
10 photoresist and the disc pattern was transferred to the resist layer using a standard EBL technique. After development in methyl isobutyl ketone (MIBK) and rinsing in IPA, the samples were treated briefly with oxygen plasma to remove any resist residues from the exposed areas. After plasma treatment they were etched for 20 s in
15 4% hydrofluoric acid to remove surface oxide. The samples were then immediately transferred to a vacuum chamber where a gold film was deposited (thickness ranging from 17 to 45 nm and diameters of 125 nm) via thermal evaporation. The thickness was measured using a quartz crystal monitor. After metal lift-off by dissolution of the photoresist layer in hot acetone for 10 min, followed by 5 min in hot IPA, structures
20 such as those shown in Figure 1(a) were obtained. The samples were then transferred to a laminar flow MOVPE reactor cell and placed on a graphite susceptor. A hydrogen carrier gas flow of 6 l min^{-1} at a pressure of 100 mbar (10 kPa) was used. A constant phosphine flow at a molar fraction of 1.5×10^{-2} was supplied to the reactor cell and the samples were annealed at 580°C for 10 min before growth. During this
25 step the surface oxide is desorbed and the gold discs on the substrate surface alloy with the InP substrate. The temperature was then ramped down to 400°C and growth of nanowires started when trimethylindium (TMI) was introduced into the reactor cell. TMI molar fractions between 3 and 6×10^{-6} were used, giving V/III (PH₃/TMI) ratios between 2500 and 5000. The growth time determines the wire length and a
30 typical choice was 8 min. Figure 1(b) shows structure (a) after growth. The wires have a top diameter of 140 nm and base diameter of 200 nm. Sample characterization was then carried out using a JSM 6400 F field emission scanning electron microscope, operated at 15 kV. It can be seen by comparison of the scanning electron

micrographs (SEMs) before and after growth that the nanowiskers have been grown essentially at the locations of the catalytic particles.

Example 2

This example is based on nano-imprint lithography (NIL). NIL is in many respects
5 capable of producing results comparable to those of electron beam lithography (EBL), but at a considerably lower cost and with a much higher throughput. NIL was used to pattern InP substrates with growth-catalyzing gold particles. Growth of vertically aligned InP nanowires then took place in a metal-organic vapor phase epitaxy (MOVPE) system via the vapor-liquid-solid (VLS) growth. The material of
10 choice was InP, but the method is effective equally well with other III-V materials. The (111)B substrate orientation was used since the preferred growth direction of nanowires is $\langle 111 \rangle_B$, and vertically aligned arrays were desired.

The stamp for the nano-imprint process was made on a one-inch Si wafer using EBL and dry etching. A bi-layer of resist was used comprising
15 ZEP520A7/PMMA950k that was exposed at 35 kV with a probe current of 20 pA. After resist development, 30 nm of Chromium was thermally evaporated and lifted-off in hot Microposit Remover S-1165 (Shipley). The metal layer was then used as etch mask to create the morphological structure of the stamp. Reactive ion etching in SF_6/O_2 chemistry was used yielding a structure height of 300 nm, as measured by
20 atomic force microscope (AFM). The columns are arranged in a hexagonal pattern with a nearest neighbor distance of 1 micrometer. The remaining Cr was removed by wet etching. The stamp was then treated for anti-sticking, by monolayer deposition of tridecafluoro-(1,1,2,2)-tetrahydrooctyltrichlorosilane (F13-TCS) in a nitrogen atmosphere. A scanning electron microscopy (SEM) image of the stamp after use is
25 shown in Figure 2.

To pattern the substrates with catalyzing gold dots, imprint was used followed by metal evaporation and lift-off. A bi-layer resist scheme of a lift-off layer (LOL) and PMMA was used. First a 200 nm LOL film was spin-coated and soft-baked at 180 °C. On top 100 nm of PMMA 50k was deposited and baked. Imprinting was done
30 at 220 °C, 50 bar and 3 minutes hold time. The samples were then ashed in oxygen plasma for 12 s and 5 mBar before development in MF319. The developer dissolves the LOL layer isotropically and thus creates the undercut profile necessary for good metal liftoff. The samples were then treated briefly with oxygen plasma, 12 s and 5 mbar, to remove any resist residues from the imprinted areas. After plasma treatment

the samples were etched for 20 s in 4% hydrofluoric acid to remove surface oxide. The samples were then immediately transferred to a vacuum chamber where a 40 nm thick gold film was deposited via thermal evaporation. Metal liftoff was then performed in Remover S-1165 on a hotplate.

5 Nanowhiskers were then grown on the NIL defined sample using a laminar flow MOVPE system where the samples are placed on a RF-heated graphite susceptor. A hydrogen carrier gas flow of 6 l/min at a pressure of 100 mBar (10 kPa) was used. A constant phosphine flow at a molar fraction of 1.5×10^{-2} was supplied to the reactor cell and the samples were annealed at 580 °C for ten minutes before
10 growth. During this step the surface oxide is desorbed and the gold disks on the substrate surface alloy with the InP substrate. The temperature was then ramped down to 400 °C, and growth of nanowires started when trimethylindium (TMI) was introduced into the reactor cell. A TMI molar fraction of 3×10^{-6} was used and the growth time was 16 minutes. Sample characterization was then carried out using a
15 JSM 6400 F field emission scanning electron microscope, operated at 15 kV.

The lithographic method provides considerable freedom in design and a number of different patterns for various applications can be envisioned. Two structures with different wire densities and different wire diameters are shown in Figures 3 and 4 forming a first embodiment of the invention. In Figure 3, a scanning
20 electron microscope (SEM) image of a high-density array is presented. This $8 \times 8 \mu\text{m}^2$ array consists of hexagonal unit cells with a nearest neighbour distance of 250 nm. The catalysing particles consisted of gold discs with a diameter of 45 nm and a thickness of 17 nm. The importance of the thickness-to-diameter ratio will be discussed below. After growth, the resulting wires had a length of approximately 3
25 μm and a top diameter of 50 nm, while the base diameter (measured where the actual wire starts, just above the heavy 'foot') was larger, about 110 nm. The inset shows the shape of individual wires.

The structure in Figure 4 is a pattern from the field of photonic crystals. In a photonic crystal the electromagnetic waves experience periodic modulation of the dielectric constant resulting in a photonic band gap, analogous to an electronic band
30 gap in a semiconductor. For a two-dimensional photonic crystal this means that electromagnetic waves of a certain wavelength cannot propagate in the plane. However, defects in the photonic crystal will allow electromagnetic modes within the band gap and by engineering these defects the flow of light can be controlled and

devices such as laser cavities and waveguides can be achieved. Figure 4 is an example of a nanowire-based photonic crystal structure. This pattern consists of high-refractive-index pillars in air, forming a honeycomb lattice with an exceptionally large photonic band gap. A wire distance of 500 nm and a wire diameter of 140 nm were chosen which, for a dielectric constant of 11.4, are calculated to give a photonic band gap in the wavelength region around 500 nm. The lithographic nature of the method readily allows introduction of defects into the photonic lattice by changing the diameter of some wires, or by exclusion of certain wires altogether, as demonstrated in Figure 3. Choosing the gold disc diameter prior to growth to be 125 nm with a thickness of 47 nm, the top wire diameter after growth was close to 140 nm, which was the desired value. The wire length was approximately 1 μ m.

