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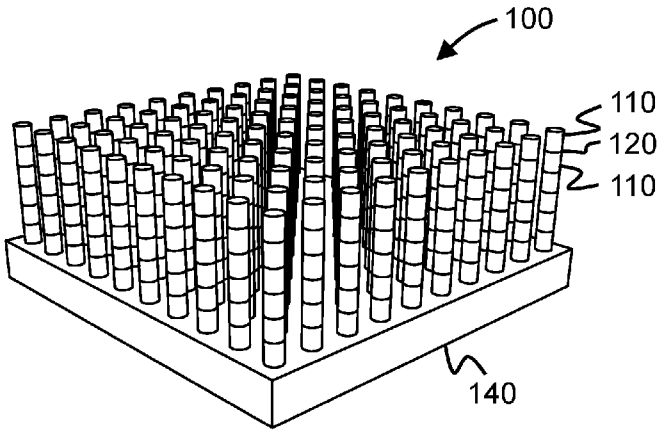

Fig. 2

(57) Abstract: A product and process of nanoforming, in which the process includes applying a cyclic loading to a contact area on a workpiece via a nanojackhammer such that at least a part of the workpiece is displaced to form one or more nanostructures adjacent the contact area, the cyclic loading being applied for a process time and wherein the workpiece is in a solid state throughout the process time.

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A PRODUCT AND PROCESS OF NANOFORMING

The present application claims priority from the Singapore patent application no. 10202008172X, the contents of which are incorporated herein in entirety by reference.

TECHNICAL FIELD

[0001] The present disclosure relates to nanotechnology and more particularly to a product and process of nanoforming.

BACKGROUND

[0002] Metal nanostructures are conventionally produced via chemical synthesis using precursors, with some nanostructures involving electroplating. Understandably, not all metals are suitable for electroplating, and only a limited range of precursors are suitable for use in such chemical synthesis. As a result, the types of metal nanostructures available are limited.

[0003] Conventional nanoimprinting involves the use of high-energy laser or other forms of heating to bring a substrate above its glass transition temperature or to a temperature higher than half of its melting point, so that the substrate will undergo a phase change (from its stable state under ambient conditions) into a super plastic state suitable for receiving an imprint from a mold. The substrate is then cooled so that it undergoes a phase change reverting back to its stable state in ambient conditions. In view of the melting point of metals (e.g., zinc has a melting point of 419.5 degrees Celsius, copper has a melting point of 1084 degrees Celsius, tungsten has a melting point of 3400 degrees Celsius, etc.), clearly conventional nanoimprinting operates at fairly high temperatures. At the elevated temperatures involved, metals also tend to be more reactive, and are likely to undergo oxidation or alloying with contaminants, introducing defects to the resulting product. Conventional nanoimprinting is therefore carried out in a cleanroom environment, vacuum, or an inert gas environment.

SUMMARY

[0004] In one aspect, the present disclosure provides a method including: applying a cyclic

loading to a contact area on a workpiece via a nanojackhammer such that at least a part of the workpiece is displaced to form one or more nanostructures adjacent the contact area, wherein the cyclic loading is applied for a process time and wherein the workpiece is in a solid state throughout the process time.

[0005] The method according to the above, wherein the one or more nanostructures comprises at least one material, and wherein the one or more nanostructures are formed at a process temperature below a hot embossing temperature characteristic of the at least one material.

[0006] The method according to any of the above, wherein the at least one material includes at least one metal.

[0007] The method according to any of the above, wherein the nanojackhammer is of nanoscale, and wherein the nanojackhammer forms a part of a nanowall, the nanowall defining at least one nanocavity configured to receive the one or more nanostructures.

[0008] The method according to any one of the above, wherein the one or more nanostructures includes one material or at least two dissimilar materials, and wherein the one or more nanostructures are formed at a process temperature at which the one material or all of the at least two dissimilar materials are in a solid state. The method according to any one of the above, wherein the one or more nanostructures are formed under ambient conditions.

[0009] The method according to any one of the above, wherein the cyclic loading includes alternating loading half-cycles in which the nanojackhammer applies pressure to the contact area and retreating half-cycles in which the nanojackhammer releases pressure on the contact area.

[0010] The method according to any one of the above, wherein the cyclic loading is configured to promote generation of dislocations in the loading half-cycles and to enable recovery of at least some of the dislocations in the retreating half-cycles.

[0011] The method according to any one of the above, wherein the process time is in a range from a few seconds to a few minutes.

[0012] The method according to any one of the above, wherein the material of the workpiece includes a plurality of dissimilar materials, and wherein each nanostructure includes segments of the materials.

[0013] The method according to any one of the above, further including modifying the one or more nanostructures by etching away at least some of one of the dissimilar materials.

[0014] The method according to any one of the above, further including removing some of one of the materials to form a nanogap between two of the segments.

[0015] The method according to any one of the above, further including forming compounds with one of the materials on the one or more nanostructures to form features on the one or more nanostructures.

[0016] A product comprising nanostructures formed by the method according to any one of the above, wherein each of the nanostructures has at least one segment characterized by a crystallinity similar to a crystallinity of a corresponding layer in the workpiece.

[0017] The product according to any one of the above, wherein each of the nanostructures includes two contiguous segments of dissimilar materials having different physical properties and/or chemical properties.

[0018] The product according to any one of the above, wherein each of the nanostructures includes a spacer segment contiguous with two other segments, the spacer segment being of a material dissimilar to each material of the two other segments, and wherein the spacer segment is configured to define a nanogap between the two other segments.

[0019] The product according to any one of the above, wherein each of the plurality of nanostructures includes at least one heterojunction defined by an abrupt interface between two segments.

[0020] A product comprising at least one nanostructure formed from a material by cyclic loading, the at least one nanostructure being characterized by a crystallinity consistent with the material being in a solid state throughout the process time.

[0021] The product according to any one of the above, wherein the at least one

nanostructure includes at least one heterojunction, the at least one heterojunction being defined by an abrupt interface between two segments.

[0022] The product according to any one of the above, wherein the at least one nanostructure includes at least two segments of dissimilar materials, the at least two segments being one of contiguous segments or spaced apart segments.

[0023] The product according to any one of the above, wherein the at least two segments include a segment of a first material and a segment of a compound of a second material.

[0024] The product according to any one of the above, wherein the at least one nanostructure includes a spacer segment contiguous with two other segments, the spacer segment being configured to define a nanogap between the two other segments.

[0025] In another aspect, there is provided an apparatus for use with a workpiece, the apparatus including: a tool with at least one nanojackhammer, the at least one nanojackhammer being of nanoscale; and an actuator configured to intermittent apply pressure on one or both of the tool and the workpiece to form the product according to any described above.

BRIEF DESCRIPTION OF DRAWINGS

[0026] Fig. 1 illustrates nanostructures according to one embodiment of the present disclosure.

[0027] Fig. 2 illustrates nanostructures according to another embodiment.

[0028] Fig. 3A and Fig. 3B illustrate nanostructures according to yet another embodiment;

[0029] Fig. 4A and Fig. 4B show flowcharts of methods of nanoforming according to embodiments of the present disclosure;

[0030] Fig. 5A shows an apparatus for nanoforming;

[0031] Fig. 5B and Fig. 5C illustrate various configurations for nanoforming according to embodiments of the present disclosure;

[0032] Figs. 6A to 6J compare load requirements with and without cyclic loading and schematically represent the effect of cyclic loading on dislocation generation and recovery;

[0033] Figs. 7A to 7E and Figs. 8A to 8E illustrate the nanojackhammer effect of nanojackhammers of different profiles;

[0034] Fig. 9 shows a plot of aspect ratio against force at frequency of 20 KHz;

[0035] Fig. 10 shows plots of aspect ratio against vibration amplitude at frequency of 20 KHz;

[0036] Figs. 11A to 11D are SEM images of silver nanowires of different lengths but similar diameters formed according to embodiments of the present disclosure;

[0037] Figs. 12A to 12D are SEM images of gold nanowires of different diameters but similar lengths formed according to embodiments of the present disclosure;

[0038] Figs. 13A to 13F are SEM images of nanorods of different materials formed according to embodiments of the present disclosure;

[0039] Fig. 14 illustrates the volume fraction of FCC phase after direct loading and cyclic loading respectively;

[0040] Fig. 15A and Fig. 15B are schematic diagrams showing the grain structure in a nanoformed product and in a conventional product respectively;

[0041] Fig. 16A and Fig. 16B are schematic diagrams showing a multilayered workpiece and a corresponding multi-segment nanostructure respectively;

[0042] Fig. 17A and Fig. 17B are schematic diagrams showing an abrupt interface and a diffused interface respectively;

[0043] Figs. 18A to 18C are SEM, TEM and EDS images of Au-Bi heterojunctions;

[0044] Figs. 19A to 19C are SEM, TEM and EDS images of Sn-Au heterojunctions;

[0045] Figs. 20A to 20C are SEM, TEM and EDS images of Cu-Au heterojunctions;

[0046] Fig. 21A and Fig. 21B are SEM and TEM images of nanostructures with Au-Al_2O_3-Au heterojunctions;

[0047] Fig. 22 shows Raman intensity plots of quorum sensing signal using different nanostructures; and

[0048] Fig. 23 is a schematic drawing to illustrate examples of post-processing.

DETAILED DESCRIPTION

[0049] References throughout this specification to "one embodiment", "another embodiment" or "an embodiment" (or the like) means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment. Thus, the appearance of the phrases "in one embodiment" or "in an embodiment" or the like in various places throughout this specification are not necessarily all referring to the same embodiment. Furthermore, the described features, structures, or characteristics may be combined in any suitable manner in one or more embodiments. In the following description, numerous specific details are provided to give a thorough understanding of embodiments. One skilled in the relevant art will recognize, that the various embodiments be practiced without one or more of the specific details, or with other methods, components, materials, etc. In other instances, some or all known structures, materials, or operations may not be shown or described in detail to avoid obfuscation.

[0050] The word "exemplary" is used herein to mean "serving as an example, instance, or illustration." Any embodiment described herein as "exemplary" is not necessarily to be construed as preferred or advantageous over other embodiments. As used herein, the singular 'a' and 'an' may be construed as including the plural "one or more" unless apparent from the context to be otherwise.

[0051] The terms "first" and "second" are used in the description and claims only for the sake of brevity and clarity, and do not necessarily imply a priority or order, unless required by the context. The terms "about" and "approximately" as applied to a stated numeric value encompasses the exact value and a reasonable variance as will be understood by one of ordinary skill in the art. The terms "generally" and "substantially" are to be understood in a

similar manner.

[0052] Conventional nanoimprinting or nanopatterning is carried out at elevated temperatures. Conventional hot embossing temperature is material specific (i.e., characteristic of the material), and is typically lower than the material's melting point but much higher than room temperature. For example, bismuth (Bi) is characterized by a hot embossing temperature of around 260 degrees Celsius (under a force of 8 kN) that is slightly lower than its melting point of about 273 degrees Celsius but significantly higher than room temperature or any ambient temperature. Conventional hot embossing of silver (Ag) requires a hot embossing temperature of at least 700 degrees Celsius while being subject to a force of 15 kN for one and a half hours. Copper (Cu) is characterized by a hot embossing temperature of at least about 550 degrees Celsius and platinum (Pt) is characterized by a hot embossing temperature of at least about 820 degrees Celsius. For example, aluminum alloys (such as Al 6061T6) would require a hot embossing temperature in the region of 582 to 652 degrees Celsius. For example, conventional nanoimprinting of gold requires a processing temperature of at least 0.5 Tm and preferably close to Tm, where Tm is the melting point of gold (approximately 1064 degrees Celsius), so as to enable plastic deformation and conformance of the gold with the nanoimprint mold. Non-metals are also characterized by relatively high hot embossing temperatures. For example, polycarbonate is associated with a hot embossing temperature of at least 150 degrees Celsius under pressure of 150 bar. From these examples, it is clear that previous to the present disclosure it is inconceivable that nanostructures could be formed at temperatures and pressures well below those of hot embossing. Within the temperature range required for one material to undergo nanoimprinting, another material might have melted or vaporized, or would have oxidized if nanoimprinting is not performed in vacuum or an inert gas environment. It is thus impossible to form nanostructures of two metals by conventional nanoimprinting when one of the metals oxidizes at the elevated temperature required to imprint another metal.

[0053] In one aspect, the nanoforming method (400) according to embodiments of the present disclosure forms nanostructures by a different mechanism, such that elevated temperatures and such special processing conditions are not necessary although not precluded. In addition to circumventing heating-related issues in manufacturing, the nanoforming method enables a greater variety of nanostructures to be fabricated. The

nanoforming method (400) can be carried out at a temperature lower than that required of the conventional hot embossing of metal. Contrary to conventional expectations, the nanoforming method (400) of the present disclosure is able to form nanostructures of a material at various temperatures below the hot embossing temperature characteristic of the material. The nanoforming method (400) enables the formation of nanostructures at a greater range of temperatures compared to conventional methods. The nanoforming method (400) is even able to form nanostructures at room temperature (ambient temperature). For avoidance of doubt, room temperature and ambient temperature are used interchangeably in the present disclosure. Room temperature will be generally understood to be above a freezing temperature (at which the material is "frozen" and will crack) and lower than a glass transition temperature or a melting temperature. Room temperature may also be described as any temperature selected from a range of temperatures to which human beings are accustomed. Although room temperature is variable and dependent on various factors such as location, climate, time of the day, etc., the nanoforming method (400) can nevertheless be performed successfully under such variable room temperature conditions. This advantageously enables the nanoforming method (400) to be carried out in a large variety of environments, including outdoors or even harsh environments. The nanoforming method (400) can be performed at a temperature selected from a range, in which the range is defined by an upper bound temperature that is lower the hot embossing temperature characteristic of the materials involved. The nanoforming method (400) can be performed at a temperature selected from a range, in which the range is defined by a lower bound temperature that is higher than the freezing temperatures characteristic of the materials involved. The nanoforming method (400) can be performed at a temperature selected from a range, in which the range is defined by a lower bound temperature that is at or higher than room temperature.

[0054] According to embodiments of the nanoforming method (400), products such as nanostructures (100) as illustrated in Fig. 1 can be formed. Nanostructures refer to products with dimensions smaller than 1000 nm (nanometer). Nanostructures include but are not limited to nanowires, nanorods, and nanodisks. The nanoforming method (400) enables a one-step fabrication process to form nanostructures in which each nanostructure is made of one material (Fig. 1) or of more than one material (Fig. 2), including materials of greatly

differing properties. Each nanostructure is formed as a unitary or integral element having contiguous segments (110) of different materials. Adjacent segments (110) have an abrupt (distinct and planar) interface (120) in between. The nanoforming method (400) further enables the formation of nanostructures (100) with nanogaps (130) between the segments (110), as shown in Fig. 3A and magnified in Fig. 3B. The nanoforming method (400) can form heterojunctions between contiguous segments of dissimilar materials (e.g., Fig. 2) or between segments of similar materials separated by a nanogap (e.g., Fig. 3A and Fig. 3B). The nanoforming method (400) may form the nanostructures on a substrate (140) or as free-standing nanostructures unconnected by a substrate.

