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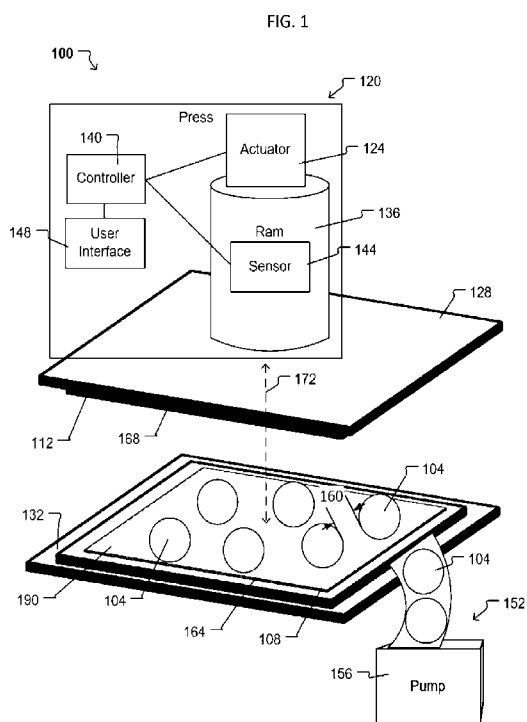
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(57) Abstract: The present disclosure provides methods and systems for preparing a metal nanostructure. The nanostructure can have a unique two-dimensional (2D) anisotropic morphology and a thickness of below 10 nm. In various embodiments, colloiddally synthesized gold nanoparticles can be used for the present methods and systems. Advantageously, the present disclosure provides an effective approach to prepare nanofilms useful for many applications.

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METHODS AND SYSTEMS FOR PREPARING METAL NANOSTRUCTURES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 63/518,726, filed August 10, 2023, the content of which is hereby incorporated by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] This invention was made with government support under DMR-1720633 awarded by National Science Foundation. The government has certain rights in the invention.

[0003] This invention was made with government support under CMMI-1944638 awarded by National Science Foundation. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

[0004] Bulk metal, in particular, gold, can be processed through mechanical deformation to form thin films (e.g., gossamer, sheets, or leaves). Over time, the thinness of the gold leaf progressed towards the nanoscale regime from ~300 nm in the Eighteenth Dynasty of ancient Egypt towards to about 100 nm, achievable with modern mechanized systems. However, this lower limit of ~100 nm achieved by goldbeating is still much thicker than the single-digit nanometer gold thin films achievable via modern metallization technologies such as electrochemical deposition, atomic layer deposition, vacuum-based evaporation, molecular epitaxy, etc.

[0005] Conventionally, achieving thinner films, for example, down to the single-digit nanoscale regime are limited to complex, bottom-up formation techniques like vapor deposition, chemical lithography, etc. A need exists for improved methods for producing nanoscale thin films in a more cost-effective manner.

SUMMARY OF THE INVENTION

[0006] In one aspect, the present disclosure provides a method for producing metal nanostructure. The method comprises applying a uniaxial deformation to a plurality of nanoparticles (e.g., an assembly of nanoparticles) comprising a metal, whereby the plurality of nanoparticles is compressed under the uniaxial deformation to produce a metal nanostructure having a thickness of 100 nm or less.

[0007] The nanoparticles can include, for example, gold, silver, platinum, copper, gallium, cobalt, bismuth, iron, cadmium, manganese, zinc, nickel, palladium, titanium, iridium, aluminum,

tin, indium, antimony, magnesium, chromium, molybdenum, tungsten, silicon, arsenic, tellurium, an alloy thereof, or a combination thereof. In some embodiments, the nanoparticles comprise gold.