For ideal nanowire array growth, parameters such as the shape of the seed particles, the gas flows and temperature during growth must be optimized. The ability to produce a single vertical nanowire from each gold dot was found to be strongly dependent on the shape of the seeding particle. Figure 5 shows the results obtained from discs with a thickness of 17 nm and with different diameters. Starting from the left the disc diameters prior to growth were approximately 50, 100, 200, 400 and 800 nm. The general trend is clear: a thin disc tends to break up and form many small catalysing particles, whereas a disc with a greater thickness-to-diameter ratio is more stable. An empirical thickness-to-diameter ratio of around 1/3 gives good results (in agreement with the very simple model of a disc transforming into a molten hemisphere during annealing without changing its diameter). In Figure 5 the aspect ratio is optimized for the leftmost structure; however, the second structure from the left, with a ratio of 1/6, also shows good results, indicating a certain tolerance. The other extreme, with a very high thickness-to-diameter ratio, may be expected to cause problems with site control when the more pillar-like structure is to transform into a hemisphere during annealing. If wires with very different diameters are desired in the same structure, e.g. for photonic crystal applications, multiple EBL patterning and metal evaporation might be necessary to obtain the optimal aspect ratio for each wire diameter. The catalysing particle consists of gold plus a certain amount of indium incorporated from the substrate during alloying. To a first approximation the wire diameter is then defined by the diameter of this catalysing particle. However, competing growth mechanisms on the {110} side facets make this true only for the top diameter. The base is often larger and tapering of the wires can be observed, as

also reported in prior investigations. The tapering becomes stronger at higher temperatures and thus, for rod-like wires, low growth temperatures are preferable. The structures presented in Figures 3 and 4 contain a low density of unwanted defects. Such defects are caused by nanowiskers or wires nucleating and growing at
5 undesired positions, as well as wires that change growth direction during growth (kinking). Temperature and V/III ratio were observed to affect the tendency of the wires to kink. For the V/III ratios two extremes could be observed: a low V/III ratio caused frequent wire kinking, whereas a high V/III ratio caused problems associated with wire nucleation and low wire growth rates. When the V/III ratio is kept constant,
10 the problem of wire kinking also becomes more severe for low temperatures, in agreement with previously reported results. Thus, if high-aspect-ratio, rod-like wires or nanowiskers are desired one must find a compromise between low growth temperature, to minimize the tapering effect, and a higher temperature, to avoid kinking. A temperature of 400°C was found to be suitable for these structures based
15 on InP wires. Further optimization of fabrication parameters should minimize the presence of such defects, or eliminate them altogether

This example demonstrates the synthesis of highly uniform arrays of vertical InP nanowires, as shown in Figures 3 and 4. The wires are individually seeded from catalytic gold particles and the method provides control over the location, diameter
20 and length of the wires. Such a fabrication technique is important for nanowires as building blocks for specific applications. Applications based on arrays of nanowire devices may include producing two-dimensional photonic crystals and FEDs (Field Emission Displays) with nanowire cathodes. In combination with a technique for contacting vertically standing wires, single nanowire components (such as SETs and
25 RTDs) could be combined to form more complex devices.

This example illustrates the use of MOVPE (MOCVD) process for achieving high positional accuracy of nanowiskers within an array. With the MOVPE process, a relatively large amount of indium, present as TMI vapour molecules, is present at the nanowisker growth sites, by reason of the relatively high pressure (10 millibars)
30 within the reaction chamber. An additional factor is the working temperature. The working temperature is chosen for MOVPE at a relatively low value of about 400°C so that there is little bulk growth on the substrate surface. However, the indium ions, when released after cracking of the TMI, may move a long distance to a growth site.

An additional factor is the activity of the phosphorous ions present when the phosphine gas is cracked at the growth site. The working temperature is chosen so that the activity matches the amount of indium present at the growth site so as to sustain growth without forcing the catalytic particle to gather more indium by moving
5 from its predetermined site.

A further process for growth of nanowhiskers in accordance with the invention is chemical beam epitaxy (CBE) this is described in our co-pending US Patent Application No. 10/613,071 filed July 7, 2003. In CBE, the pressure within the reaction chamber is considerably lower by several orders of magnitude than that
10 of MOVPE, and essentially one beam of material, TMI, and phosphorus in gaseous form, is used for formation of indium phosphide. The phosphorus containing molecules are cracked remote from the growth site. This implies that it is easier to control the process, since working temperature and phosphorus activity can be separated, and to maintain positional accuracy of the catalytic particles.

It has been found that the initial shape of the mass deposited on the substrate is important for accurate positioning of the catalytic particle formed from the mass, whether or not a mask is used. Figure 6 illustrates an ideal situation, where the melted mass occupies exactly the same surface area as the initial mass. Figure 6a shows a gold catalytic mass formed as a disc, and Figure 6b illustrates that melting of
20 the disk has created a perfect hemisphere. A calculation, neglecting the fact that the gold droplet absorbs material from the substrate, shows that to keep the same diameter at the interface with the substrate, in the molten droplet as in the original disk, the diameter should be three times the gold thickness. Let the unprimed quantities be before heating and the primed after heating. Let t be the gold thickness
25 and r the radius. The volumes V and V' are assumed the same

$$\begin{aligned} V &= V' \\ \pi r^2 \times t &= 4\pi r'^3/3 \cdot 2 \\ t &= 2r'/3 \quad \text{or} \quad d = 3t \end{aligned}$$

In practice, it has been found that a $d:t$ ratio between 12:1 and 2:1 can produce
30 acceptable results.

While it is possible by accurate and precise control over the operating parameters within a CBE process, to provide accurately positioned nanowhiskers within a nanowhisker array, an alternative and preferred technique, in accordance with a second embodiment of the invention, is to provide a mask on the substrate

surface which performs two functions, firstly that of preventing bulk growth on the surface, and secondly inhibiting movement of the catalytic particles. A mask in accordance with the invention is termed an epi-mask (epitaxy inhibitor).

Turning to Figure 7a, a substrate 20 of gallium arsenide with a (111) surface has formed thereon an epi-mask 22. This may be an inorganic material such as silicon dioxide, or it may be an organic polymer material of which various types are commercially available.

As shown in Figure 7b a photoresist material 24 is applied to layer 22 and is patterned for example using an electron beam. The photoresist material is then etched to produce a predetermined pattern as shown in Figure 7c wherein apertures are produced in the photoresist material and the underlying epi-mask to define the predetermined sites for nanowhisker growth.

Subsequently, as shown in Figure 7d a layer of gold of predetermined depth is applied as at 30. A subsequent etching process removes the photoresist material layer 24 and the gold therein 30 so as to leave the epi-mask 22 with the gold present to a predetermined depth (one third of the width of the aperture) within each site aperture 30 (Figure 7e).

The substrate as shown in Figure 7e, after appropriate cleansing operations, is transferred to a CBE reaction chamber 34 as shown in Figure 7f. The substrate 20 is mounted on a metal sample holder 36 connected to a heater 38. Around the chamber a ring 40 is filled with liquid nitrogen to provide a cryoshroud. Vacuum pumps 42 are provided.

Sources 44, 46 of TMI_n, TBP in liquid phase are stored in constant temperature baths and by controlling the temperature for liquid source the partial pressure of the vapour above the liquid is regulated. The vapour is fed into the chamber through a pipe complex 48 to a source injector 50. Source injector 50 injects a molecular beam into the chamber with stable and uniform intensity. The group III material decomposes at the substrate surface i.e. gallium. As opposed to this the group V phosphorous material will be decomposed before injection into the growth chamber at high temperatures in the injectors. These injectors are called cracking cells and their temperature is kept around 900°C. The source beam impinges directly on the heated substrate surface. Either the molecule gets enough thermal energy from the surface substrate to dissociate all of its three alkyl radicals, leaving the elemental atom on the surface, or the molecule gets dispelled in an undissociated

or partially dissociated shape. Which of these processes dominates depends on the temperature of the substrate and the arrival rate of the molecules. At higher temperatures this growth rate will desorption that will block sites.

5 By providing the mask 22, imbalances in the annealing step and nanowhisker growth step are prevented from causing movement of the gold catalytic seed particles on the substrate surface. When the seed particle is formed, its distance from the edge of the mask aperture is less than the diameter of the nanowhisker. This applies equally to the resultant nanowhisker.

Example 3

10 As shown in Figure 8, a mask of silicon nitride, 27nm thick, was formed on an InP substrate. Circular apertures were formed in the mask by a lithographic process. Gold catalytic particles were formed in the circular apertures within the mask. Nanowhiskers were grown from the gold catalytic particles. The nanowhiskers substantially filled the mask apertures, with a narrow gap between the nanowhisker and the edge of the mask aperture.