[0055] Referring to Fig. 4A, the nanoforming method (400) includes applying a cyclic loading (410) to a contact area on a first surface of a workpiece via a nanojackhammer to displace an amount of material of the workpiece such that at least a part of the displaced material forms one or more nanostructures adjacent the contact area, wherein the nanojackhammer and the one or more nanostructures are of nanoscale. The one or more nanostructures are formed from the material in a solid state. The one or more nanostructures are formed without the material undergoing a phase change. The workpiece may be one of an amorphous metal, a crystalline metal, or a polymer, or any combination of at least two of such materials. At the beginning of the nanoforming process, the workpiece can be a generally planar piece of one material, or the workpiece may be a stack of generally planar pieces of different materials. Each piece of material may be a (solid) film or foil of a crystallinity similar to the target crystallinity in the nanostructure to be formed. To form a nanostructure having segments of dissimilar materials or segments of similar materials with different crystallinity in a particular order, the workpiece may be provided as a stack of corresponding layers of the materials arranged in the same order.

[0056] In some examples, the step of applying cyclic loading may be preceded by providing a lubricant (440) to the workpiece (600) and/or a tool (520), in which the nanojackhammer (550) is configured on a first tool surface (521) of the tool (520). A solid lubricant, for example (but not limited to) buckminsterfullerene or carbon nanotubes, may be provided at a first tool surface (521) of the tool (520). As the nanoforming process displaces or dislocates some of the material of the workpiece into some of the channels of the tool, some of the lubricant may be carried along with the displaced material such that there is some

lubricant between the nanostructures (formed from the displaced or dislocated material) and the tool (520). In other examples, the tool is coated with thin carbon nanotubes. Examples of carbon nanotubes suitable for use includes (but are not limited to) carbon nanotubes having a diameter of about 1 nm (nanometer) and a length in a range of about 100 nm to 200 nm. In some examples, other fine nanoparticle lubricants may be used in place of thin carbon nanotubes. The carbon nanotubes facilitate the flow of material into/in the cavities such that longer nanostructures can be formed in a shorter period of time (all other process conditions being the same).

[0057] The nanoforming method (400) may include removing the tool from the product after the nanostructures have been formed (420). The tool may be dissolved or removed in a manner that enables it to be re-used or recycled. In some examples, the tool may be simply decoupled or disengaged from the product (e.g., in air). Use of a lubricant as described above may help in pulling the tool and the product apart, for example, in cases where the nanostructures formed have relatively lower aspect ratios, such as nanodisks, nanorods, etc. In cases where the product includes nanostructures with relatively high aspect ratios (such as some relatively long nanowires), a sonicating bath (e.g., an ethanol bath) may be useful for removing the tool from the product formed. Alternatively, the tool may be removed by dissolving it in a suitable solvent (420). For example, potassium hyrdroxide (KOH) may be used to dissolve a tool made of anodized aluminum oxide (AAO), leaving behind the nanoformed product. If the workpiece (and hence the nanoformed product) includes aluminum or zinc, or a material that may dissolve in potassium hydroxide, a different solvent may be selected. For example, chromic acid may be used to dissolve AAO to leave behind aluminum nanostructures.

[0058] Referring to Fig. 4B, the nanostructures formed by cyclic loading (410) via a nanojackhammer may undergo post-processing (450) to form a great variety of products. Examples of the processing (450) includes but are not limited to removing material from the nanostructures (452) and/or adding features to the nanostructures (454). These will be further described in this document.

[0059] In another aspect, as illustrated schematically in Fig. 5A, a nanoforming apparatus (500) includes a source of excitation or an actuator (510) coupled to a horn (512). The terms

"horn", "vibratory horn", and "sonotrode" are used interchangeably to refer to a device configured to transfer vibratory energy towards the workpiece (600) and/or a tool (520). A computing device (514) may be coupled with the horn (512) and an actuator (510) such that a repeated loading force or a cyclic loading can be controllably applied to the workpiece and/or tool via the horn (512). The actuator may be operable by means of an alternating current excitation to drive the tool in repetitious movement toward and/or against the workpiece. The repeated movement of the tool may be periodic, with a regular or constant interval between sequential movements. The repeated movement of the tool may be aperiodic or irregular, with a different time interval between the movements. The horn (512) may be configured in various shapes and sizes. In some instances, the horn (512) may be made of titanium or other suitable metal. In some examples, the horn may be axisymmetric about a longitudinal axis. A workpiece holder (516) may be provided to hold the workpiece (600) in a desired position and/or orientation relative to the horn (512). The workpiece holder (516) may be adapted for the purpose of securing the workpiece (600). In some examples, the workpiece holder (516) includes a stage on which a workpiece (600) and a tool (520) are disposed in alignment with the longitudinal axis (517) defined by a longitudinal vibration (519) of horn. In some examples, the tool (520) is disposed between the horn (512) and the workpiece (600), as illustrated in Fig. 5A. In some other examples, the workpiece (600) is disposed between the horn (512) and the tool (520). In some examples, the tool (520) is separate from the horn (512), as illustrated in Fig. 5A. In some other examples, the tool (520) can be detachably coupled to the horn (512).

[0060] In some examples, the horn (512) is configured such that the horn (512) applies a loading force that is parallel to the longitudinal axis (517) and directed towards the tool (520) and the workpiece (600). In operation, the horn (512) is configured to apply a cyclic loading on the tool and the workpiece. The horn (512) is made to oscillate longitudinally (parallel to the longitudinal axis) with standing waves at a vibration amplitude. The horn (512) may be described as expanding and contacting in opposite directions along the longitudinal axis, such that the horn (512) intermittently or periodically pushes against the workpiece (600) and the tool (520) in one half cycle (loading half-cycle), and such that the horn retracts or releases pressure on the workpiece (600) and the tool (520) in a next half cycle (retreating half-cycle).

[0061] The nanoforming apparatus may be of various scale and configured to operate at different ranges of process parameters, depending on the desired scale of production. Some examples of process parameters are given here simply for the purpose of illustration, and it will be understood that embodiments of the present disclosure are not limited to these examples. In some examples, the horn (512) is configured to operate at an ultrasonic frequency. In some examples, the horn (512) may be configured to operate at any of the following frequencies: 15 kilohertz (kHz), 20 kHz, 30 kHz, 40 kHz, 70 kHz, 80 kHz, etc. For the purpose of illustration and not to be limiting, the examples of nanostructures described below can be formed by providing a cyclic loading of 20 kHz, with the loading force in a range of about 300 N (newton) to about 1600 N for a workpiece presenting a sample area of about 0.25 cm^2 (square centimeter). This relates to a nominal pressure in a range of about 12 MPa (megapascal) to about 64 MPa. The vibration amplitude of the horn may be within a range from 4 μm to 12 μm (depending on the apparatus, this could correspond to about 10% to 30% of the maximum amplitude of 40 μm).

[0062] The tool (520) is configured to present at least one nanojackhammer (550) to the workpiece (600). The tool (520) may be defined by a first tool surface (521) and a second tool surface (522) spaced apart from the first tool surface. Referring to Fig. 5B, for convenient reference, the first tool surface (521) refers to the part of the tool (520) that faces or that comes into contact with the workpiece (600). The second tool surface (522) faces away in an opposite direction from the first tool surface such that the first tool surface and the second tool surface define a tool thickness (523) therebetween. The second tool surface (522) may face the horn (512) as shown in Fig. 5A or, in other examples, the second tool surface (522) may face the workpiece holder (516). As illustrated in Fig. 5C, in some examples, the tool (520) may be sandwiched between two similar or dissimilar workpieces (600) such that the first tool surface (521) and the second tool surface (522) are used in nanoforming multiple workpieces concurrently. References in the present disclosure to the first tool surface (521) will therefore be understood to apply correspondingly to the second tool surface (522).

[0063] The tool (520) is configured with a plurality of nanowalls (530) which also serve as a corresponding plurality of nanojackhammers (550) at the first tool surface (521). The nanowalls (530) define a corresponding plurality of nanocavities (534) in the body of the

tool. The nanocavities (534) open at the first tool surface (521) to define corresponding nanopores (540). The nanojackhammers are disposed between the nanopores (540). The nanocavities (534) may be concave recesses with a recess depth shorter than the tool thickness. The nanocavities (534) may alternatively extend through the tool thickness (523) to open at the second tool surface (522). In some examples, the second tool surface (522) may be similarly configured as the first tool surface (521). In some examples, the tool (520) may be in the form of a honeycomb of nanocavities (534). In some examples, the nanocavities (534) are parallel to one another. In some examples, the nanocavities (534) are uniformly distributed in the tool. In some examples, the nanocavities (534) are distributed at different densities in different areas of the first tool surface. In some examples, all the nanocavities (534) in a tool are configured with a uniform cross-sectional shape and size. In some examples, the nanocavities (534) may be of different shapes and/or sizes. In some examples, the whole tool (520) is formed as one integral piece of anodized aluminum oxide (AAO) with an array of nanocavities (534). The tool (520) may be made of other materials, for example, the tool (520) may alternatively be made of silica or silicon, etc.

[0064] In the present disclosure, the term “nanoscale” refers to an article having a linear dimension that is in a range of a few hundreds of nanometers or in a range smaller than 1000 nm (nanometer). The nanopores (540) and the nanocavities (534) are of nanoscale. Each nanopore (540) can have a diameter or cross-sectional width of about 300 nm or smaller. A nanopore (540) is spaced apart from at least one other nanopore by less than 100 nm, to define a nanojackhammer (550) in between that is of nanoscale. That is, the nanowall (530) between adjacent nanopores (540) may be configured to serve as at least one nanojackhammer (550). The nanowall (530) between two adjacent nanocavities (534) has a wall thickness of less than 100 nm. Each nanojackhammer (550) is of nanoscale and presents a nanoscale area for contact with a surface of the workpiece (contact area 552). The nanowalls (530) / the nanojackhammers (550) may be interconnecting to form one unitary tool (520). The nanojackhammer (550) may be defined as part of the nanowall (530) or the part of the first tool surface (521) that contacts the workpiece (600), or the terms “nanojackhammer” and “nanowall” may be used interchangeably. For the sake of brevity, reference to a singular article may be construed as including a plurality of such articles, e.g., reference to “a nanojackhammer” or “the nanojackhammer” in the singular form may be

construed as including the plural form "nanojackhammers", and vice versa. Similarly, reference to "a nanowall" or "the nanowall" may be construed as including the plural form "nanowalls", and vice versa.

[0065] The nanojackhammer (550) (<100 nm in width) is configured to serve as an energy director to guide vibratory energy from the horn (512) to the contact area (552). In operation, the nanojackhammer (550) may be in contact with the workpiece at the contact area (552) throughout the process of forming the nanostructures. As the nanojackhammer applies cyclic loading to the workpiece, the nanojackhammer is alternately pushing against the workpiece (during a loading half-cycle) and releasing pressure on (retreating from) the workpiece (during a retreating half-cycle), the nanojackhammer (tool) is also progressively being displaced toward the workpiece (in a first direction parallel to the longitudinal axis).

[0066] According to embodiments of the present disclosure, the nanojackhammer (550) acts as a "highly energetic nanoblade" or as a chisel-like nanoscale bit to promote the formation of dislocations at the atomic/molecular level in the workpiece. Under cyclic loading (rapid and repeated application of forces/pressure to the workpiece by the nanojackhammer), the material of the workpiece (600) alternately experiences extremely high local stress near the contact area and a relaxation of the stresses. Fig. 6B and Fig. 6C schematically illustrate the different local lattice symmetries present at the end of a loading half-cycle and at the end of a retreating half-cycle respectively of a nth cycle of the cyclic loading on a silver workpiece (e.g., face-centered cubic FCC, hexagonal close packed HCP, body-centered cubic BCC lattice symmetries). Fig. 6D and Fig. 6E schematically illustrate the local lattice symmetries at the end of the loading half-cycle and at the end of the retreating half-cycle respectively of a (n+1)th cycle of the cyclic loading. At the end of the nth loading half-cycle, dislocations (810) are present and generally concentrated at the "root" or "corner" (reference line/plane 820) of the nanostructure (100), i.e., near the contact area or where the nanojackhammer interacts with the workpiece. The dislocations in the material are such that plastic deformation occurs in multiple locations in the workpiece. Lattice dislocation breaks a single grain of the material into smaller grains. The resulting smaller grains elongate and rotate, and migrate into the nanocavity.

[0067] The material of the workpiece thus exhibits an overall displacement alongside the

nanojackhammer (or parallel to the longitudinal axis), generally in a direction opposite to the direction in which forces are applied to the contact area (advancing direction / loading direction). At the end of the nth retreating half-cycle, some of the dislocations disappear through a recovery mechanism. Nevertheless, residual dislocations from the end of the nth retreating half-cycle facilitate the generation of more dislocations at the following (n+1)th loading half-cycle. This reduces the loading force required to advance or displace the nanojackhammer toward the workpiece. Displacement of the nanojackhammer results in displacing some of the material of the workpiece where there is less resistance, e.g., adjacent the nanowall and into a nanocavity. This can happen at a relatively low loading force because the deformation resistance of the material in the workpiece has been weakened by the alternating generation and recovery of dislocations (caused by the cyclic loading).

[0068] Again, at the (n+1)th retreating cycle, some but not all of the dislocations disappear, serving to facilitate the next cycle of dislocation generation. The retreating half-cycles allow the dislocations to recover partially and thus stop the dislocations from accumulating and piling up. The material in the workpiece can thus dislocate and move towards where there is less resistance (e.g., nanocavities).

[0069] Fig. 6F to Fig. 6I show the corresponding volume fractions of dislocations along a z-axis (i.e., along the longitudinal axis), with $z = 0$ corresponding to the reference line/plane 820. The graphs similarly show a greater volume of dislocations at the end of a loading half-cycle, near where an edge of the nanojackhammer or an edge of the nanopore would have come into contact with the workpiece. At the retreating half-cycles, the volume fraction of dislocations is smaller and almost zero at the root of the nanostructure. The resulting nanojackhammer effect can be described as a cyclic-loading induced softening of the material. The cyclic-loading induced softening enables the material to be reshaped at a lower loading force.

[0070] Hence, it is not necessary to heat up the material for the purpose of softening the material. The whole nanoforming process can thus take place with the material remaining in a solid state throughout the formation of the nanostructures. Nanoforming clearly involves a mechanism different from conventional nanoimprinting, forging, material deposition or growth.

[0071] To aid comparison, a dimensionless loading parameter δ is introduced to characterize the normalized net displacement of a nanojackhammer at each cycle as the nanojackhammer undergoes multiple cycles of advancing and retreating. As shown in Equation (1) below, δ is defined with respect to d1 and d2, where d1 denotes the displacement during each loading (advancing) half-cycle relative, and d2 denotes the displacement during each retreating half-cycle relative to the same reference:

$$\delta = (d1 - d2)/(d1+d2) \quad (1)$$

[0072] Thus, loading parameter δ=1 corresponds to a case where the loading force is applied in only the "loading" direction at a constant magnitude consistently throughout the whole process. For the sake of brevity, this is referred to as a "direct loading". $0 < \delta < 1$ describes "cyclic loading" with loading half-cycles and retreating half-cycles alternating according to a selected frequency.