[0008] In some embodiments, the nanoparticles are colloiddally synthesized nanoparticles. In some embodiments, the nanoparticles further comprise a polymer, or wherein the nanoparticles further comprise a ceramic coating. For example, the polymer can include polyethylene glycol, polyvinyl alcohol, polystyrene sulfonate, chitosan, polyvinylpyrrolidone, polyacrylic acid, polyethyleneimine, polylactic acid, polyglycolic acid, dextran, poly(2-ethyl-2-oxazoline, poly(N-isopropylacrylamide), or a combination thereof. In some embodiments, the polymer is polyethylene glycol. In some embodiments, the nanoparticle has a size of about 1 nm to about 150 nm. In some embodiments, the polymer has a molecular weight of about 1 kDa to about 100 kDa. The polymer can have a hydrodynamic length of about 10 nm to about 50 nm. In some embodiments, the polymer in the nanoparticles has crystallinity between 30 and 70%. In some embodiments, the plurality of nanoparticles is a monolayer and/or sub-monolayer and/or multilayer of the nanoparticles having a thickness of less than 1 μm .

[0009] In some embodiments, the method may comprise depositing the plurality of nanoparticles onto a bottom substrate, thereby forming an assembly of nanoparticles on the bottom substrate, placing a top substrate over the assembly of nanoparticles, such that the assembly of nanoparticles is between the top substrate and the bottom substrate, and reducing the physical spacing between the top substrate and the bottom substrate, whereby the assembly of nanoparticles is deformed under the uniaxial compression. The bottom substrate can comprise a silicon wafer surface, onto which the nanoparticles are deposited. In some embodiments, the uniaxial deformation is applied by applying a uniaxial pressure to the plurality of nanoparticles. The uniaxial pressure can be, for example, about 2.0 GPa to 5.0 GPa.

[0010] In some embodiments, the metal nanostructure produced by the present method has a thickness of 1 nm or less. In some embodiments, the plurality of nanoparticles has a surface area. The compression under the uniaxial deformation can cause an increase of the surface area, for example, by about 25% to about 50%.

[0011] In some embodiments, the present disclosure further provides a metal nanostructure produced by the methods described herein.

[0012] In another aspect, the present method provides a metal nanostructure comprising a plurality of nanoparticles, wherein the plurality of nanoparticles comprise a metal, and wherein the

metal nanosheet has a thickness of 10 nm or less. For example, the nanoparticles can comprise gold.

[0013] The metal nanostructure as described herein can have a two-dimensional anisotropic morphology. In some embodiments, the nanostructure has a shape, which is round, hexagonal, octagonal, square, rectangular, triangular, ribbon, or irregular. In some embodiments, the nanostructure has a Schmid factor about 0.25 to about 0.50. In some embodiments, the nanostructure has a compression-induced vertical deformation between 1 unit cell and 1000 unit cells thick.

[0014] In another aspect, the present disclosure further provides an article or device comprising the metal nanostructure as described herein.

[0015] In another aspect, the present disclosure details a pressing system for producing a contiguous nanofilm. The pressing system comprises a first pressing member configured to receive a plurality of dispersed nanoparticles, a second pressing member in an opposed configuration with the first pressing member, and an actuator configured to move at least one of the first pressing member and the second pressing member to apply a uniaxial compression to the plurality of nanoparticles between the first pressing member and the second pressing member, the uniaxial compression causing the plurality of nanoparticles to expand into one another to form the contiguous nanofilm.

[0016] In some embodiments, the plurality of nanoparticles have an average particle size between about 1 nanometers and about 50 nanometers. In some embodiments, the plurality of nanoparticles has an average interparticle distance of between 1 nanometer and 1000 nanometers. In some embodiments, a ratio of an average particle size of the plurality of nanoparticles and an average interparticle distance is between about 0.006 and 200.

[0017] In some embodiments, at least one of the first pressing member and the second pressing member is moved so that a shortest distance between the first pressing member and the second pressing member is less than about 1000 nanometers. In some embodiments, a ratio of a shortest distance between the first pressing member and the second pressing member and an average particle size of the plurality of nanoparticles is between about 0.01 and about 1.