Example 4

Gold catalytic particles were formed on a GaAs substrate. By depositing a thin oxide of SiO_x over the entire structure just before the particles were formed, movement of the gold particle over the substrate was restricted. The result is shown in
20 Figures 9a and 9b, where two samples are shown. They are identical with respect to manufacturing and heat treatment. The only difference is that Figure 9a has a thin (7 nm) layer of SiO_x oxide. This oxide is thermally evaporated from a source of SiO. Whether the oxide on the sample is SiO or SiO₂ depends on the vacuum conditions in the evaporation chamber. As seen the thin oxide drastically changes the behaviour of
25 the sample when heated. The migration is much less although a triangular formation can be seen. The melt migrates along the surface under the oxide. The original disk can be seen, indicating that the oxide forms a shell over the gold disk. Successful whisker growth was performed with a covering oxide. This means that the oxide is removed at growth temperature that is typically about 550°.

Example 5 - InAs (100) substrate

30 At 451°C with 38.4% In, for an Au-In mixture, there is a eutectic point. This composition was evaporated onto a sample in a 45 nm thick film. Au and In cannot be evaporated together at the same time, so a Au-In-Au sandwich was used with a thickness of ~ 14:17:14 nm respectively. A sample with pure gold was also fabricated

for comparison. The samples were then heated at 455° for 20 minutes and the result can be seen in Figures 10a and 10b. Figure 10a shows the sample with the Au-In-Au sandwich whereas Figure 10b shows the sample with pure Au. The sample with In forms a droplet on the surface seemingly without having to incorporate a lot of In from the substrate. In the case of pure gold a lot of In has to be incorporated and the droplet digs its way down into the substrate. Thus it does not form a droplet on the surface but the top of the droplet is almost levelled with the surface. The droplets follow the crystal symmetries. The square, and sometimes rectangular, shape can be understood from the rectangular structure of the (100) surface. As a rule of thumb the smaller the feature sizes the more they tend to follow the crystal symmetry. The largest structures remained quite rounded whereas the smallest were almost entirely rectangular. Although the result was better for the sample with the mix of Au and In, the sample with pure Au also shows a very good result considering positioning. This means that either InAs is a better-suited material than GaAs or that the (100) surface is more suitable than the (111) surface considering positioning.

Example 6 Au-In-Au sandwich on GaAs (111)B

A sandwich of Au-In-Au on a GaAs substrate was employed. A GaAs (111) substrate is used since preferential growth direction for the whiskers in this system is (111). The sample above was evaporated with a 45 nm thick metal film comprising 14 nm Au : 17 nm In : 14 nm Au. The sample was then heated to 450° for 15 minutes. Figures 11a and 11b show satisfactory positioning of the catalytic particles. In this embodiment the In may the droplet, preventing it from absorbing a large amount of Ga from the substrate. The temperature, ~450°, is well within the temperature range suitable for growth of InAs whiskers which are usually grown between 410 and 460° in our system.

Referring to Figure 12, there is shown a third embodiment of the invention for providing a three-dimensional photonic bandgap structure. The process described above with reference to Figure 7 of the second embodiment is employed for providing gold catalytic masses 101 at each nanowhisker growth site. The result is shown in Figure 12a wherein a substrate 100 of silicon has a 111 upper surface. Growth is initiated by means of a CBE process in order to grow segments 102 of silicon nanowhiskers. After a predetermined time, the constituents in the molecular beams injected into the reaction chamber are rapidly switched so as to induce growth of a germanium segment of nanowhisker 104 on top of the silicon segment. The

process for forming abrupt heterojunctions between different materials within a nanowhisker is fully described in our co-pending US Patent Application No. 10/613,071, filed July 7, 2003.

5 The result as shown is a nanowhisker comprising a large numbers of alternating segments of germanium and silicon. As an alternative, aluminium may be used instead of germanium. The nanowhisker is then subjected to heat in an oxidising environment so that the segments of silicon and germanium are transformed to their oxides, silicon dioxide and germanium oxide. Alternatively, if aluminium is used this is transformed to aluminium oxide (sapphire). As shown in Figure 12b, the result is a nanowhisker with regions 106, 108 of different refractive index along its length. The length of the regions 106, 108 may be adjusted, and the result is a three-dimensional photonic bandgap structure where the site positions of the nanowhiskers provides the bandgap properties within two-dimensions, and the variations in refractive index along the length of the nanowhiskers provide the third dimension of the photonic bandgap structure.

15 In a fourth embodiment, as shown in Figures 13a and b, there is shown a nanoengineered structure forming a photonic band gap array, together with integrated light sources for transmitting light through the array. The process described above with reference to Figure 7 of the second embodiment is employed for providing gold catalytic masses at each nanowhisker growth site. The result is shown in Figure 13a wherein a substrate 130 of indium phosphide has gold catalytic particles 132 formed thereon. Growth is initiated by means of a CBE process in order to grow segments 134 of InP nanowhiskers. After a predetermined time, the constituents in the molecular beams injected into the reaction chamber are rapidly switched so as to induce growth of an Indium Arsenide segment of nanowhisker 136 on top of the InP segment. A further segment of InP 138 is then grown on top of the InAs segment 136. The process for forming abrupt heterojunctions between different materials within a nanowhisker is fully described in our co-pending US Patent Application No. 10/613,071, filed July 7, 2003. The array is then encapsulated in a transparent matrix medium 140.

30 As shown in Figure 13b, the result is an extremely small LED quantum dot structure. A whisker 150, selected from the whisker array has anode and cathode outer regions 134, 138 of indium phosphide either side of an inner region 136 formed of indium arsenide, so as to define a quantum well. Regions 134, 138 are connected

to respective anode and cathode electrical contacts, formed as metallisation areas 152, 154. In contrast to planar devices, where because of the need for lattice matching and for relieving mismatch strain, only certain wavelengths are possible, an important point of this embodiment is that the wavelength of the LED is fully variable since the materials making up the diode may be of any desired composition to achieve a
5 desired wavelength of emission.

Figure 14 shows a fifth embodiment of the invention for use as a stamp in nano imprint lithography. A substrate 300 has an array of nanowhiskers 302 formed thereon, according to the process described in example 1, at respective
10 sites 304 (only some of the nanowhiskers are shown for clarity). The nanowhiskers are grouped and configured so as to form a pattern 304, that when applied in the NIL process, produces a required nanostructure formation. The length of the nanowhiskers may be as long as required, more than 1 micrometer that permits nanostructures of arbitrary depth to be formed.

15 **Example 7**

This example illustrates the precision with which nanowhisker arrays of the invention can be fabricated.

Figure 15 shows a plan view of a nanowhisker array prepared according to the invention wherein the nanowhiskers are arranged in hexagonal pattern, the sides of
20 the hexagons having a length of 1 μm .

Figure 16 shows an enlarged view of a portion of the array shown in Figure 15 in which the positions of the nanowhiskers as determined by a computer program for analyzing such images have been determined for each nanowhisker and the positions have been indicated by crosses, such as cross 60. Also indicated in the Figure 16 are
25 the positions of the points of a lattice grid (the target positions of the nanowhiskers) generated by the computer program, indicated, for example by points such as cross 62. After the positions of the grid points and the locations of the individual nanowhiskers were determined by the computer program, differences between the grid points and the actual positions were generated for each nanowhisker.

Figure 17 is a representation of the differences in the form of a histogram plot. Based
30 on the data displayed in Figure 17 it was determined that the mean displacement of the actual positions from the computer-generated lattice grid was 36 nm, with a standard deviation of 23 nm. For the structure illustrated these results can be

compared with the lattice parameter (=side of the hexagonal cell) to yield the values in percent of mean displacement, 3.6% and standard deviation 2.3%. Moreover, for nearly all of the nanowhiskers, the deviation of each whisker from its target position is less than the diameter of the whisker, indeed less than half the diameter in most cases, with many of the whiskers deviating less than 20% of the diameter from the target position and even being within 1% to 5% of the diameter, or even essentially coincident with the target position (no more than 0.5% deviation).

WE CLAIM:

- 5 1. A method for producing a structure including at least one nanowhisker on a substrate, the method comprising:
 providing a substrate of a predetermined material,
 providing at least one mass of a catalytic material on a surface of the substrate
 at a predetermined position on the surface,
10 applying heat and introducing at least one material in gaseous form such as to create a catalytic seed particle from each said mass, and to grow, from the catalytic seed particle, epitaxially, a nanowhisker of a predetermined material,
 and wherein each said mass is such that during the formation of the catalytic seed particle, forces causing the mass to migrate across said surface are less than a
15 holding force across a wetted interface on the substrate surface.
2. A method according to claim 1, wherein each said mass, upon melting, retains approximately the same interface with the substrate surface.
- 20 3. A method according to claim 1, wherein each said mass has a diameter and a height, and a ratio of diameter to height of between 1:2 and 1:12.
4. A method according to claim 3, wherein said ratio is about 1:3.
- 25 5. A method according to claim 1 wherein each said mass comprises a first region of a catalytic material, and a second region of an alloying material for forming said catalytic seed particle.
6. A method according to claim 5 wherein the mass comprises first and third
30 layers of said catalytic material, with an intervening second layer of said alloying material.