[0073] Fig. 6A shows the load-displacement curves for a case with no cyclic loading (i.e., $\delta = 1$) and for cases with cyclic loading at different δ (namely, at $\delta = 0.05$, 0.10. 0.14, 0.19, and 0.24). Fig. 6J shows the steady-state mean loading force as a function of the loading parameter δ. It can be seen that, in a case with no cyclic loading ($\delta = 1$), displacement of the tool or an indenter beyond 0.5 nm would have required a force two or more times greater than that required with cyclic loading ($0 < \delta < 1$). On the other hand, it has been experimentally verified that direct loading or mechanical stress alone without cyclic loading barely made a dent on a piece of copper (Cu) metal foil, even when a force as high as 88,000 N is applied. In fact, the tool (made of AAO) broke into pieces when the direct loading force was increased to 250,000 N. One explanation for the high level of resistance encountered by direct loading is that as dislocations continuously nucleate, glide, accumulate, pile up and interact, these dislocations themselves serve to resist plastic deformation. Thus, the loading force required in conventional direct loading is so high that it would often exceed the limit of the apparatus unless one resorts to heating the substrate material.

[0074] Advantageously, a significantly smaller amount of energy is required to deliver the nanojackhammer effect, compared to the case where there is direct loading and no cyclic loading. There is no necessity to heat up the workpiece for the purpose of softening the material since the required loading force for nanoforming the material in the solid state is

relatively low. Advantageously, the nanoforming method of the present embodiments can be carried out under whichever conditions are convenient or available, including but not limited to ambient temperature, ambient pressure, etc. This means that the nanoforming method according to embodiment of the present disclosure can be performed in a wide variety of environments, such as those in manufacturing, laboratory, indoor and/or outdoor situations. Although the nanoforming method does not require a clean room environment, current clean room facilities may be used to carry out the methods of nanoforming disclosed herein. This advantageously facilitates the integration of the nanoforming method with existing infrastructure and existing manufacturing environments, without the need for replacing existing facilities.

[0075] Figs. 7A to 7E and Figs. 8A to 8E show that the nanoforming method can be used with nanojackhammers of different shapes or profiles. The nanojackhammer of Fig. 7A has a nanowall that meets the first tool surface at a right angle, and the nanojackhammer of Fig. 8A has a nanowall configured at an obtuse angle α (e.g., 102 degrees) to the first tool surface. Fig. 7B and FIG. 7C show sectional views of a silver (Ag) workpiece under deformation at the 9th loading half-cycle 9 and at the 9th retreating half-cycle respectively. FIG. 7D and FIG. 7E show sectional views of the same workpiece under deformation at the 10th loading half-cycle and at the 10th retreating half-cycle respectively. Figs. 8B to 8E show the corresponding diagrams for the nanojackhammer of Fig. 8A. In both cases, similar dislocations are generated at the loading half-cycles, and similar recovery mechanisms are observed at the retreating half-cycles. Thus, the nanojackhammer need not be limited to the profiles illustrated in the present disclosure. The examples illustrated herein are merely to aid understanding and are not intended to be limiting.

[0076] The loading force may be varied according to the desired aspect ratio of the nanostructures being formed. Fig. 9 shows a plot of aspect ratio (length/diameter) against loading force at a constant amplitude and frequency (20 kHz) based on experimental data from nanoforming of silver nanowires. Silver foils, each with a thickness of 100 μm were formed into nanostructures. The tool was 50 μm thick and the nanocavities have diameters of 300 nm. The results show a generally proportional relationship between the loading force and the aspect ratio. Thus, by controlling the loading force, it is possible to control the aspect ratio or the length (height) of the nanostructures formed.

[0077] Fig. 10 shows plots of aspect ratio against vibration amplitude at constant loading forces (1200 and 1500 N) and frequency (20 kHz). Silver foils of 100 μm were formed into silver nanostructures according to a nanoforming method of the present disclosure, under loading forces of 1200 N and 1500 N respectively. The process time was 30 s (second). Thus, for a given process time and loading force, nanostructures of different aspect ratios can be formed by controlling the vibration amplitude. It is also noted that the process time (time period in which the cyclic loading is applied) is remarkably short, i.e., the nanoforming process is rapid and highly efficient.

[0078] Thus, by controlling the process parameters, different nanostructures can be obtained from the nanoforming method disclosed herein. Fig. 11A to 11D are scanning electron microscopy (SEM) images showing silver (Ag) nanowires successfully obtained using the nanoforming method. The nanowires in these examples are of 200 nm (Fig. 11A), 2 μm (Fig. 11B), 5 μm (Fig. 11C), and more than 10 μm (Fig. 11D) respectively. In other experiments, silver nanowires ranging from 1 μm to 25 μm, and having similar diameters of about 250 nm, were formed. This corresponds to aspect ratios ranging from 4 to 100. In some experiments, silver nanowires with different diameters (ranging from 50 nm to 200 nm) and similar lengths of about 10 μm, were formed, corresponding to aspect ratios ranging from 200 to 50).

[0079] Figs. 12A to 12D are SEM images of gold (Au) nanowires of different diameters, obtained by the nanoforming method. In these examples, the nanostructures have a diameter of 300 nm (Fig. 12A), 80 nm (Fig. 12B), 50 nm (Fig. 12C), and 20 nm (Fig. 12D) respectively. The nanoforming method was performed with the corresponding process parameters shown in Table 1 below. The tools used in each of these cases have nanopores sized with a diameter of 300 nm, 80 nm, 50 m, and 20 nm respectively. The experiments also show that the whole nanoforming process can be completed relatively quickly in one minute or less.

Table 1. Process parameters for nanoforming of Au nanowires

Nanopore Diameter (nm)	Force (N)	Amplitude (%)	Time (s)
300	800	20	20
80	800	18	30
50	800	15	60

20	800	10	60

[0080] The nanoforming method can be used on different materials. SEM images of silver nanorods on a silver foil substrate, aluminum nanorods on an aluminum substrate, tin nanorods on a tin substrate, copper nanorods on a copper substrate, and bismuth nanostructures are shown in Figs. 13A to 13E respectively. A few examples of the process parameters used for nanoforming nanostructures of some of these metals are shown in Table 2 below. The nanoforming process is relatively fast and can be completed in 60 s or less.

Table 2. Process parameters for different metals

Metal	Force (N)	Amplitude (%)	Time (s)
Sn	600	10	20
Al	1000	15	30
Bi	800	10	30
Cu	1200	25	60

[0081] These experimental results demonstrate that the nanoforming method disclosed herein offers outstanding controllability over the dimensions of the nanostructures formed. Nanowires of different types of materials such as tin, aluminum, bismuth and copper are successfully formed, despite the large differences in their respective physical and chemical properties. Processes such as physical vapor deposition may be used to provide a workpiece in the form of a thin film deposited on a substrate. The thickness of the thin film is configurable to determine a length or a height of the nanostructures. The lateral dimensions of the nanostructures can be configured by selecting a tool with correspondingly sized nanocavities. Examples of nanostructures formed include nanorods (generally of a lower height compared to nanowires) of a metal on a substrate of a similar metal. Examples of nanodisks (generally of a lower height/thickness compared to nanorods) formed using the nanoforming method include silver nanodisks of 30 nm thickness on a silicon substrate or a plastic (Kapton tape) substrate, and gold nanodisks of 30 nm thickness (height) on a silicon substrate. Nanoforming can also be used on non-metal materials. Fig. 13F shows an SEM image of polymer nanorods formed on a polymer substrate according to the nanoforming method disclosed here.

[0082] High-resolution transmission electron microscopy (HRTEM) images of gold

nanowires obtained from nanoforming show perfectly ordered (111) and (200) lattice planes of face-centered cubic gold. This indicates that the nanojackhammer effect retained the polycrystalline nature of the gold foil which was used as the starting material (the workpiece). In other words, the nanostructures formed are characterized by a crystallinity similar to a crystallinity of the corresponding material in the workpiece. Fig. 14 shows the volume fraction of face-centered cubic (FCC) phase in a material when there is no cyclic loading ($\delta = 1$) and when there is cyclic loading ($0 < \delta < 1$). Overall, the volume fraction of the FCC crystalline structure keeps decreasing under direct loading ($\delta = 1$). In contrast, in the nanoforming method, the volume fraction of FCC crystalline structure remains within a certain range (10.9% to 13.4%) over the whole duration of cyclic loading ($0 < \delta < 1$). The product of nanoforming ($0 < \delta < 1$) can thus be found to retain the crystallinity of the starting material / workpiece.

[0083] This suggests that the properties of the nanostructures can be configured before the nanoforming process is carried out with a good degree of predictability, and is helpful for enabling cost-efficient commercial production. In one aspect, the nanostructures can be configured by configuring the workpiece. In one aspect, the desired crystallinity of the nanostructures (target crystallinity) can be configured by selecting a material for the workpiece with a crystallinity similar to the target crystallinity. That is, the nanoforming method enables the nanostructures to be formed with a selected crystallinity. The nanostructures formed by the nanoforming method can retain or share a similar crystallinity as the corresponding material in the workpiece. This is possible because the nanoforming method can be performed without heating the workpiece, which enables the nanostructures to be formed without undergoing a phase change or re-crystallization. The term "crystallinity" as used in this document refers to the structural order or the manner in which atoms/molecules are arranged in a solid material.

[0084] Fig. 15A schematically illustrates nanostructures (1500) obtained from a nanoforming method according to an embodiment of the present disclosure. Owing to the dislocations and displacement that occur in the course of nanoforming, for the same pristine materials, it is possible to obtain nanostructures (1500) that have a comparatively smaller average grain size (1502) and a less homogenous grain orientation compared to a product obtained from a conventional method such as thermal nanoimprinting (1510, Fig. 15B).

[0085] Advantageously, new nanostructures can be formed using the nanoforming method disclosed herein. A much wider range of products can be formed by the nanoforming method because nanostructures can be formed without the need to undergo heating that may promote unwanted reactions and/or changes to the materials. The ability to form nanostructures directly from solid material under ambient temperatures means that a wide variety of dissimilar materials can be combined and formed into one integral product. As illustrated, the products of nanoforming are not limited to metal products. Materials suitable for nanoforming include non-metals as well as metals.

[0086] As schematically illustrated in Figs. 16A and 16B, according to embodiments of the present disclosure, the workpiece (600) may be in provided as a stack (or layers) of dissimilar materials (1601, 1602, 1603, 1604) in the solid state. The respective thickness of each layer may be selected according to the target dimensions of the respective segment. Each layer of material in the workpiece may be as thin as desired or as permitted by the nature of the material. For example, gold foil of a few microns thick may be used as a layer in the workpiece. The layers in the workpiece (600) are shown spaced apart (Fig. 16A) to indicate that the layers need not be bonded together prior to the nanoforming process. It suffices to align the solid pieces together to receive cyclic loading. Cyclic loading via a nanojackhammer can then be applied, with the advancing displacement of the nanojackhammer represented by the arrow (1600) parallel to a longitudinal axis 517. After a nanoforming process time of shorter than a few minutes, the resulting nanostructure (100) formed. The nanostructure (100) is one integral unit of segments of the dissimilar materials (1601, 1602, 1603, 1604), in the same order as that in the stack (Fig. 16B). Each segment of material has a crystallinity similar to the crystallinity of the respective starting layer of material. If compared to conventionally produced products, the surface (1630) of the nanostructure may be described as having a higher degree of surface roughness. The segments of dissimilar materials form heterojunctions (1620) at the interfaces of the segments. Advantageously, the segments form relatively abrupt and distinct interfaces. The term “abrupt” describes an interface (1620, Fig. 17A) that is generally more distinct, thinner, and/or flatter (planar), compared to a diffused interface (1732, Fig. 17B). A diffused interface (1732) is characteristic of a conventional product (1730) that had undergone processing at an elevated temperature that promoted atomic diffusion.

[0087] One advantage of being able to form nanostructures without subjecting the materials to elevated temperatures or phase changes is that it is now possible to form nanostructures with widely dissimilar properties on the same nanostructure, without being limited by a disparity in the respective melting points. For example, the workpiece may include one or more types of metals and/or polymers. Such nanostructures can also serve as a basis for post-processing (450, Fig. 4B) to create an even greater variety of products. Post-processing can include one or more subtractive processes and/or one or more additive processes. Examples of subtractive processes include etching. Examples of additive processes include oxidation and chemical reactions to form other compounds. Various examples will be described below, including but not limited to, removing some material from the nanostructures (452) and/or adding features to the nanostructures (454).

[0088] According to embodiments of the present disclosure, nanostructures with at least one heterojunction can be formed in a single nanoforming step. The nanojackhammer effect enables the fabrication of heterojunctions of different materials, even if the mechanical properties of the different materials are at extreme or opposite ends of a spectrum. For example, the nanoforming method can form a nanowire array with bismuth-gold (Bi-Au) heterojunctions, even though bismuth is one of the most brittle metals known and gold is one of the most malleable metals known. Fig. 18A shows a SEM image of nanostructures with Au-Bi heterojunctions. Fig. 18B is a transmission electron microscopy (TEM) image and Fig. 18C is a corresponding energy dispersive X-ray spectroscopy (EDS) image of the same. The images show that the Bi-Au heterojunction formed by nanoforming is an abrupt interface.

[0089] Another product that can be formed using nanoforming is a nanostructure with an abrupt or distinct heterojunction of Sn-Au (tin-gold). Owing to the large difference between the melting point of tin (about 232 degrees Celsius) and the melting point of gold (about 1064 degrees Celsius), tin would have vaporized before gold reaches a sufficiently high temperature required for conventional nanoimprinting. Solution-phase synthesis would not have yielded an abrupt heterojunction in the manner of nanoforming. However, as shown in the SEM, TEM and EDS images of Figs. 19A to 19C respectively, nanostructures with abrupt and distinct gold-tin (Au-Sn) heterojunctions can be obtained by nanoforming.

[0090] SEM, TEM and EDS images copper-gold (Cu-Au) nanostructures are shown in Figs. 20A to 20C respectively, as one example of hard-soft metal heterojunctions formed by nanoforming. Other heterojunctions that can be fabricated using the nanoforming method include inert-reactive metal junctions (e.g., gold-silver) and metal-plastic junctions (e.g., gold-polycarbonate). Heterojunctions of Au-Cu-Ag-Al were also successfully formed on an aluminum substrate.

[0091] In one example, nanostructures with multiple segments are formed. As shown in the SEM and TEM images of Fig. 21A and Fig. 21B respectively, the nanostructure includes a gold-aluminum oxide-gold (Au-Al_2O_3-Au) multilayered/multi-segment configuration. It is noted that the image of the nanostructure in Fig. 21B shows a distinct and abrupt interface. The Raman intensity plot for quorum sensing using Au-Al_2O_3-Au nanowires is shown in Fig. 22, together with plots for quorum sensing using Au-Al_2O_3-Au nanowires decorated with polyethylene glycol (Au-Al_2O_3-Au + PEG), gold nanowires (Au), and gold nanowires decorated with PEG (AU + PEG). The Au-Al_2O_3-Au heterojunctions provided in nanostructures of the present embodiment show significant signal enhancement over nanowires of pure metallic gold. Even when the heterojunctions are decorated by PEG and the signal intensity is slightly depressed, it still offers an improvement over that of gold nanowires and gold nanowires decorated with PEG. This demonstrates that the nanostructures disclosed herein are strong viable options for use as active elements in sensors and other products. Various compound-metal heterojunctions useful in spintronics and/or catalysis can thus be relatively easily formed on the basis of the nanoforming method disclosed herein.