[0018] In some embodiments, a substrate is positioned between the first pressing member and the second pressing member. In some embodiments, the substrate is coupled to at least one of the

first pressing member and the second pressing member. For example, the substrate can optionally fixedly couple to the plurality of nanoparticles as the uniaxial compression is applied.

[0019] In some embodiments, at least one of the first pressing member and the second pressing member includes a surface texture that is transferred to the contiguous nanofilm. For example, the at least one of the first pressing member and the second pressing member can include a projection to form a perforation in the contiguous nanofilm. For example, the projection can be one of a plurality of projections so that the contiguous nanofilm has a mesh structure.

[0020] In some embodiments, at least one of the first pressing member and the second pressing member is configured to control (lateral) expansion of at least some of the plurality of nanoparticles during the uniaxial compression. In some embodiments, the actuator system includes at least one of a hydraulic actuator, a linear actuator, toggle actuator, magnetic actuator, inductive actuator, pneumatic actuator, and a rotary actuator. In some embodiments, the pressing system further comprises an electronic controller configured to operate the actuator system. For example, the pressing system can comprise a sensor in communication with the controller, the sensor configured to generate a signal corresponding to the state of compression of the plurality of nanoparticles. For example, the sensor can include at least one of a distance sensor, a proximity sensor, a switch, a hall effect sensor, a load sensor, a pressure sensor, and a force sensor.

[0021] In some embodiments, the actuator system moves at least one of the first pressing member and the second pressing member along a first direction to control a distance between the first pressing member and the second pressing member in the first direction. In some embodiments, at least one of the first pressing member and the second pressing member is configured as a plate. In some embodiments, the pressing system further comprises a dispensing system configured to dispense the plurality of nanoparticles onto the first pressing member. For example, the dispensing system can include a pump configured to pump a colloidal solution that includes the plurality of nanoparticles.

[0022] In yet another aspect, the present disclosure discloses a method of making a nanofilm. The method comprises depositing a plurality of nanoparticles between a first pressing member and a second pressing, the plurality of nanoparticles being a dispersed configuration to define an average interparticle distance, and moving at least one of the first pressing member and the second pressing member to apply a uniaxial compression to the plurality of nanoparticles so that the plurality of nanoparticles expand in a direction substantially perpendicular to a direction of the

uniaxial compression, the plurality of nanoparticles expanding to couple to one another to form the nanofilm.

BRIEF DESCRIPTION OF DRAWINGS

[0023] FIG. 1 is a perspective view a pressing system according to aspects of the disclosure.

[0024] FIG. 2 is a side view of the pressing system of FIG. 1 in a first position prior to compressing a medium of dispersed particles.

[0025] FIG. 3 is a side view of the pressing system of FIG. 1 in a second position where the medium is being compressed.

[0026] FIG. 4 is a perspective view of the pressing system of FIG. 1 in the first position with the medium compressed into a contiguous film.

[0027] FIG. 5 is a perspective view of the pressing system of FIG. 1 in the first position in the first position with the medium compressed into a contiguous film having a plurality of openings formed therein.

[0028] FIG. 6 is a perspective view of an example plate that can be used with the pressing system of FIG. 1.

[0029] FIG. 7 is a flowchart of a method of operating a pressing system to produce a nanofilm, in accordance with aspects of the disclosure.

[0030] FIG. 8 shows a schematic of the nanoscale system experimental setup.

[0031] FIG. 9 shows the experimental setup of a nanoscale system with hydraulic press using a diamond holder.

[0032] FIG. 10 shows the experimental setup of a nanoscale system with a manual drill machine setup to apply force onto the wafer to compress metallic nanocrystal.

[0033] FIG. 11 shows the experimental setup of a nanoscale system test of the experimental setup with hydraulic press with heating with a hotplate.

[0034] FIG. 12 shows the experimental setup of a nanoscale system with a hydraulic press with heating with a custom-made conduction heater block.