7. A method according to claim 1, wherein said at least one mass is formed by a nanoimprint lithography process, employing a stamp defining the catalytic mass regions.

5 8. A method according to claim 7, wherein the stamp is formed by an array of nanowhiskers on a substrate, whereby to permit an arbitrary diameter: height ratio for the masses of catalytic material.

9. A method according to claim 1, including an initial annealing step in which
10 said catalytic seed particle is formed, and a second growth step in which a nanowhisker is grown from the catalytic seed particle.

10. A method according to claim 1, wherein nanowhisker growth conditions are regulated such that the time for growth nucleation of a nanowhisker at a said
15 predetermined position is less than a characteristic time for the mobility of the respective mass on the substrate surface such as to maintain the nanowhisker within a predetermined tolerance of position from said predetermined position.

11. A method according to claim 1, comprising providing a multiplicity of
20 masses of catalytic material in a predetermined configuration, each mass being in a respective predetermined location, and wherein each nanowhisker is sited within an accuracy from its predetermined site of 10% of the distance from its nearest neighbour.

25 12. A method according to claim 1, wherein the nanowhisker material is one of a group II-VI, III-V, or IV material.

13. A method according to claim 1, wherein the substrate material is one of a
30 group II-VI, III-V, or IV material.

14. A method as claimed in claim 1, comprising regulating activity of one or more elements of nanowhisker material in gaseous form around each site, so as to regulate growth of the nanowhisker.

15. A method as claimed in claim 14, comprising regulating the activity of a group V material during growth of a III V compound.

16. A method as claimed in claim 1, wherein the epitaxial growth process is MOVPE, and materials for nanowhisker growth are introduced in vapour form to said substrate.

17. A method as claimed in claim 1, wherein the epitaxial growth process is CBE, and materials for nanowhisker growth are introduced in the form of a beam to said substrate.

18. A method as claimed in claim 1, comprising providing a mask over the substrate surface to inhibit migration of the catalytic masses during nanowhisker growth.

15

19. A method as claimed in claim 18, wherein said mask is apertured, each aperture containing a respective mass.

20. A nanoengineered structure comprising a substrate of a predetermined material, and at least one mass of a catalytic material formed on the substrate surface in a predetermined position, wherein each said mass is such that, upon heating and melting to form a catalytic seed particle for subsequent nanowhisker growth, a wetted interface with the substrate is formed such that forces causing the mass to migrate across the surface are less than the force provided by the wetted interface holding the mass in its predetermined position.

25

21. A structure according to claim 20, wherein each said mass is such that upon melting it retains approximately the same interface with the substrate surface.

22. A structure according to claim 21, wherein said mass has a diameter and a height, and a ratio of diameter to height of between 1: 2 and 1:12.

30

23. A structure according to claim 21, wherein said ratio is about 1:3.

24. A structure according to claim 20, wherein each said mass comprises a first region of a catalytic material, and a second region of an alloying material for forming said catalytic seed particle.

5 25. A structure according to claim 24, wherein each said mass comprises first and third layers of said catalytic material, with an intervening second layer of said alloying material.

10 26. A method for producing a structure including at least one nanowhisker on a substrate, the method comprising:

 providing a substrate of a predetermined material,

 providing at least one mass of a catalytic material on a surface of the substrate at a predetermined position on the surface,

15 applying heat and introducing at least one material in gaseous form such as to grow epitaxially, from each said mass, a nanowhisker of a predetermined material,

 and wherein nanowhisker growth conditions are regulated such that the time for growth nucleation of a nanowhisker at a said predetermined position is less than a characteristic time for the mobility of the respective mass on the substrate surface such as to maintain the nanowhisker within a predetermined tolerance of position
20 from said predetermined position.

27. A method according to claim 26, comprising providing a multiplicity of masses of catalytic material in a predetermined configuration, each mass being in a respective predetermined location, and wherein each nanowhisker is sited within an
25 accuracy from its predetermined site of 10% of the distance from its nearest neighbour.

28. A method according to claim 27, wherein the nanowhisker material is one of a group II-VI, III-V, or IV material.
30

29. A method according to claim 27, wherein the substrate material is one of a group II-VI, III-V, or IV material.

30. A method according to claim 26, including an initial step of annealing the substrate and the at least one catalytic mass, whereby each catalytic mass alloys with the substrate surface.

5 31. A method as claimed in claim 26, comprising regulating activity of one or more elements of nanowhisker material in gaseous form around each site, so as to regulate growth of the nanowhisker.

10 32. A method as claimed in claim 31, comprising regulating the activity of a group V material during growth of a III-V compound.

15 33. A method as claimed in claim 26, wherein the epitaxial growth process is MOVPE, and materials for nanowhisker growth are introduced in vapour form to said substrate.

 34. A method as claimed in claim 26, wherein the epitaxial growth process is CBE, and materials for nanowhisker growth are introduced in gaseous form to said substrate.

20 35. A method as claimed in claim 26, comprising providing a mask over the substrate surface to inhibit migration of the catalytic masses during nanowhisker growth.

25 36. A method for producing a structure comprising at least one nanowhisker on a substrate, the method comprising:

 providing a substrate,

 providing at least one mass of catalytic material on a surface of the substrate, each said mass being located at a respective predetermined position on the surface,

 providing a mask on the substrate surface,

30 applying heat and introducing at least one material in vapour form such as to grow by Chemical Beam Epitaxy, a nanowhisker by way of each said mass, of controlled height, diameter and position, and wherein said mask inhibits both growth on the substrate surface and lateral movement of the catalytic masses.

37. A method for producing a nanoengineered structure, the method comprising:
- providing a substrate,
 - providing a mask on the substrate surface having at least one aperture of
 - 5 predetermined dimensions at a predetermined position on the substrate,
 - providing at least one mass of catalytic material, each said mass being located in a respective mask aperture on the surface
 - applying heat and introducing at least one material in vapour form such as to grow by Chemical Beam Epitaxy, a nanowhisker by way of each said mass, of
 - 10 controlled height, diameter and position, and wherein said mask inhibits both growth on the substrate surface and lateral movement of the catalytic masses.
38. A method according to claim 37, comprising providing a multiplicity of masses of catalytic material in a predetermined configuration, each mass being in a
- 15 respective predetermined location, and wherein each nanowhisker is sited within an accuracy from its predetermined site of 10% of the distance from its nearest neighbour.
39. A method according to claim 37, wherein the nanowhisker material is one
- 20 of a group II VI, III V, or IV material.
40. A method according to claim 37, wherein the substrate material is one of a group II VI, III V, or IV material.
- 25 41. A method according to claim 37, including an initial step of annealing the substrate and said at least one mass, whereby each catalytic mass alloys with the substrate surface.
- 30 42. A method as claimed in claim 37, comprising regulating activity of one or more elements of nanowhisker material in gaseous form around each site, so as to regulate growth of the nanowhisker.

43. A method as claimed in claim 37, wherein the base of the nanowhisker at the substrate surface is of a distance from the edge of the mask defining the respective aperture by an amount which is less than about the diameter of the nanowhisker.

5 44. A nanoengineered structure including at least one nanowhisker on a substrate, a substrate of a predetermined material, a mask of a further material on the substrate surface and being apertured with at least one aperture in a predetermined site and of predetermined diameter, and a nanowhisker projecting from each said aperture, the base of the nanowhisker at the substrate surface being of a distance from
10 the edge of the mask defining the respective aperture by an amount which is less than about the diameter of the nanowhisker.