[0092] The heterojunctions may also be configured with a nanogap between segments, in which the nanogap width (spacing between the segments) is controllable. In some examples, a sacrificial layer can be provided in the workpiece, such that in a post-processing step, at least some of the sacrificial material can be etched away. In some examples, all the sacrificial material is etched away or otherwise removed from the nanostructure formed. Referring to Fig. 23 to illustrate, a sacrificial layer/segment of chromium (222) may be formed between two other layers/segments (201, 202) of gold. After the nanostructure is formed, an etchant is introduced to etch away some of the chromium (222), leaving behind a spacer segment (224) of a smaller diameter than one or both of the neighboring segments

(201, 202). A nanogap can thus be formed between two segments (201, 202). The two segments (201, 202) may be of similar or dissimilar materials. The size of the separation between the two segments (201, 202) may be configured by controlling the dimensions of the sacrificial segment (222) and/or the amount of the sacrificial material that is removed in post-processing. Previous to the nanoforming method disclosed herein, such a resultant product would be difficult to form. For example, using conventional nanoimprinting, the elevated temperature required during conventional thermal nanoimprinting would have caused the chromium metal to form chromium oxide, and it would have been significantly more difficult to etch away chromium oxide.

[0093] In some examples, the sacrificial layer is also the substrate such that removal of the sacrificial layer in entirety (212) leaves behind free-standing or unconnected nanostructures (214), as opposed to nanostructures that are connected to a common substrate (252). In another example, it may be desired to etch away only a part of the substrate so as to create different thicknesses (242) at different locations of the substrate.

[0094] Post-processing can also include subjecting the plurality of nanostructures to conditions conducive to oxidation (or other reactions) of selected segments while leaving other segments unchanged. Thus, additional features (232) may be formed on selected segments (203) of the nanostructures by introducing one or more reactants to undergo chemical reaction with one or more of the segments of the nanostructure. The diameter of nanostructures may similarly be varied at selected locations through one or both of an oxidation process and an etching process (252, 262). Of course, oxidation is only one of many possible reactions or processes that can be carried out as part of post-processing. These are only a few non-limiting examples. The actual possible range of products that can be formed is too wide to enumerate in the present document.

[0095] It can be appreciated from the disclosure herein that the use of solid starting materials can greatly improve the uniformity of the product (as compared with the solution-phase synthesis) and enable more precise control over the fabrication process as well as the resultant products. All segments of dissimilar materials in one nanostructure can be formed simultaneously by one nanoforming process, if so desired. There is no need for new processing parameters, tool changes or additional intermediate processing steps between the

formation of different segments of dissimilar materials. In other words, a nanostructure with segments of dissimilar materials can be formed in a one-step nanoforming method. This is possible even when the target product or the target nanostructures include materials of dissimilar properties with distinctly different properties. It is noteworthy that each nanostructure remains as one integral unit even though it may include contiguous (or immediately adjacent and adjoining) segments of dissimilar materials having widely different properties. In one aspect, the nanoforming method provides a less costly and no less precise process for manufacturing heterojunctions, when compared to conventional processes such as chemical vapor deposition or molecular beam epitaxy.

[0096] To provide another example, a surface-enhanced Raman spectroscopy (SERS) platform for quorum sensing (QS) can be made using the nanoforming method of the present disclosure, as illustrated in Fig. 22. The SERS platform includes plasmonic nanostructures made by a nanojackhammer tool. QS is a phenomenon of cell-to-cell communication which is often deployed by bacteria to detect and respond to cell population density by producing, secreting, and sensing autoinducers. In this example, *Pseudomonas aeruginosa* is chosen as a model bacterium to form biofilms on the sensing platform. The QS-controlled metabolite pyrocyanin is Raman active, and its Raman signals can be measured to reflect the level of QS inside the biofilms. The sensing platform is configured as an array of nanorods generally aligned in a preferred direction. The nanorods are formed from a workpiece that is a silver-alumina-silver tri-layer thin film deposited on a silver foil substrate, using the nanojackhammer tool. After the nanorods are formed, a partial etching of the alumina segment is carried out in a sodium hydroxide solution. The resulting product is an array of nanorods, each nanorod being about 360 nm in length (height) and about 130 nm thick (in terms of a diameter or a lateral dimension), with 13 nm nanogaps between two consecutive silver segments. Pure silver nanorods with similar overall dimensions but without nanogaps are also fabricated for comparison. Numerical calculations show that the electric field enhancement insider the nanogap is increased by a factor of 1180. In contrast, the electric field of pure silver nanorods (without nanogaps) is enhanced by only 15 times between nanorods. To experimentally verify that the Raman enhancement originates from the nanogap, two groups of samples are prepared for comparison: Sample S1 in which Raman dye 4-mercaptopyridine (4-MPy) is adsorbed on the entire surface of the nanorods

(including the silver surfaces and the nanogaps), and Sample S2 in which the 4-MPy is selectively adsorbed inside the nanogaps. Sample S2 is prepared by blocking/masking the nanorod surfaces with thiolated polyethylene glycol (HS-PEG) before etching the alumina segments to form the nanogaps. The Raman intensity is found to be similar in S1 and S2, suggesting the dominant role of the nanogap in SERS signal enhancement. In contrast, the Raman intensity of 4-MPy is greatly reduced after the nanorod surface is blocked with HS-PEG in the control sample of pure silver nanorods (without nanogaps).

[0097] After culturing bacteria on the sensing platform for 18 hours, an aggregation of bacteria is evident, indicating the formation of a biofilm. The nanorods with nanogaps exhibit a strong Raman spectrum comparable to a conventional sensing platform that has more than 50 layers of closely packed gold nanorods (each about 91 nm long and 27 nm thick) with supercrystals. The sensing platform made using the nanojackhammer delivers a homogenous Raman intensity, as reflected by the high degree of similarity (variation below 10%) between spectra collected from six different locations across the sensing platform. In addition, considering that the sensing platform made using the nanojackhammer takes only a few minutes to fabricate nanostructures that are four times longer than what the conventional sensing platform takes a few days to fabricate, one can conclude that the sensing platform made using the nanojackhammer outperforms the conventional sensing platform. The successful detection of QS-modulated molecules by the nanoformed sensing platform suggests additional applications in the screening of potential QS inhibitors for bacterial infection treatment.

[0098] Products of the nanoforming method can be useful in a wide variety of applications. For example, nanostructures with gold segments can be used to enhance the surface electromagnetic field in SERS, or to enhance surface plasmon for enhanced optical absorption and detection. Nanostructures with noble metal segments formed by the nanoforming method can be used in diagnostic biomedical imaging, physiotherapy, drug delivery, and other biomedical applications. Nanostructures with segments of transitional metals can be used as catalysts in chemical reactions.

[0099] The nanoforming method is useful for processing reactive metals, metal junctions and other structures, including very reactive metals. For example, the nanoforming method

can form products having heterojunctions of metal-metal and/or metal-metal compound in a scalable manner suitable for a wide range of applications. Examples of applications include in catalysis, including but not limited to hydrogenation of carbon dioxide to methanol, water-gas shifting, dry reforming of methane, direct methane-to-methanol conversion, and other chemical synthesis processes. Such heterojunctions also find applications in areas of transport, such as carbon monoxide oxidation (to remove carbon monoxide in emitted gas) in vehicles, and hydrogen electrolyzer and fuel cells in electrical vehicles. Nanoforming enables the high-index facets of crystals (crucial for enhanced catalytic activity in catalysis but thermodynamically unstable at high temperatures) to be retained in the final nanostructures since nanoforming can be carried out at room temperature (ambient temperature). Nanoforming also provides a more viable way of processing metallic catalysts, especially those of reactive metals that tend to undergo oxidation, alloying or phase change in high-temperature processes.

[0100] Advantageously, the nanoforming process is highly energy efficient, requiring relatively low amounts of energy (compared with most conventional manufacturing processes), and can be carried out at room temperature and atmospheric pressure, or other temperatures/pressures if needed. The nanoforming process can be described as a rapid forming method. It is highly efficient in terms of the process time required. In the examples described, the average process time to form nanostructures of the desired dimensions is in the range of tens of seconds to a few minutes.

[0101] The variety of heterojunctions, nanostructures, and products of nanoforming, etc., is too great to be enumerated herein. All examples described herein, whether of apparatus, methods, materials, or products, are presented for the purpose of illustration and to aid understanding, and are not intended to be limiting or exhaustive. Various changes and modifications may be made by one of ordinary skill in the art without departing from the scope of the invention as claimed.

CLAIMS

1. A method comprising:

applying a cyclic loading to a contact area on a workpiece via a nanojackhammer such that at least a part of the workpiece is displaced to form one or more nanostructures adjacent the contact area, wherein the cyclic loading is applied for a process time and wherein the workpiece is in a solid state throughout the process time.

2. The method according to claim 1, wherein the one or more nanostructures comprises at least one material, and wherein the one or more nanostructures are formed at a process temperature below a hot embossing temperature characteristic of the at least one material.

3. The method according to claim 2, wherein the at least one material comprises at least one metal.

4. The method according to any one of claims 1 to 3, wherein the nanojackhammer is of nanoscale, and wherein the nanojackhammer forms a part of a nanowall, the nanowall defining at least one nanocavity configured to receive the one or more nanostructures.

5. The method according to any one of claims 1 to 4, wherein the one or more nanostructures comprises one material or at least two dissimilar materials, and wherein the one or more nanostructures are formed at a process temperature at which the one material or all of the at least two dissimilar materials are in a solid state.

6. The method according to any one of claims 1 to 5, wherein the one or more nanostructures are formed under ambient conditions.

7. The method according to any one of claims 1 to 6, wherein the cyclic loading comprises alternating loading half-cycles in which the nanojackhammer applies pressure to the contact area and retreating half-cycles in which the nanojackhammer releases pressure on the contact area.

8. The method according to any one of claims 1 to 7, wherein the cyclic loading is configured to promote generation of dislocations in the loading half-cycles and to enable recovery of at least some of the dislocations in the retreating half-cycles.

9. The method according to any one of claims 1 to 8, wherein the process time is in a range from a few seconds to a few minutes.

10. The method according to any one of claims 1 to 9, wherein the material of the workpiece comprises a plurality of dissimilar materials, and wherein each nanostructure includes segments of the materials.

11. The method according to claim 10, further comprising modifying the one or more nanostructures by etching away at least some of one of the dissimilar materials.

12. The method according to claim 10, further comprising removing some of one of the materials to form a nanogap between two of the segments.

13. The method according to claim 10, further comprising forming compounds with one of the materials on the one or more nanostructures to form features on the one or more nanostructures.

14. A product comprising nanostructures formed by the method according to any one of claims 1 to 13, wherein each of the nanostructures has at least one segment characterized by a crystallinity similar to a crystallinity of a corresponding layer in the workpiece.

15. The product according to claim 14, wherein each of the nanostructures comprises two contiguous segments of dissimilar materials having different physical properties and/or chemical properties.

16. The product according to claim 14 or claim 15, wherein each of the nanostructures comprises a spacer segment contiguous with two other segments, the spacer segment being

of a material dissimilar to each material of the two other segments, and wherein the spacer segment is configured to define a nanogap between the two other segments.

17. The product according to any one of claims 14 to 16, wherein each of the plurality of nanostructures comprises at least one heterojunction defined by an abrupt interface between two segments.

18. A product comprising at least one nanostructure formed from a material by cyclic loading according to any one of claims 1 to 13, the at least one nanostructure being characterized by a crystallinity consistent with the material being in a solid state throughout the process time.

19. The product according to claim 18, wherein the at least one nanostructure comprises at least one heterojunction, the at least one heterojunction being defined by an abrupt interface between two segments.

20. The product according to claim 18 or claim 19, wherein the at least one nanostructure comprises at least two segments of dissimilar materials, the at least two segments being one of contiguous segments or spaced apart segments.

21. The product according to any one of claims 18 to 20, wherein the at least two segments comprise a segment of a first material and a segment of a compound of a second material.

22. The product according to any one of claims 18 to 21, wherein the at least one nanostructure comprises a spacer segment contiguous with two other segments, the spacer segment being configured to define a nanogap between the two other segments.