[0035] FIG. 13 (A) Schematic showing the compression of monolayer surface assembly of gold nanospheres (AuNPs) on silicon substrate. The top silicon compression wafer is compressed uniaxially onto the AuNS/Si. The total lateral area of the compressed 2D gold domain equals the top compression silicon wafer dimension. SEM (50° tilted view) images of (B) large AuNS (103 nm) as-assembled on the silicon substrate and (C) after compression. The flattened 2D gold leaf-

like morphology is evident from the SEM images. All scale bars are 500 nm. AFM height maps of (D) as-assembled and (E) compressed AuNS morphology, indicating the severe plastic deformation and flattening of the AuNSs due to uniaxial compression.

[0036] FIG. 14 Morphological transformation of various sizes of AuNSs via uniaxial compression. SEM of as-assembled AuNSs of various sizes with 5k PEG: (A) small - 18 nm, (B) medium - 59 nm, and (C) large - 103 nm. The inset FFT shows diffused rings with hexagonal spots, indicative of a hexagonal closed-packed assembly of the AuNSs. SEM of transformed 2D morphology after compression of AuNSs of sizes (D) small, (E) medium, and (F) large. The AuNS's deformation could be influenced by the stochastic crystal facet orientation of the individual particles and the number of neighboring AuNSs, leading to different deformed morphologies under the same applied normalized compressive stress. The inset FFTs indicate the appearance of anisotropy due to the 2D transformation. All scale bars are 500 nm. (G) Thickness evolution and z-strain from the as-assembled to the compressed small, medium, and large AuNSs. The represented data indicates an induced vertical out-of-plane z-strain (ϵ_z) of $38.12 \pm 0.1\%$ (from 18.8 ± 0.4 nm to 11.6 ± 0.8 nm) for small AuNS, $57.06 \pm 0.1\%$ (from 51.6 ± 0.6 nm to 22.1 ± 2.9 nm) for medium AuNS, and $55.71 \pm 0.1\%$ (from 83.6 ± 0.7 nm to 37.0 ± 1.7 nm) for large AuNS under applied normalized compressive stress.

[0037] FIG. 15 Transformation of small AuNSs into anisotropic 2D morphologies with varied interparticle separation. As-assembled small (20 nm) AuNSs with (A) shorter (5k) PEG, (B) longer (40k) PEG, and after compression: (C) 5k PEG, (D) 40k PEG. The (C) 5k PEG AuNSs yield lower interparticle distance ($\sim 4.5 \pm 4.7$ nm) and form 2D morphologies with some interparticle sintering after compression, whereas the (D) 40k PEG with larger interparticle distance ($\sim 126.2 \pm 65.5$ nm) and maintains the large interparticle separation and exhibit a higher degree of 2D transformation. The deformation could be influenced by the stochastic crystal facet orientation of the individual AuNSs in isolation. All scale bars 500 nm. (E) Thickness evolution and z-strain from the as-assembled to the compressed small AuNSs with 5k PEG and 40k PEG. Under the same applied normalized compressive stress, the AuNSs with 40k PEG experience z-strain (ϵ_z) of $64.88 \pm 0.1\%$ (from 20.8 ± 2.8 nm to 7.3 ± 0.6 nm), compared to $38.12 \pm 0.1\%$ (from 18.8 ± 0.4 nm to 11.6 ± 0.8 nm) for AuNS with 5k PEG.

[0038] FIG. 16 Molecular dynamics simulation of a single AuNS. (A) Simulation domain of small AuNS (20 nm in diameter) placed between two planar force fields with an (inset of A)

zoomed-in view showing the top few atomic layers of the AuNS. (B) Top view of the compressed AuNS at ~38% strain. Atoms are colored using dislocation analysis (DXA) in OVITO; yellow refers to the FCC structure, and red refers to the HCP structure on the slipping plane. Here, the surface atoms are removed for better visualization. (C) Compressive stress variation with respect to engineering strain. The true yield stress and engineering yield stress are calculated to be 4.9 GPa and 0.18 GPa, respectively, at an engineering strain of 2.9%, (D) Contact area and dislocation density variation with respect to compression depth at compression velocity of 0.001 nm/ps.