45. A method for producing an array of more than about 1000 nanowhiskers on a substrate to form a photonic band gap array, the method comprising:
15 providing a substrate of a predetermined material,
 providing an array of masses of a catalytic material on a surface of the substrate masses of catalytic material in a predetermined configuration, each mass being in a respective predetermined location on the surface,
 applying heat and introducing sequentially a plurality of materials in gaseous
20 form such as to grow from each catalytic mass, a nanowhisker comprising segments of different materials, with sharp heterojunctions between the segments
 wherein nanowhisker growth conditions are regulated such as to maintain the nanowhisker sited within an accuracy from its predetermined site of 10% of the distance from its nearest neighbour.

25 46. A method according to claim 45, wherein each nanowhisker comprises a series of alternating segments of two different materials,
 and oxidising said nanowhiskers whereby to form from said segments, alternating regions of different refractive index.

30 47. A method according to claim 46, wherein said two different materials are Si and Al, and the regions are formed of Silica and Sapphire.

48. A method according to claim 46, wherein said two different materials are Si and Ge, and the regions are formed of Silica and GeO_x.

49. A method according to claim 45, wherein said segments provide a
5 quantum dot LED structure,
and providing electrical contacts to one or more selected nanowhiskers to enable operation of the LED structure.

50. A nanoengineered structure comprising at least one nanowhisker on a
10 substrate, wherein a positional deviation of the nanowhisker from a predetermined target location is no more than a diameter of the nanowhisker.

51. A nanoengineered structure according to claim 50, wherein the positional deviation is no more than half the diameter of the nanowhisker.
15

52. A nanoengineered structure according to claim 50, wherein the positional deviation is no more than 20% of the diameter of the nanowhisker.

53. A nanoengineered structure according to claim 50, wherein the positional deviation is no more than 5% of the diameter of the nanowhisker.
20

54. A nanoengineered structure according to claim 50, wherein the positional deviation is no more than 1% of the diameter of the nanowhisker.

25 55. A nanoengineered structure according to claim 50, wherein the positional deviation is no more than 0.5% of the diameter of the nanowhisker.

56. A method for producing a structure including at least one nanowhisker on a substrate, the method comprising:
30 providing a substrate of a predetermined material,
providing at least one mass of a catalytic material on a surface of the substrate at a predetermined position on the surface,

applying heat and introducing at least one material in gaseous form such as to create a catalytic seed particle from each said mass, and to grow, from the catalytic seed particle, epitaxially, a nanowhisker of a predetermined material,

5 and wherein a positional deviation of the nanowhisker from a predetermined target location is no more than a diameter of the nanowhisker.

57. A method according to claim 56, wherein the positional deviation is no more than half the diameter of the nanowhisker.

10 58. A method according to claim 56, wherein the positional deviation is no more than 20% of the diameter of the nanowhisker.

59. A method according to claim 56, wherein the positional deviation is no more than 5% of the diameter of the nanowhisker.

15

60. A method according to claim 56, wherein the positional deviation is no more than 1% of the diameter of the nanowhisker.

20 61. A method according to claim 56, wherein the positional deviation is no more than 0.5% of the diameter of the nanowhisker.

Fig.1a.

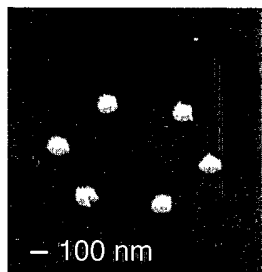


Fig.1b.

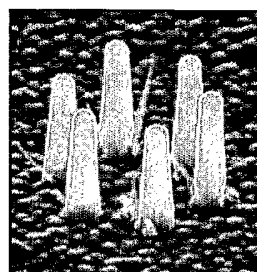


Fig.2.

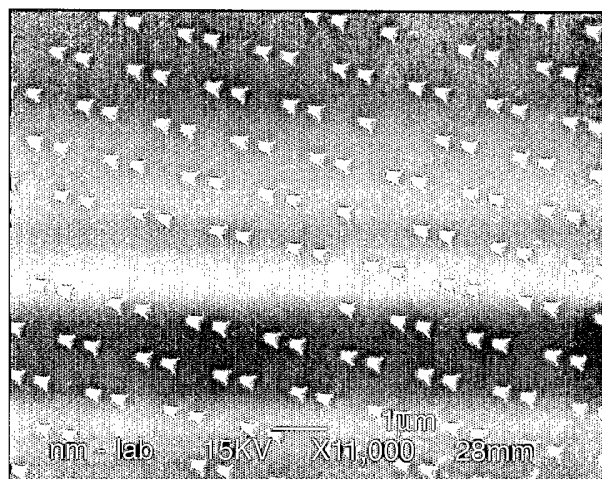


Fig.3.

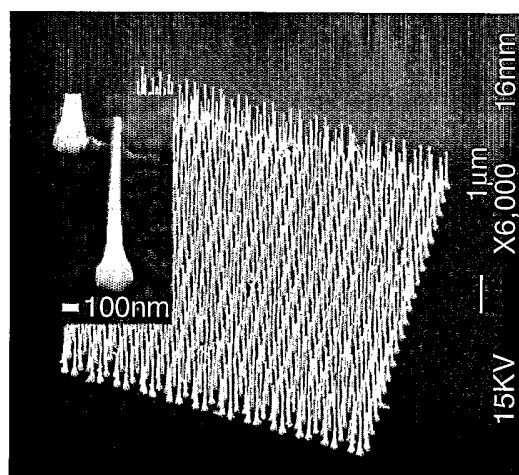


Fig.4a.

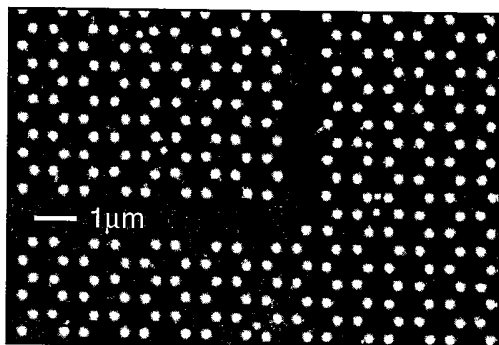


Fig.4b.

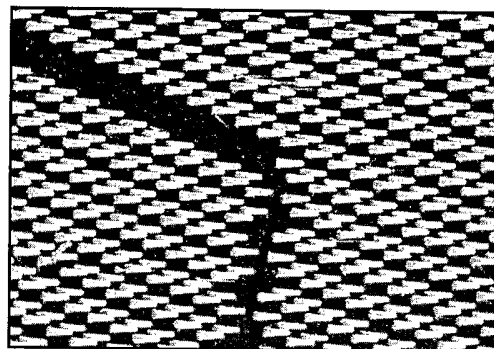


Fig.5.

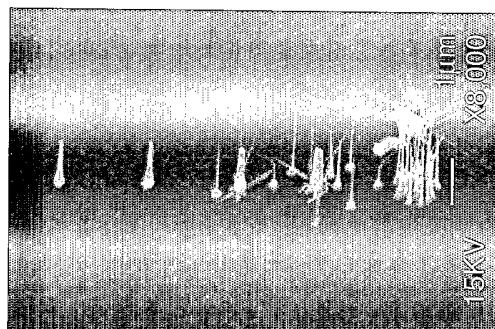


Fig.6a.

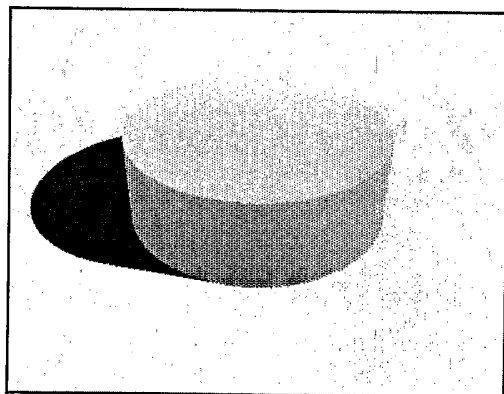


Fig.6b.

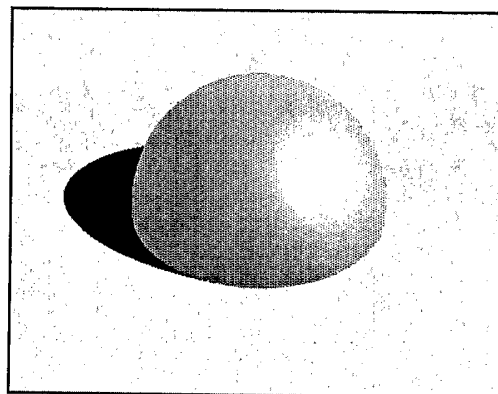


Fig.7a.