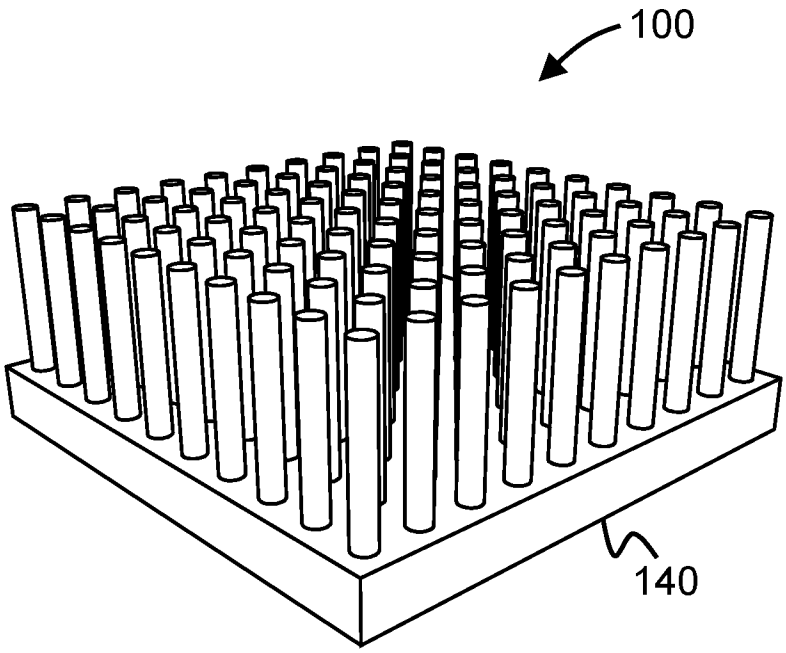

Fig. 1

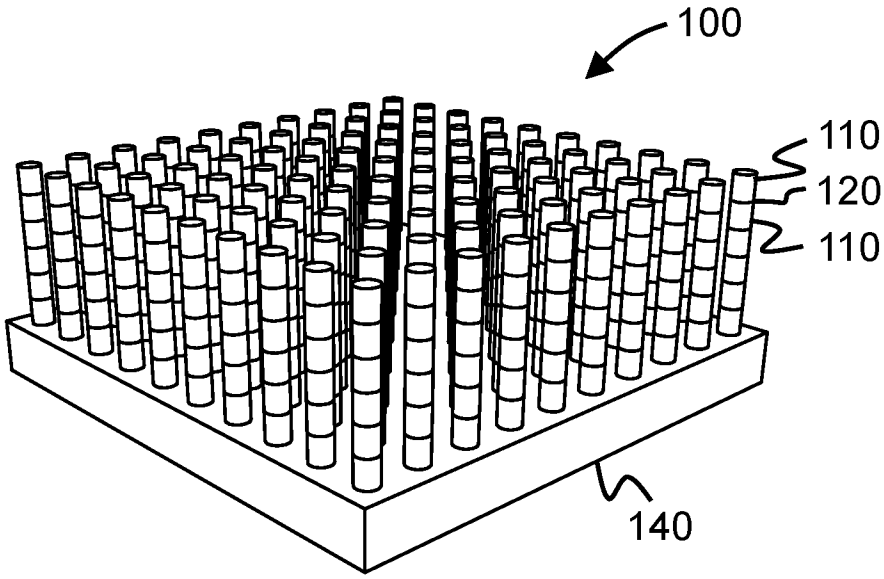

Fig. 2

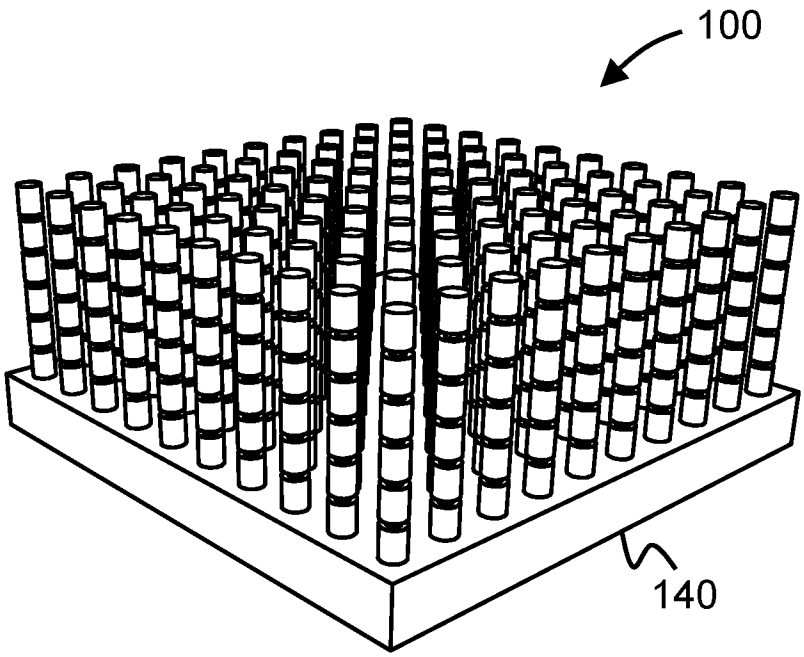

Fig. 3A

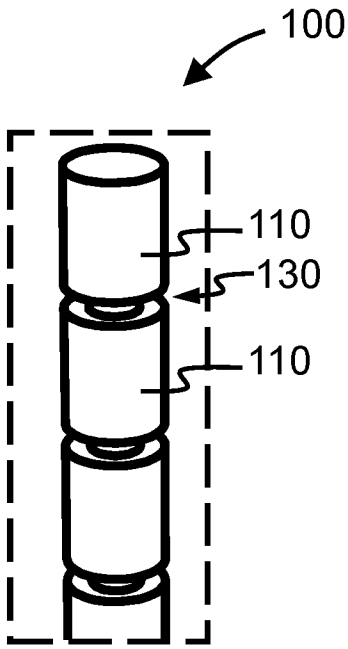

Fig. 3B

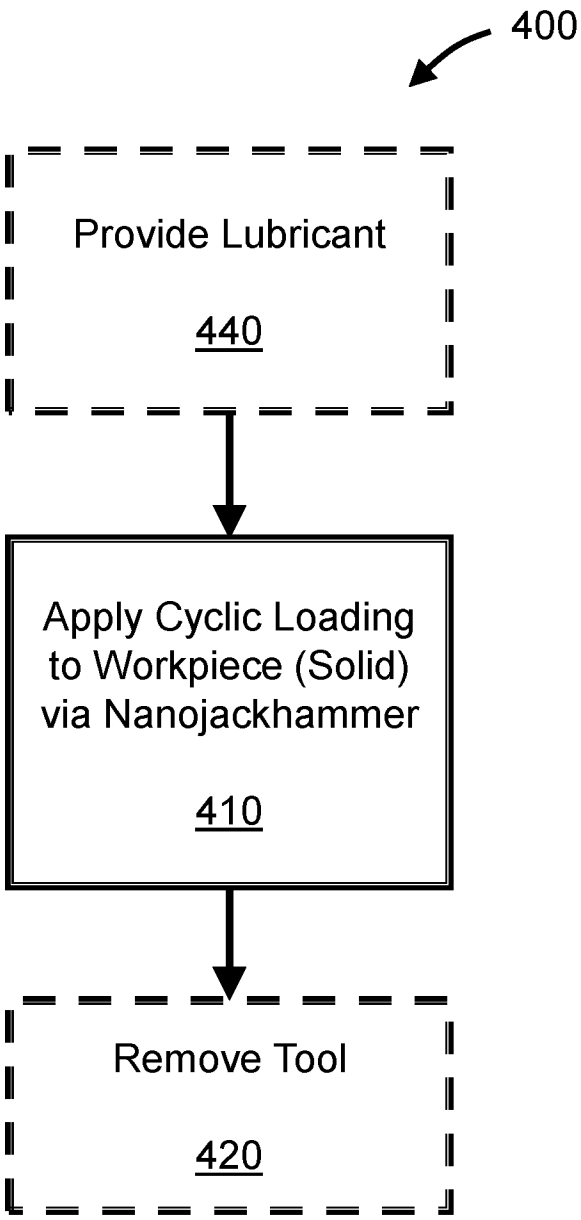
400
Provide Lubricant
440
Apply Cyclic Loading to Workpiece (Solid) via Nanojackhammer
410
Remove Tool
420

Fig. 4A

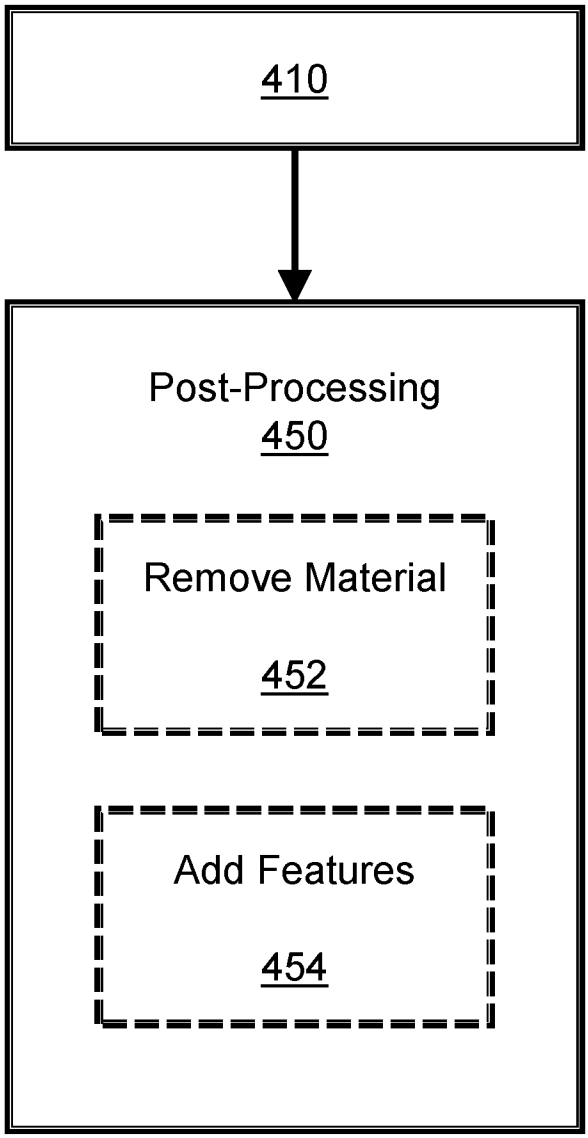
410
Post-Processing
450
Remove Material
452
Add Features
454

Fig. 4B

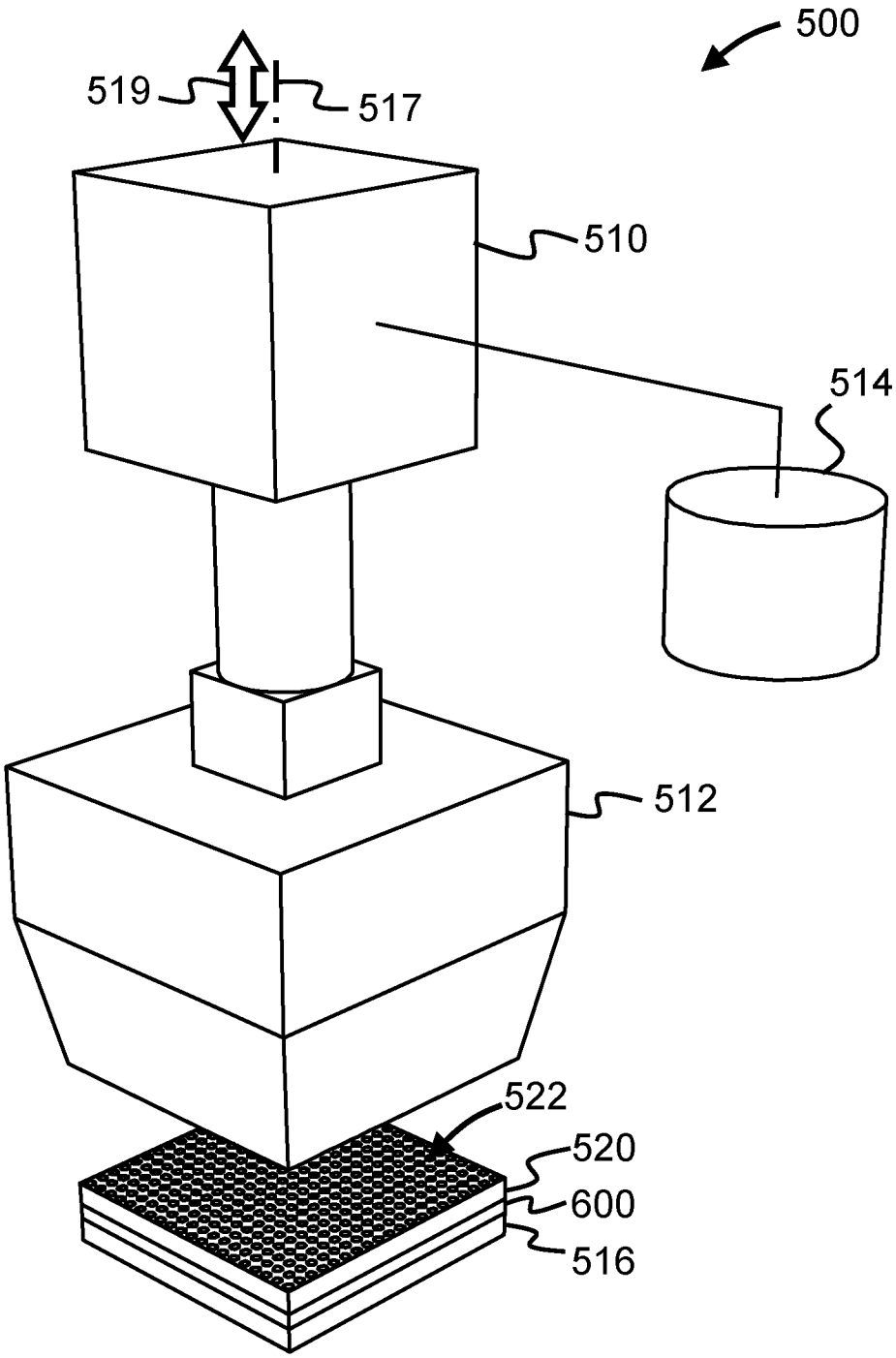

Fig. 5A

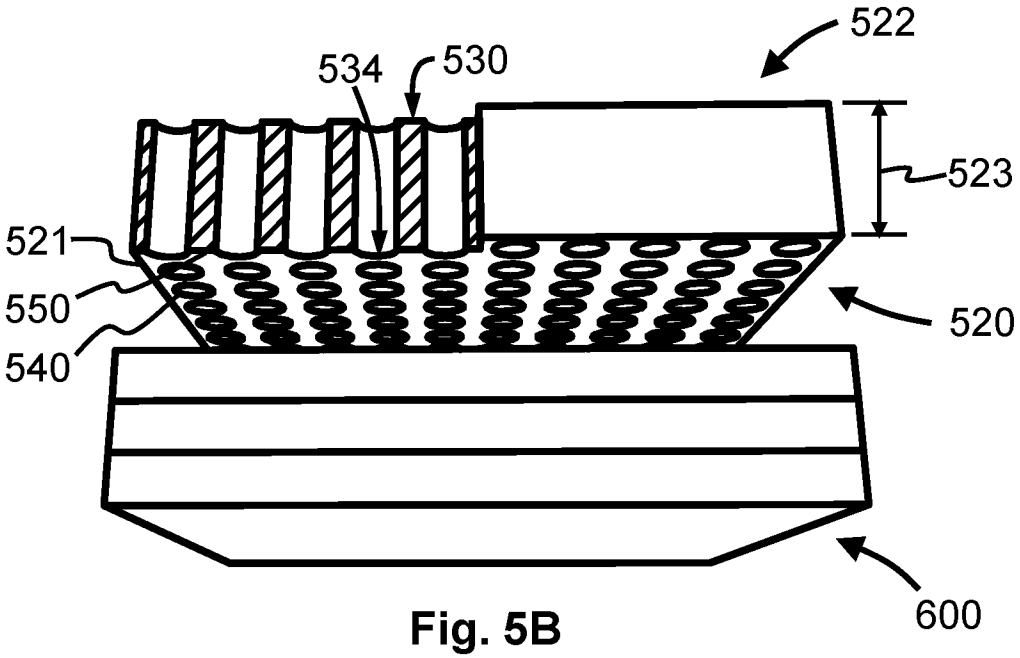
522
534
530
523
521
550
520
540
600

Fig. 5B

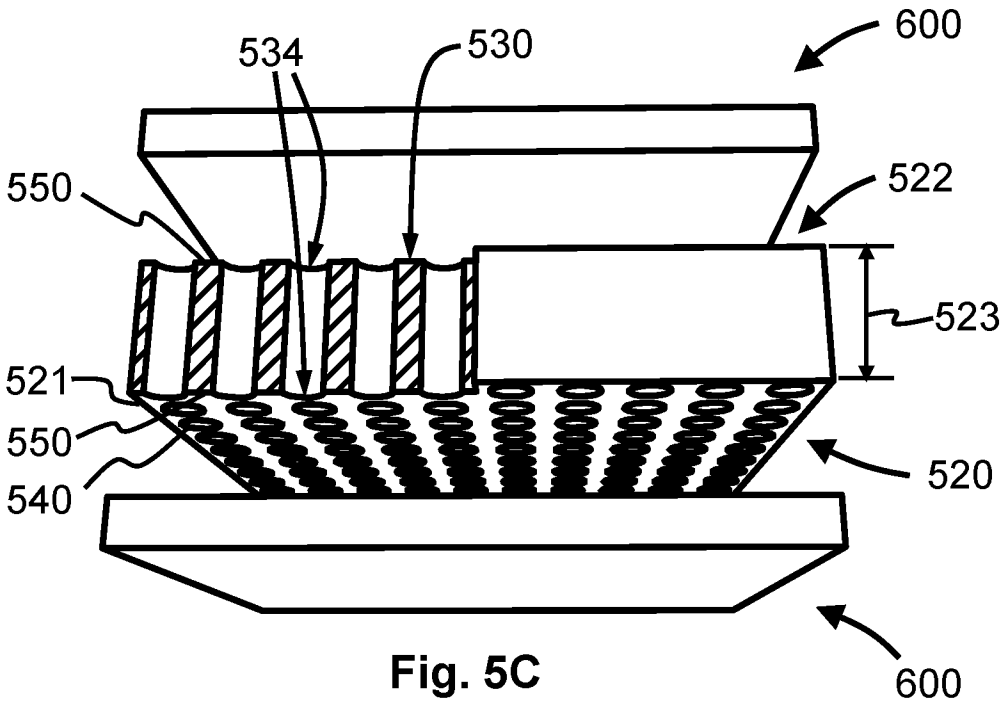
600
534
530
550
522
523
521
550
520
540
600