[0039] FIG. 17 Generalizability of the top-down compression technique to 1D nanorods (AuNRs). Monolayer (A) as-assembled and (D) compressed morphologies of short AuNR (60x20 nm, 5k PEG, and AR 3). (C) After compression, the lateral area was estimated to be increased by 80% for the short AuNR (from $1162.4 \pm 41.0 \text{ nm}^2$ to $2093.2 \pm 98.0 \text{ nm}^2$). Monolayer (B) as-assembled and (E) compressed morphologies of long AuNR (99x14 nm, 5k PEG, and “AR 7”). All scale bars are 500 nm. (F) After compression, the lateral area was increased by 37.68% for the long AuNR (from $2155.0 \pm 28.8 \text{ nm}^2$ to $2967.0 \pm 39.0 \text{ nm}^2$). (G) The elongation in the lateral dimension (estimated using ellipse fitting) of the short and long AuNR is demonstrated in the scatter plots. For the short AuNR, the length (major axis) increased from $57.9 \pm 0.7 \text{ nm}$ to $85.8 \pm 1.9 \text{ nm}$, and the width (minor axis) increased from $25.2 \pm 0.3 \text{ nm}$ to $29.9 \pm 0.7 \text{ nm}$ after compression. For the long AuNR, the length (major axis) has expanded from $117.6 \pm 0.9 \text{ nm}$ to $139.6 \pm 1.6 \text{ nm}$, and the width (minor axis) expanded from $23.1 \pm 0.2 \text{ nm}$ to $26.8 \pm 0.3 \text{ nm}$ after compression. (H) The induced z-strain of short AuNR due to compression is estimated to be ϵ_Z , short AuNR = $49.33 \pm 0.1\%$ from ($18.1 \pm 2.4 \text{ nm}$ to $9.2 \pm 0.7 \text{ nm}$), whereas, for long AuNR, the induced z-strain is estimated to be ϵ_Z , long AuNR = $42.1 \pm 0.1\%$ (from $14.4 \pm 1.2 \text{ nm}$ to $8.4 \pm 0.6 \text{ nm}$).

[0040] FIG. 18 Example of centroid-to-centroid distance calculation for small AuNS with 5k PEG, position 1. SEM image is converted to binary; subsequently, centroid to centroid distance was extracted from the FFT.

[0041] FIG. 19 The AuNSs undergo severe plastic deformation during uniaxial solid-state compression. The shear bands are prominent (pink dotted line) in the post-mortem SEM images for A) small AuNSs with 5k PEG, B) medium AuNSs with 5k PEG, C) large AuNSs with 5k PEG, and D) small AuNSs with 40k PEG. All scale bars are 100 nm.

[0042] **FIG. 20** The AuNRs undergo severe plastic deformation during uniaxial solid-state compression. The shear bands are prominent (pink dotted line) in the post-mortem SEM images for A) short AuNR 5k PEG and B) long AuNR with 5k PEG. All scale bars are 100 nm.

[0043] **FIG. 21** Crystallographic evolution of AuNSs characterized via EBSD. The SEM images of A) as-assembled and B) compressed large AuNSs; The corresponding inverse pole figures (left) and {001} pole figures (right) indicate the crystallographic orientation of the C) as-assembled and D) compressed large AuNSs. The corresponding inverse pole figure orientation maps show the spatial distribution of the preferential crystallographic orientations E) before and F) after compression of the AuNSs. All scale bars are 200 nm.

[0044] **FIG. 22** (A) Schematic of ten sampling positions across the substrate for statistical quantification of thickness evolution of the AuNS via compression. B) AFM map of medium AuNSs with 5k PEG from position 5. C) Histogram extraction and Gaussian fit to statistically determine the thickness profile of the as-assembled medium AuNSs 5k PEG for position 5.