Fig.7b.

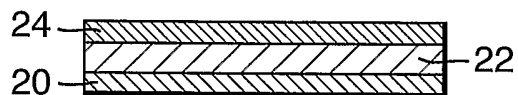


Fig.7c.

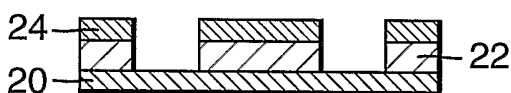


Fig.7d.

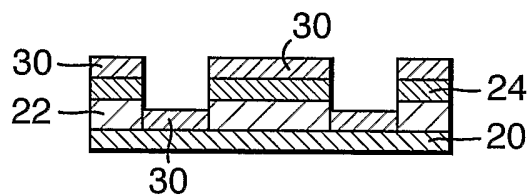


Fig.7e.

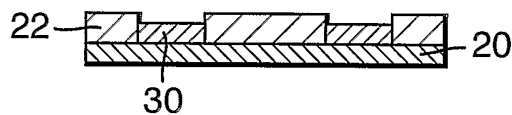


Fig.7f.

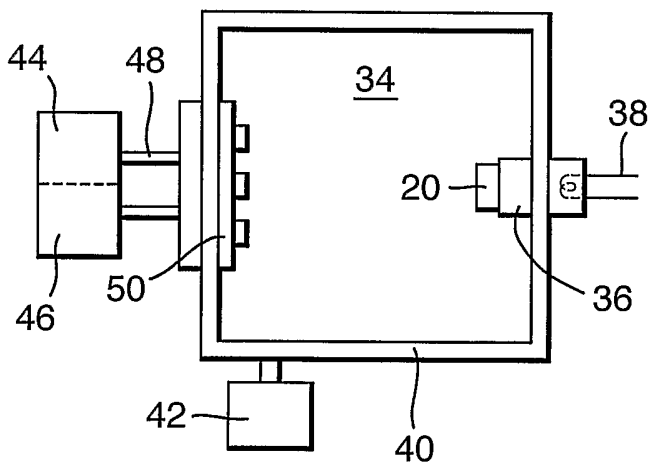


Fig.8.

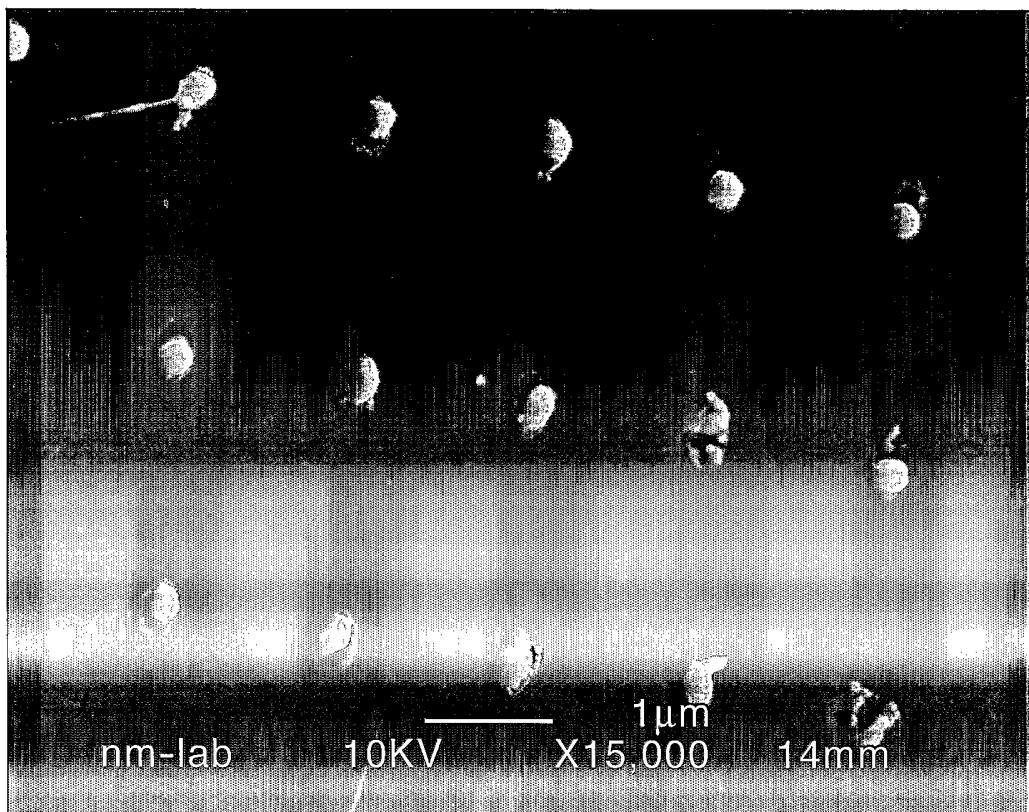


Fig.9a.

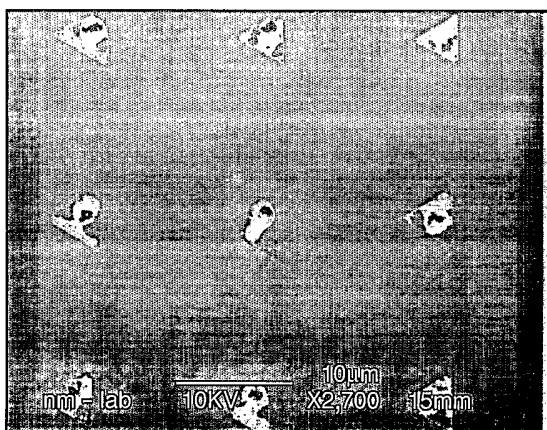


Fig.9b.

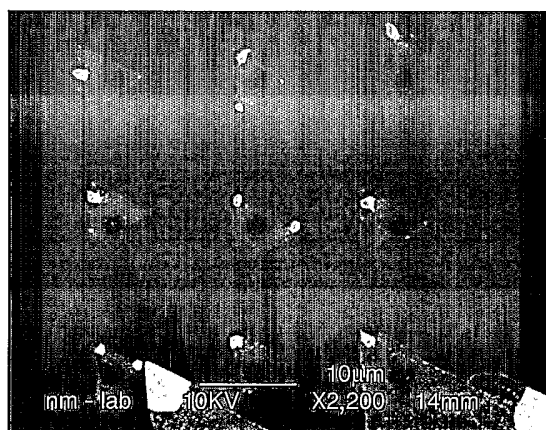


Fig.10a.

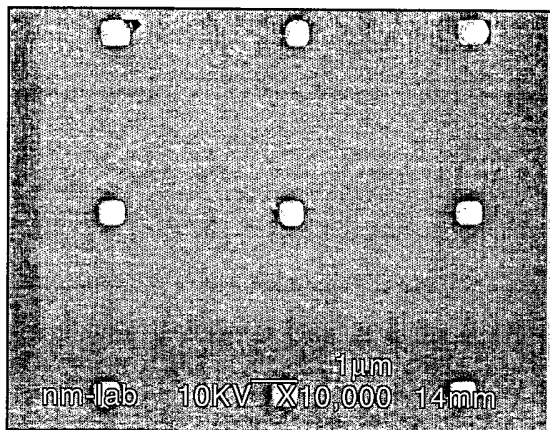


Fig.10b.

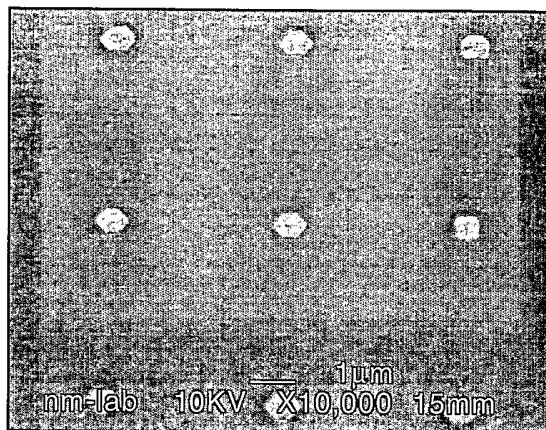


Fig.11a.