Fig. 5C

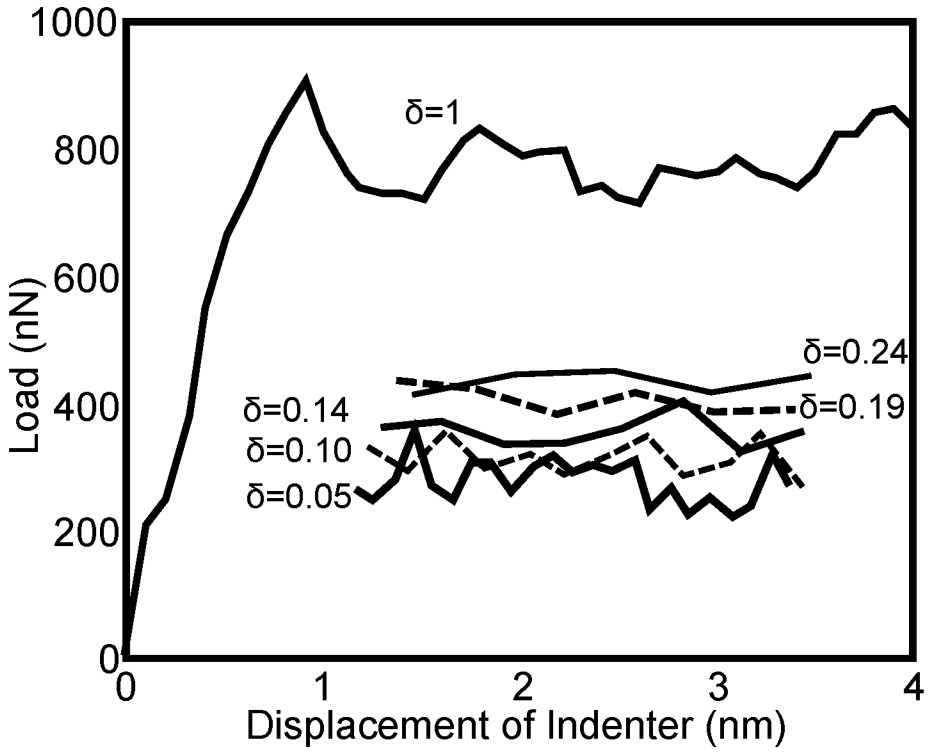
1000
800
600
400
200
0
Load (nN)
δ=1
δ=0.24
δ=0.19
δ=0.14
δ=0.10
δ=0.05
0
1
2
3
4
Displacement of Indenter (nm)

Fig. 6A

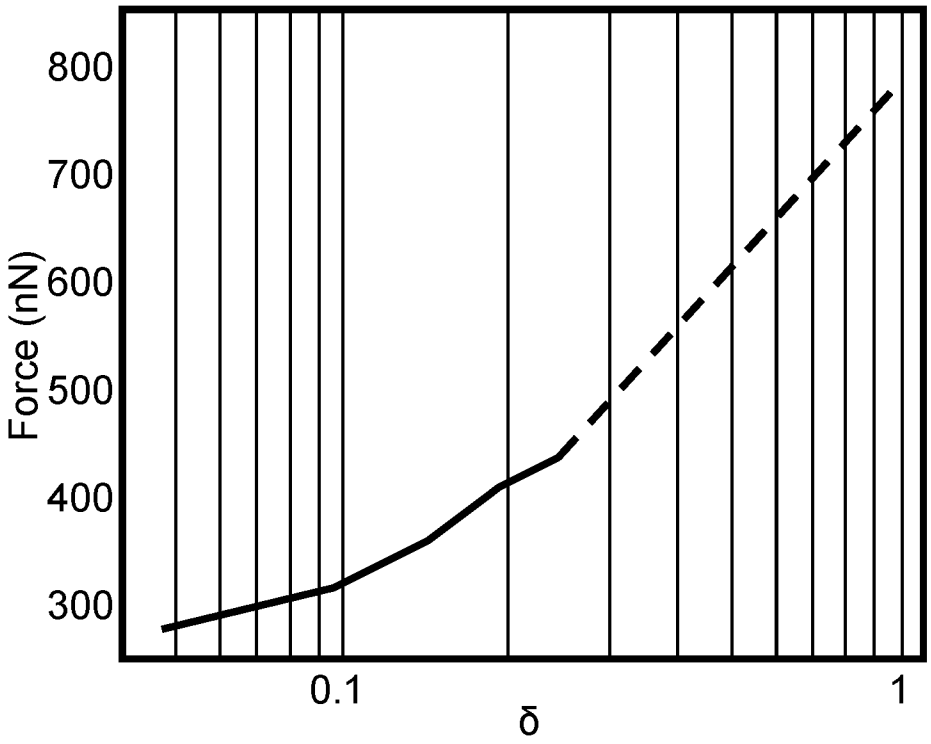
800
700
600
500
400
300
Force (nN)
0.1
1
δ

Fig. 6J

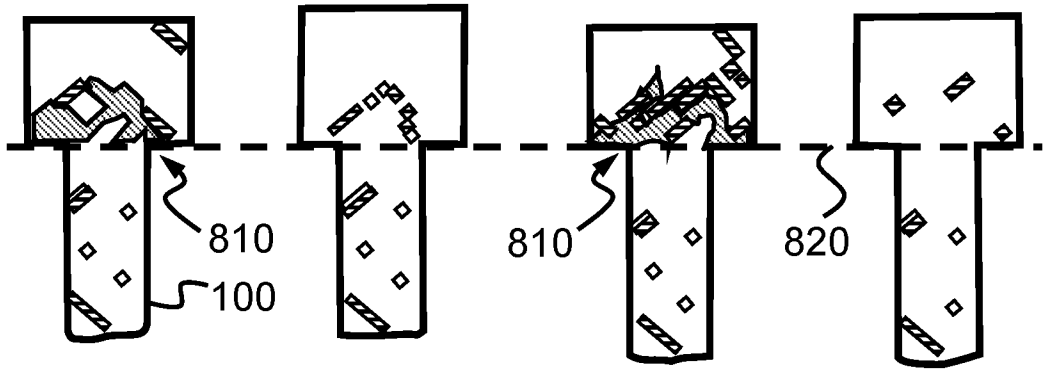

Fig. 6B Fig. 6C Fig. 6D Fig. 6E

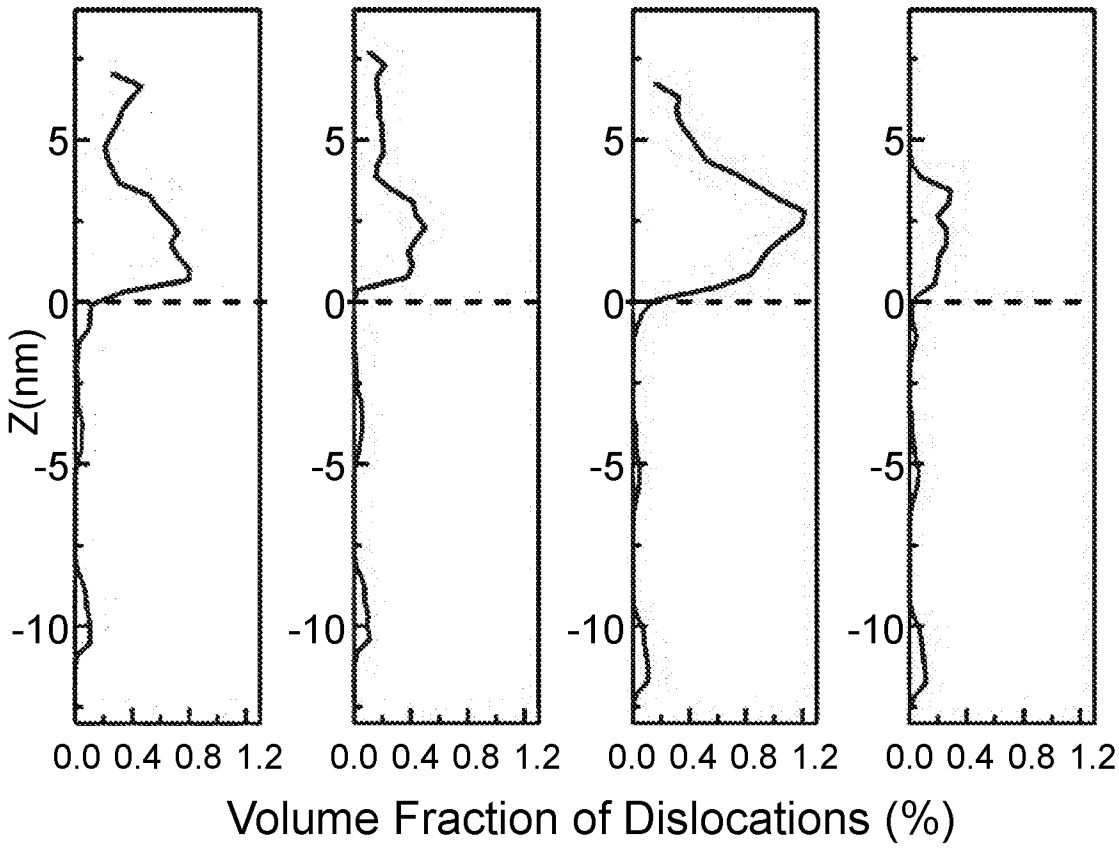

Fig. 6F Fig. 6G Fig. 6H Fig. 6I

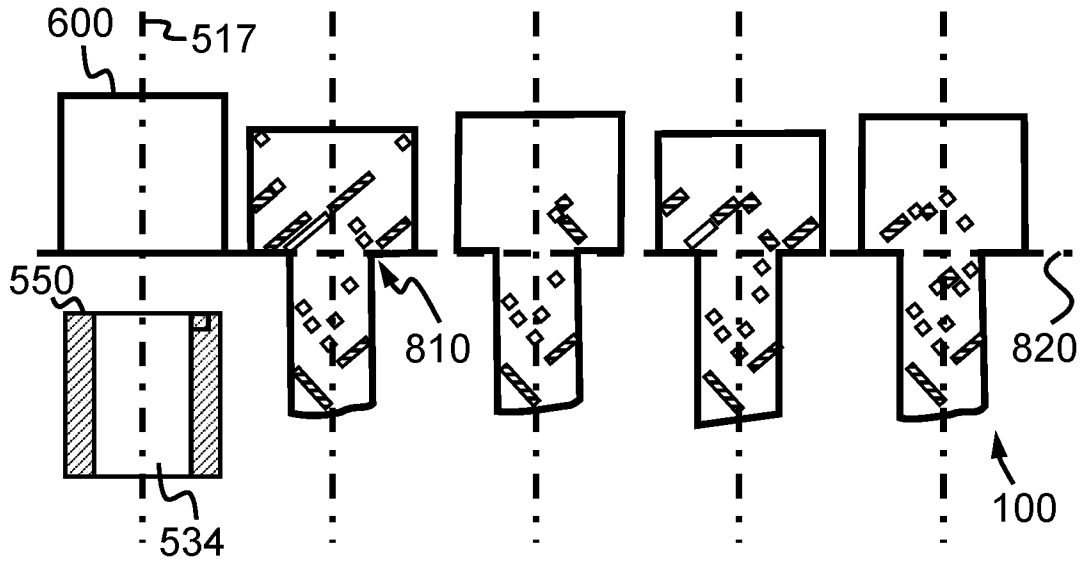

Fig. 7A Fig. 7B Fig. 7C Fig. 7D Fig. 7E

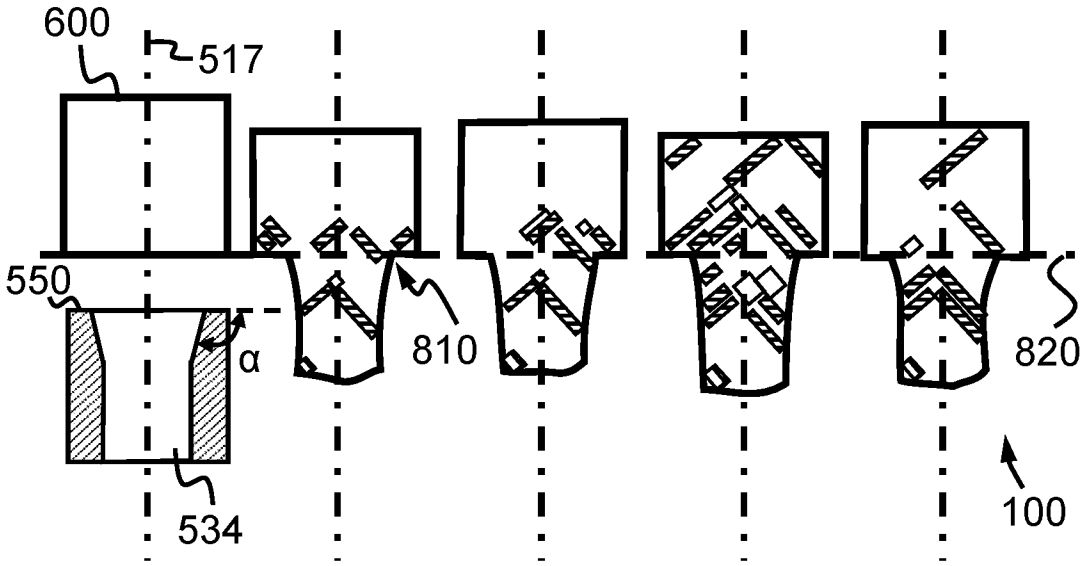

Fig. 8A Fig. 8B Fig. 8C Fig. 8D Fig. 8E

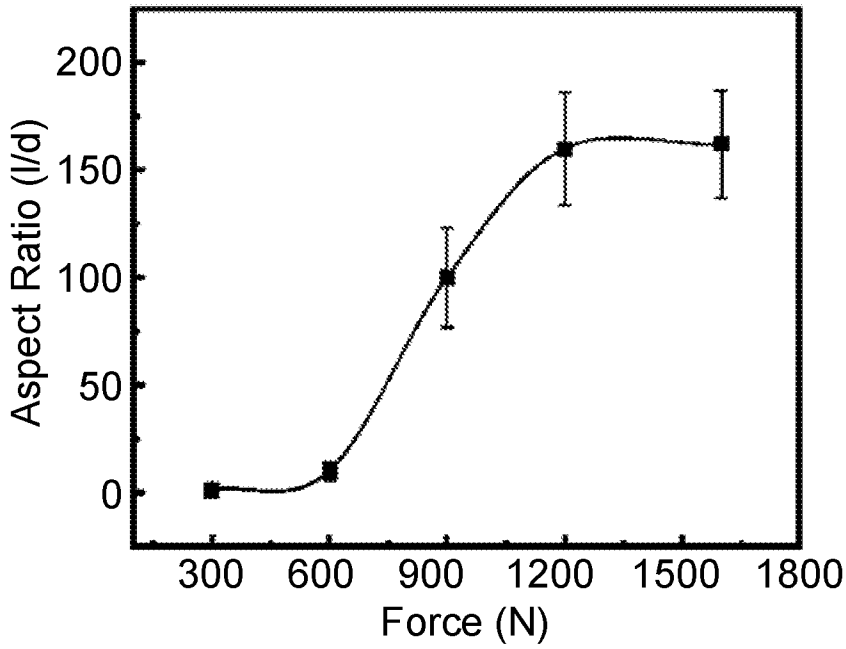
Aspect Ratio (l/d)
200
150
100
50
0
300
600
900
1200
1500
1800
Force (N)

Fig. 9

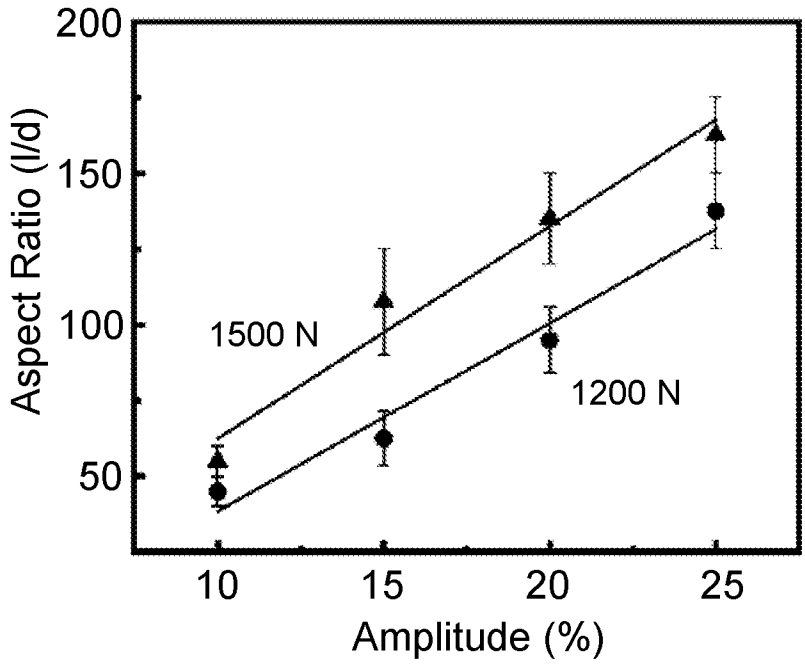
Aspect Ratio (l/d)
200
150
100
50
1500 N
1200 N
10
15
20
25
Amplitude (%)

Fig. 10

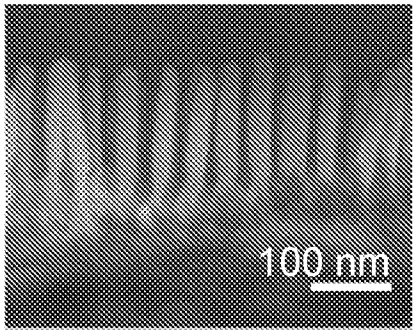

Fig. 11A

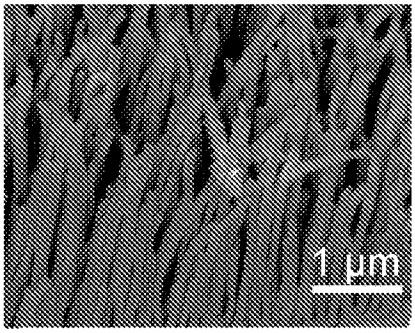

Fig. 11B

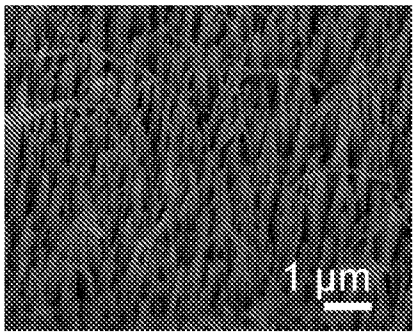

Fig. 11C

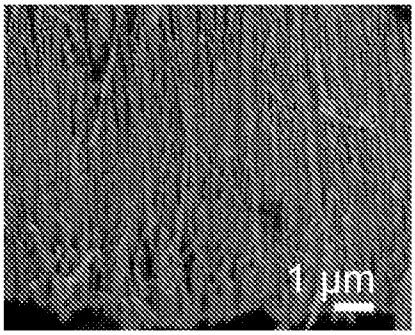

Fig. 11D

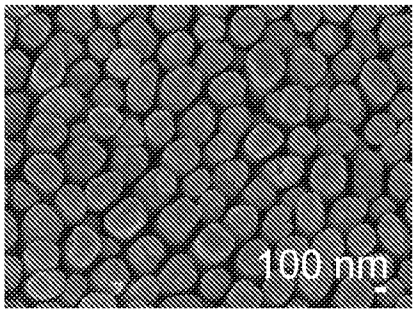

Fig. 12A

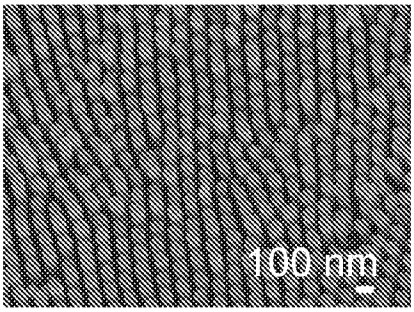

Fig. 12B

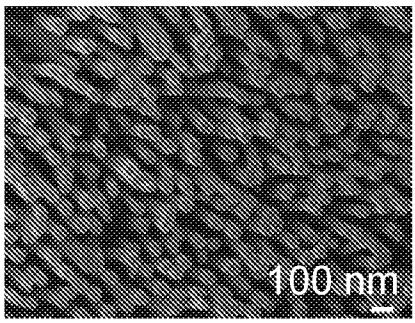

Fig. 12C

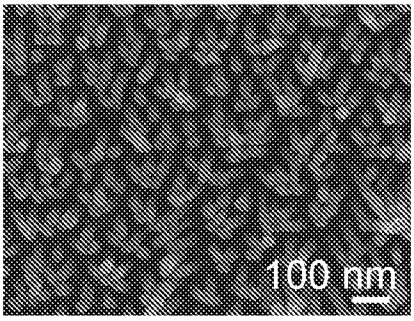

Fig. 12D

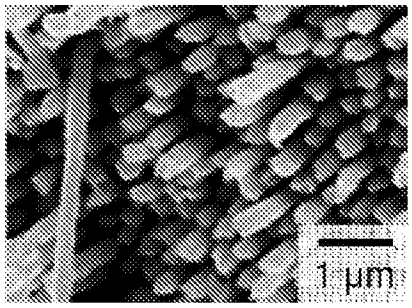

Fig. 13A

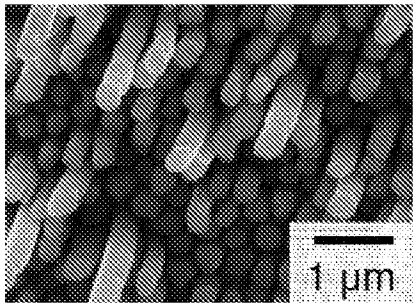

Fig. 13B

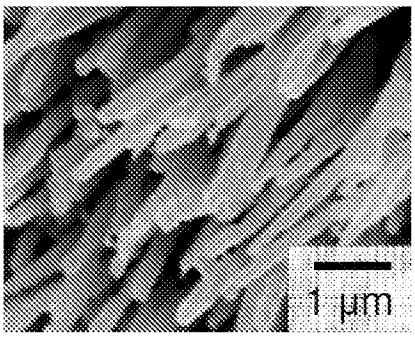

Fig. 13C

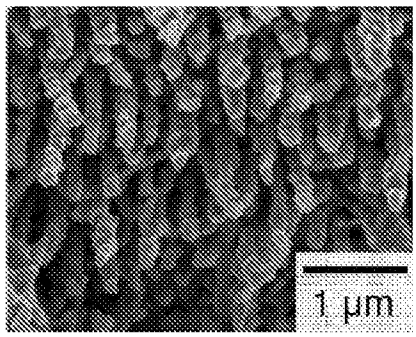

Fig. 13D

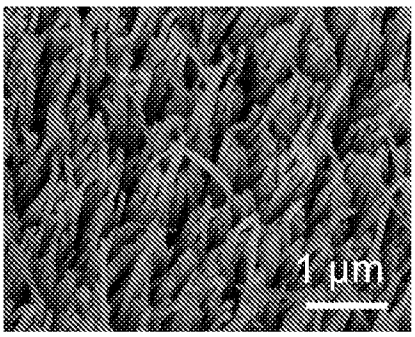

Fig. 13E

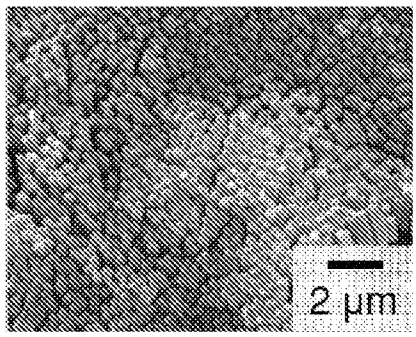

Fig. 13F

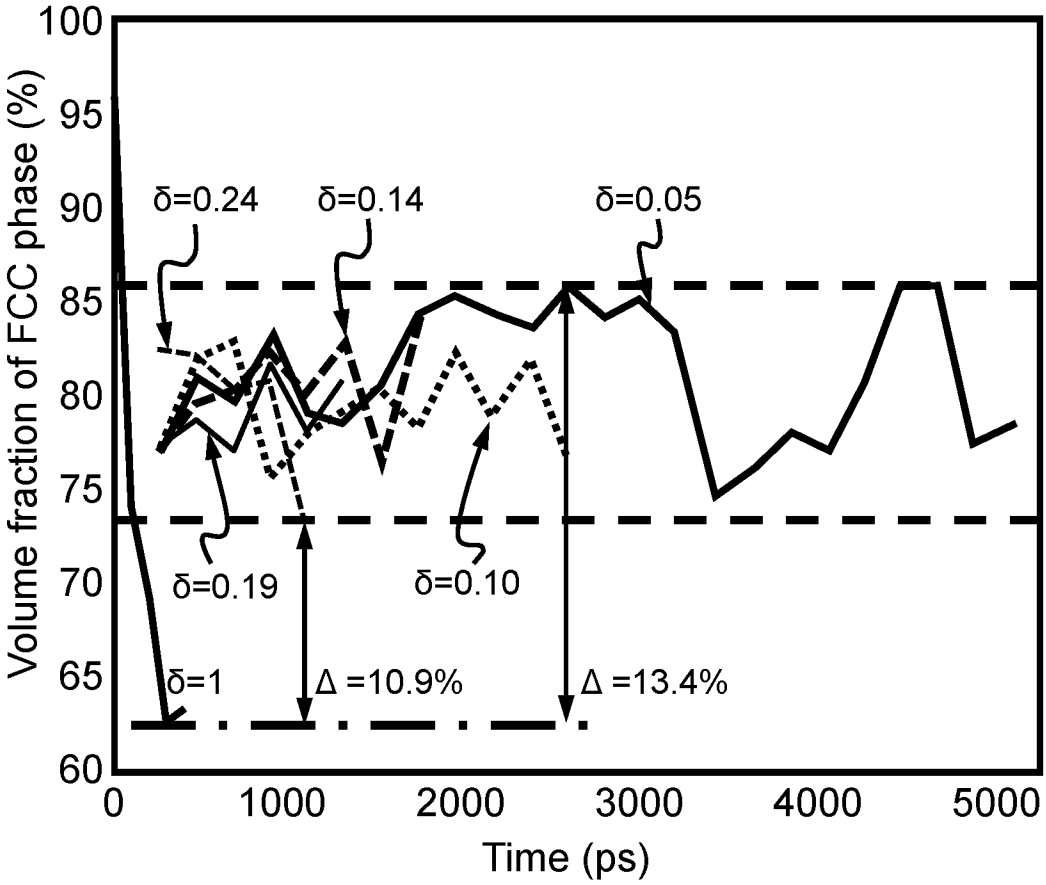
100
95
90
85
80
75
70
65
60
Volume fraction of FCC phase (%)
0
1000
2000
3000
4000
5000
Time (ps)
δ=0.24
δ=0.14
δ=0.05
δ=0.19
δ=0.10
δ=1
Δ =10.9%
Δ =13.4%