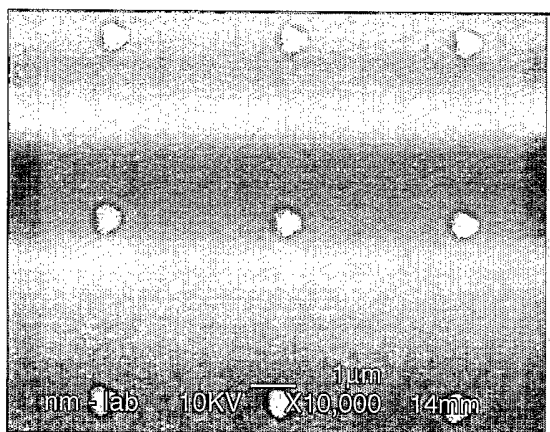


Fig.11b.

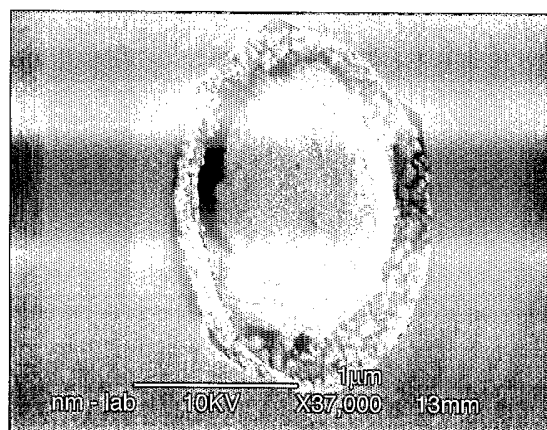


Fig.12a.

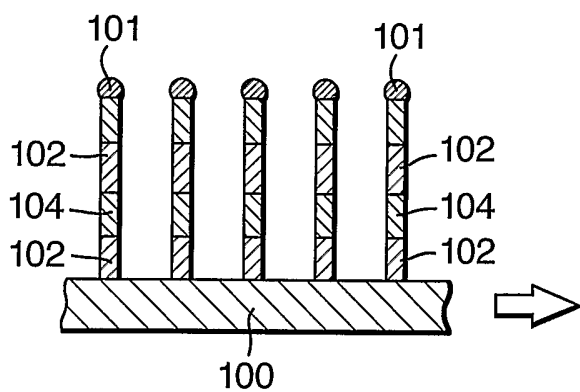


Fig.12b.

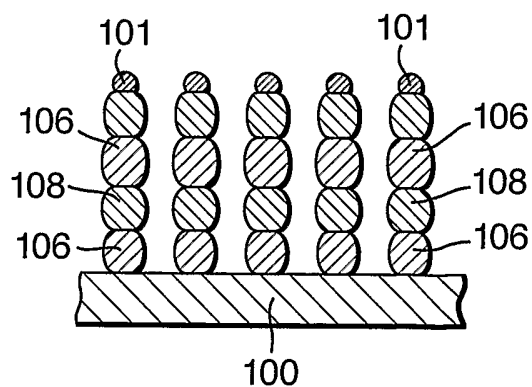


Fig.13a.

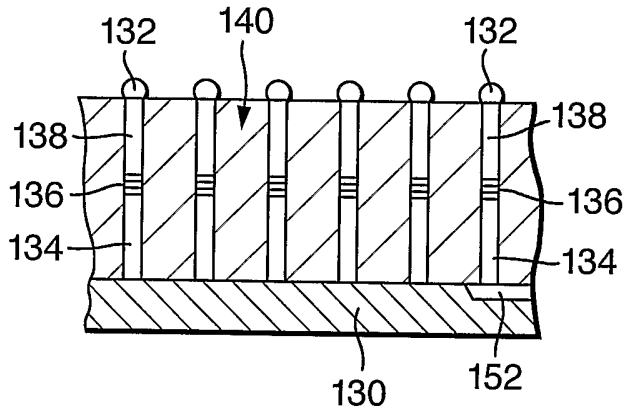


Fig.13b.

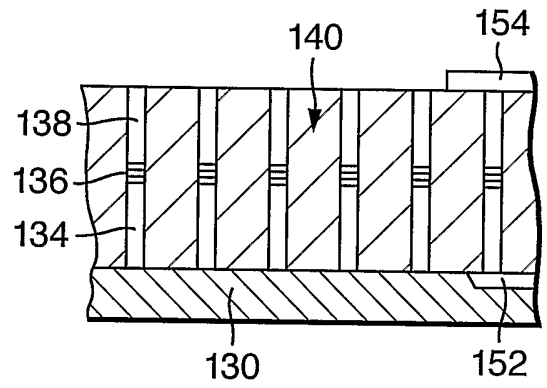


Fig.14.

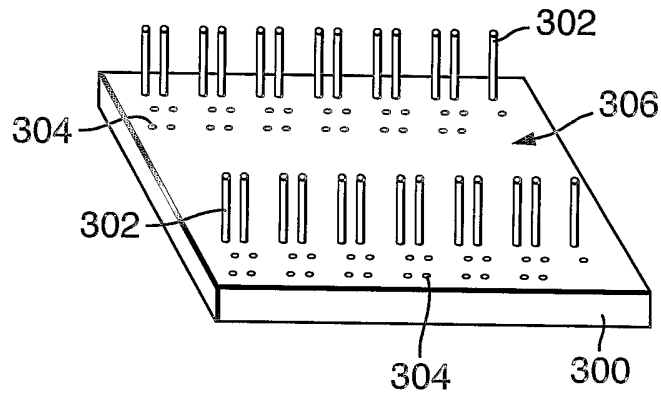


Fig.15.

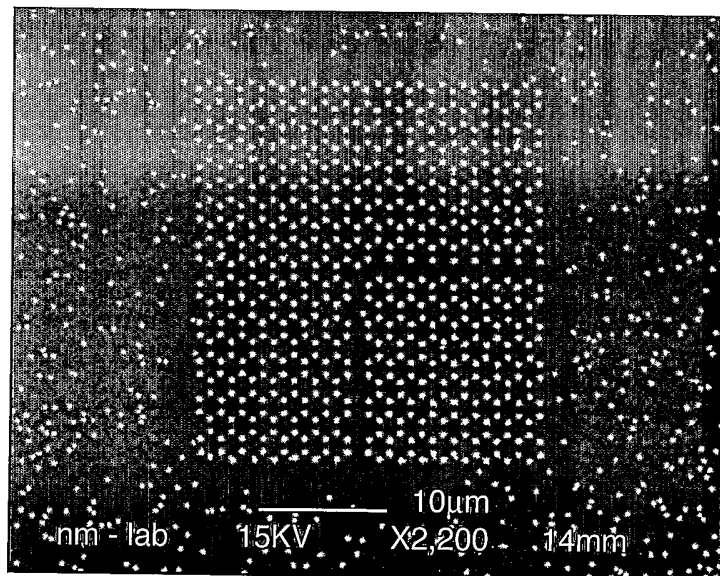


Fig.16.