Fig. 14

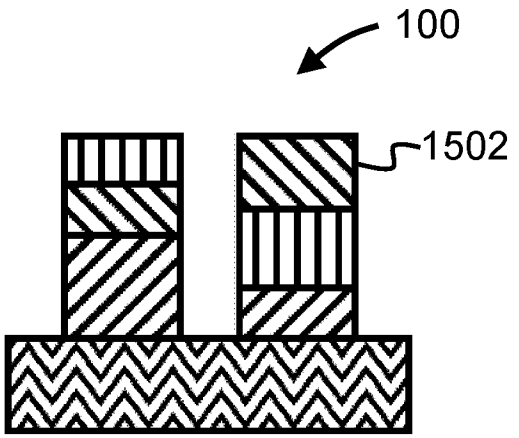

Fig. 15A

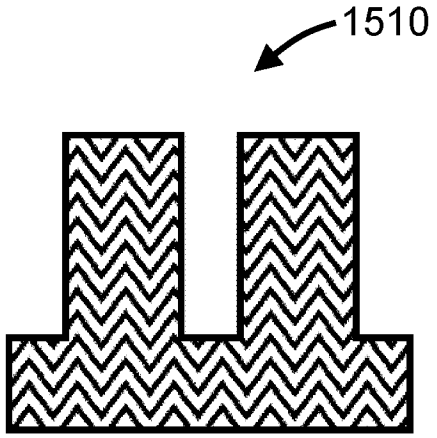

Fig. 15B

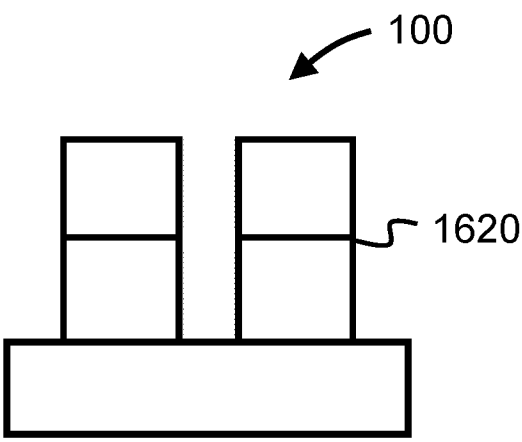

Fig. 17A

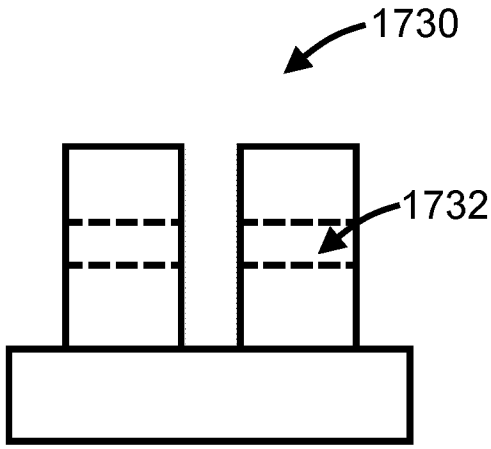

Fig. 17B

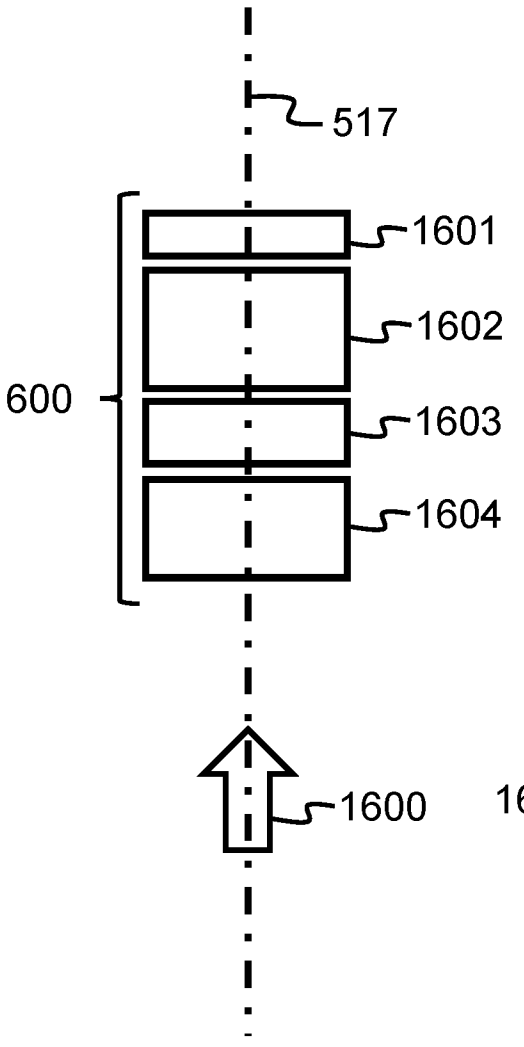

Fig. 16A

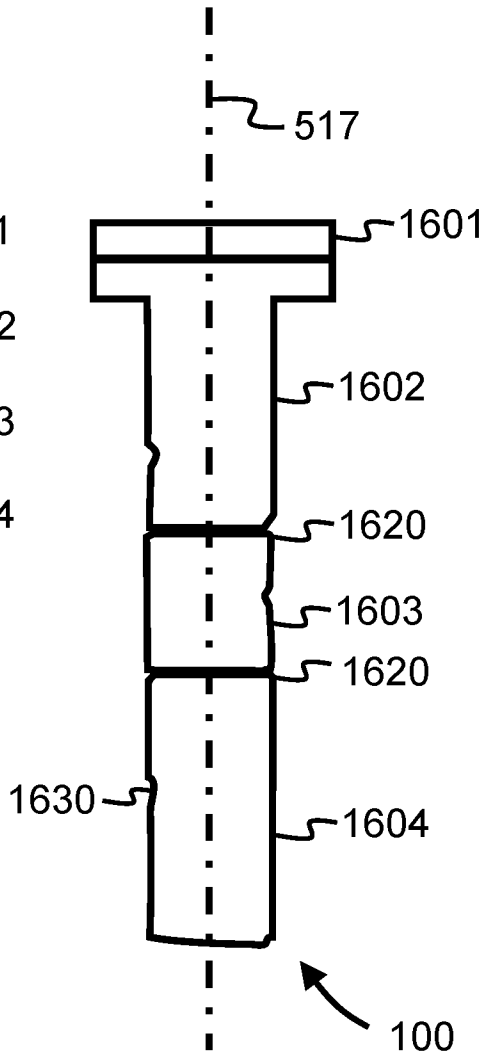

Fig. 16B

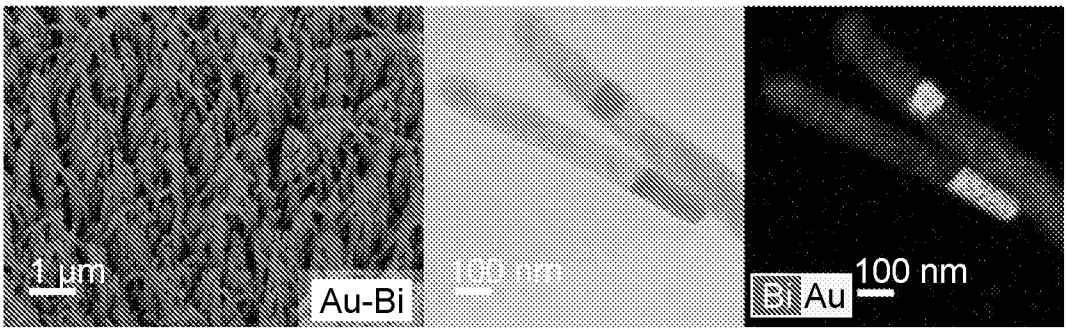

Fig. 18A Fig. 18B Fig. 18C

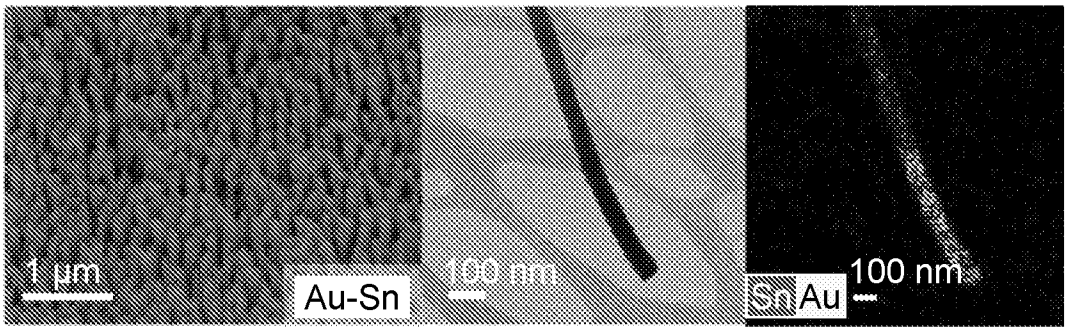

Fig. 19A Fig. 19B Fig. 19C

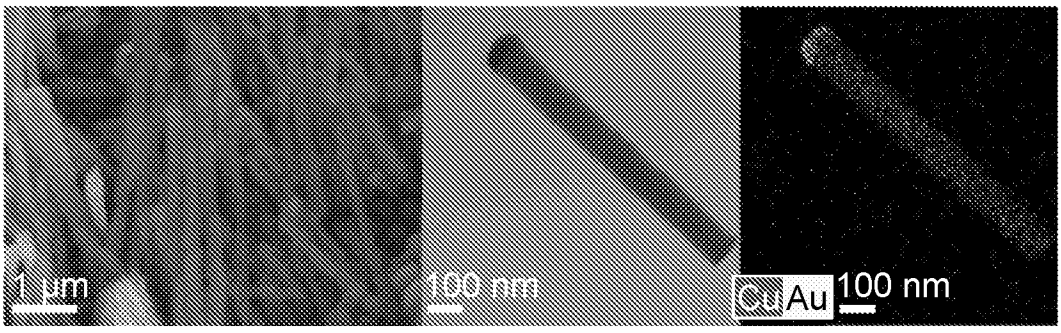

Fig. 20A Fig. 20B Fig. 20C

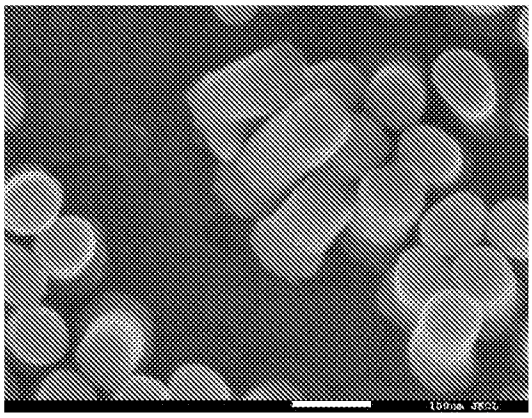

Fig. 21A

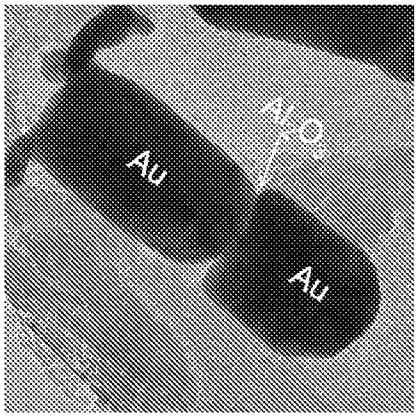

Fig. 21B

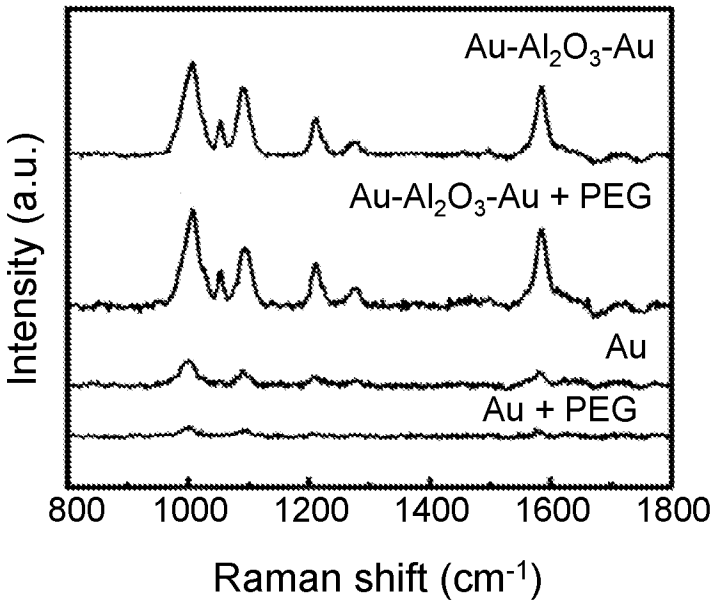

Fig. 22

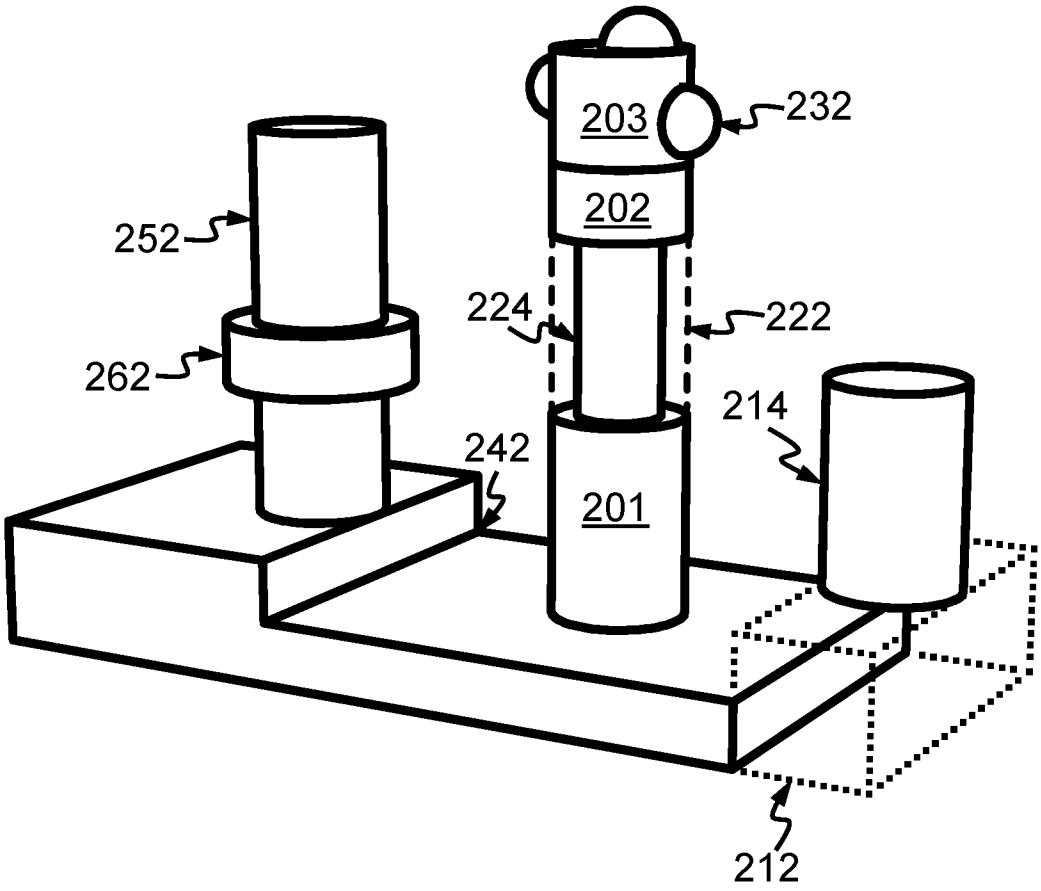

Fig. 23

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2021/050452

A. CLASSIFICATION OF SUBJECT MATTER

B29C 59/02 (2006.01) ***B29C 43/36 (2006.01)*** *B82Y 15/00 (2011.01)* *B82Y 40/00 (2011.01)*

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B29C, B82Y, G03F

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 practicable, search terms used)

Databases: FAMPAT, COMPENDEX, INSPEC
Keywords: ultrasonic, imprinting, embossing, molding, nanoforming, nanojackhammer, rod, wire, disk, fiber, anodized aluminum oxide, sonotrode and similar terms.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MEKARU H., Effect of Applying Ultrasonic Vibration in Hot Embossing and Nanoimprint. *Lithography*, 1 September 2010, pages 517-542 [Retrieved on 2021-10-19] <DOI: 10.5772/8191> Whole document, in particular Section 4.1, 4.2, 4.4; Fig. 22	1-22
A	GE J. ET AL., Vertical Silver@Silver Chloride Core–Shell Nanowire Array for Carbon Dioxide Electroreduction. *ACS Appl. Energy Mater.*, 23 August 2019, Vol. 2, No. 9, pages 6163–6169 [Retrieved on 2021-10-19] <DOI: 10.1021/ACSAEM.9B01286> Supporting Information	
A	CN 102020253 A (UNIV BEIJING) 20 April 2011 Whole document of the machine translation	

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

*Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19/10/2021 *(day/month/year)*	*21/10/2021* *(day/month/year)*

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2021/050452

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 102063950 A (UNIV BEIJING) 18 May 2011 Whole document of the machine translation	
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/SG2021/050452

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

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