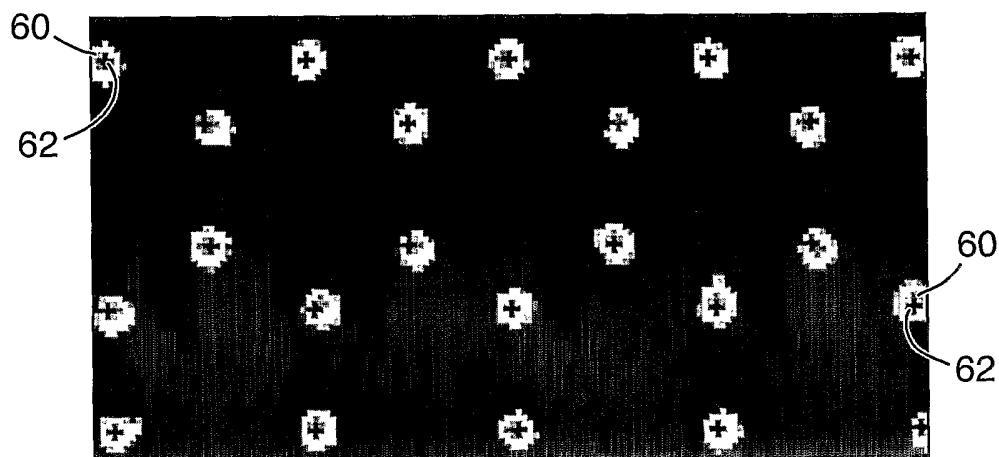
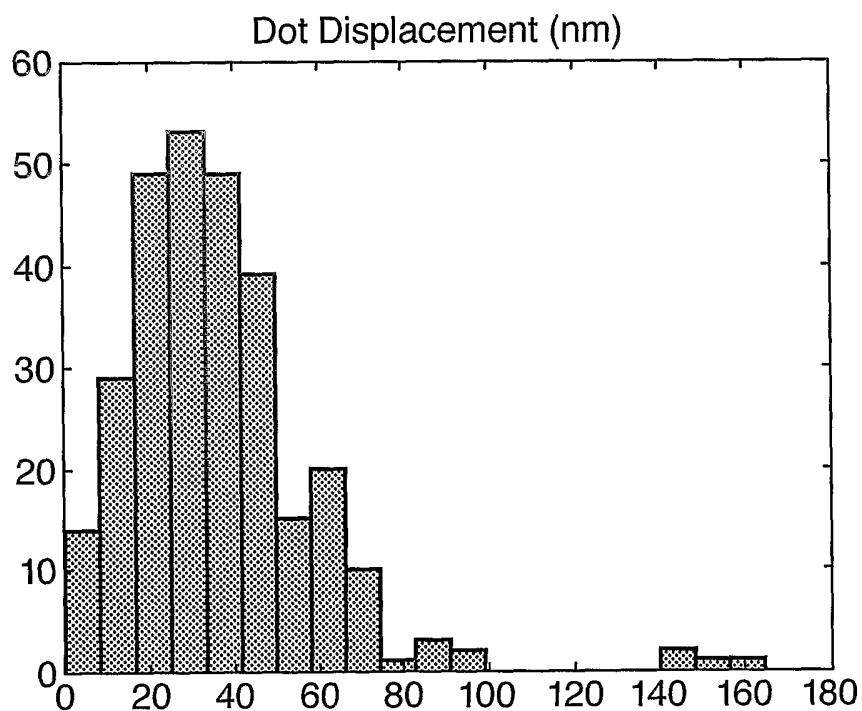


Fig.17.



INTERNATIONAL SEARCH REPORT

PCT/GB2004/000037

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 B82B3/00 C30B11/12 C30B29/62				
According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols) IPC 7 C30B				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal, INSPEC, PAJ				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	WESTWATER J ET AL: "Control of the size and position of silicon nanowires grown via the vapor-liquid-solid technique" JPN. J. APPL. PHYS. 1, REGUL. PAP. SHORT NOTES REV. PAP. (JAPAN), JAPANESE JOURNAL OF APPLIED PHYSICS, PART 1 (REGULAR PAPERS, SHORT NOTES & REVIEW PAPERS), OCT. 1997, PUBLICATION OFFICE, JAPANESE JOURNAL APPL. PHYS, JAPAN, vol. 36, no. 10, 1997, pages 6204-6209, XP002282358 ISSN: 0021-4922	1,10-13, 18-21, 26-29, 31,35, 44,45, 50-61		
Y	page 6206 - page 6209; figures 5-9 ----- -/--	36,37		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. </td> <td style="width: 50%; border: none;"> <input checked="" type="checkbox"/> Patent family members are listed in annex. </td> </tr> </table>			<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.	<input checked="" type="checkbox"/> Patent family members are listed in annex.
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Date of the actual completion of the international search <p style="text-align: center; font-size: 1.2em;">27 May 2004</p>		Date of mailing of the international search report <p style="text-align: center; font-size: 1.2em;">14/06/2004</p>		
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer <p style="text-align: center; font-size: 1.2em;">Cook, S</p>		

INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>LIU J L ET AL: "Gas-source MBE growth of freestanding Si nano-wires on Au/Si substrate" SUPERLATTICES MICROSTRUCT. (UK), SUPERLATTICES AND MICROSTRUCTURES, 1999, ACADEMIC PRESS, UK, vol. 25, no. 1-2, 1999, pages 477-479, XP002282455 ISSN: 0749-6036 the whole document</p>	36, 37
A	<p>SHIMADA T ET AL: "Size, position and direction control on GaAs and InAs nanowhisker growth" SUPERLATTICES AND MICROSTRUCTURES, ACADEMIC PRESS, LONDON, GB, vol. 24, no. 6, December 1998 (1998-12), pages 453-458, XP004445273 ISSN: 0749-6036 page 456</p>	1-61
A	<p>US 2002/172820 A1 (KIND HANNES ET AL) 21 November 2002 (2002-11-21) paragraph '0092! - paragraph '0094!; claims 83,95-97; figure 25</p>	50
A	<p>WO 01/84238 A (KRINKE THOMAS JOHANNES ; BTG INT LTD (GB); DEPPERT KNUT WILFRIED (SE);) 8 November 2001 (2001-11-08) cited in the application</p>	
A	<p>HIRUMA K ET AL: "SELF-ORGANIZED GROWTH OF GAAS/INAs HETEROSTRUCTURE NANOCYLINDERS BY ORGANOMETALLIC VAPOR PHASE EPITAXY" JOURNAL OF CRYSTAL GROWTH, NORTH-HOLLAND PUBLISHING CO. AMSTERDAM, NL, vol. 163, no. 3, 1 June 1996 (1996-06-01), pages 226-231, XP000627505 ISSN: 0022-0248 cited in the application</p>	
A	<p>SATO T ET AL: "Site-controlled growth of nanowhiskers" APPL. PHYS. LETT. (USA), APPLIED PHYSICS LETTERS, 9 JAN. 1995, USA, vol. 66, no. 2, 1995, pages 159-161, XP002282359 ISSN: 0003-6951 cited in the application the whole document</p>	
A	<p>US 2002/129761 A1 (TAKAMI TOMOHIDE) 19 September 2002 (2002-09-19)</p>	
	<p>----- -/-- -----</p>	

INTERNATIONAL SEARCH REPORT

PCT/GB2004/000037

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>HIRUMA K ET AL: "GAAS AND INAS NANOWIRE GROWTH TECHNOLOGY" PROCEEDINGS OF THE SCIENCE AND TECHNOLOGY OF ATOMICALLY ENGINEERED MATERIALS, XX, XX, 30 October 1995 (1995-10-30), pages 563-570, XP009030014</p> <p style="text-align: center;">-----</p>	
A	<p>PEIDONG YANG ET AL: "CONTROLLED GROWTH OF ZNO NANOWIRES AND THEIR OPTICAL PROPERTIES" ADVANCED FUNCTIONAL MATERIALS, WILEY INTERSCIENCES, WIENHEIM, DE, vol. 12, no. 5, May 2002 (2002-05), pages 323-331, XP001123883 ISSN: 1616-301X</p> <p style="text-align: center;">-----</p>	
A	<p>SHIRAI M ET AL: "Gold cluster formation using an atomic force microscope and its applications to GaAs whisker growth" SUPERLATTICES AND MICROSTRUCTURES, ACADEMIC PRESS, LONDON, GB, vol. 24, no. 2, August 1998 (1998-08), pages 157-162, XP004445312 ISSN: 0749-6036</p> <p style="text-align: center;">-----</p>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/GB2004/000037

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002172820 A1	21-11-2002	CA 2442985 A1	10-10-2002
		EP 1374309 A1	02-01-2004
		TW 554388 B	21-09-2003
		WO 02080280 A1	10-10-2002
		US 2002175408 A1	28-11-2002
WO 0184238 A	08-11-2001	AU 5493301 A	12-11-2001
		CA 2406006 A1	08-11-2001
		CN 1427962 T	02-07-2003
		EP 1279068 A1	29-01-2003
		WO 0184238 A1	08-11-2001
		JP 2003531738 T	28-10-2003
		US 2003102444 A1	05-06-2003
US 2002129761 A1	19-09-2002	JP 2002220300 A	09-08-2002