[0045] **FIG. 23** Estimation of hydrodynamic length of PEG on small AuNSs, indicating significantly larger length for 40k PEG compared to 5k PEG.

[0046] **FIG. 24** A) Graphical representation of area occupied by the as-assembled and compressed small AuNS with 40k PEG, which is B) $702.5 \pm 24.7 \text{ nm}^2$ and C) $1337.9 \pm 74.6 \text{ nm}^2$, respectively (xc refers to the center of the peak for Gaussian fitting). As can be seen, there is a ~ 1.9 times increment of the lateral area due to compression.

[0047] **FIG. 25** A) - M) SEM images of as-assembled isolated large AuNSs with 40k PEG from position 1 through position 13. All scale bars are 500 nm.

[0048] **FIG. 26** A) - M) SEM images of compressed isolated large AuNSs with 40k PEG from position 1 through position 13. All scale bars are 500 nm.

[0049] **FIG. 27** A) - J) AFM maps of as-assembled isolated large AuNS with 40k PEG. All scale bars are 500 nm.

[0050] **FIG. 28** A) - J) AFM maps of compressed isolated large AuNS with 40k PEG. All scale bars are 500 nm.

[0051] **FIG. 29** Thickness evolution and z-strain from the as-assembled to the compressed large AuNS with 5k PEG (close-packed) and 40k PEG (isolated). The represented data indicate an induced vertical out-of-plane z-strain (ϵ_Z) of $55.71 \pm 0.1\%$ (from $83.6 \pm 0.7 \text{ nm}$ to $37.0 \pm 1.7 \text{ nm}$)

for large AuNS with 5k PEG and $75.54 \pm 0.1\%$ (from 152.7 ± 32.1 nm to 37.3 ± 6.9 nm) for large AuNS with 40k PEG under applied normalized compressive stress.

[0052] FIG. 30 Schematic and SEM images (at five different positions on the substrate) of repeatedly compressed close-packed large AuNSs with 5k PEG with progressively larger applied normalized stresses, emulating the conventional nanoscale system process and introducing concomitant progressive reshaping and thinning of the AuNSs. The as-assembled, close-packed large AuNSs with 5k PEG were first compressed under $\sigma_{\text{norm}} = 1$ GPa, and then subsequently compressed again under $\sigma_{\text{norm}} = 2.15$ GPa, where the progressive reshaping is evident from the SEM images. All scale bars are 200 nm.

[0053] FIG. 31 A) - M) SEM images of as-assembled isolated large AuNS with 40k PEG from position 1 through position 13. All scale bars are 500 nm.

[0054] FIG. 32 A) - M) SEM images of compressed ($\sigma_{\text{norm}} = 6$ GPa) isolated large AuNS with 40k PEG from position 1 through position 13. The average $\epsilon_Z = 80.16 \pm 0.1\%$. All scale bars are 500 nm.

[0055] FIG. 33 A) - J) AFM maps of as-assembled large AuNS with 40k PEG. All scale bars are 500 nm.

[0056] FIG. 34 A) - J) AFM maps of compressed ($\sigma_{\text{norm}} = 6$ GPa) isolated large AuNS with 40k PEG. The average $\epsilon_Z = 80.16 \pm 0.1\%$. All scale bars are 500 nm.

[0057] FIG. 35 Thickness evolution and z-strain from the as-assembled, isolated large AuNS with 40k PEG to post-compression at $\sigma_{\text{norm}} = 3.6$ GPa and $\sigma_{\text{norm}} = 6$ GPa. The represented data indicate an induced vertical out-of-plane z-strain (ϵ_Z) of $75.54 \pm 0.1\%$ (from 152.7 ± 32.1 nm to 37.3 ± 6.9 nm) for isolated large AuNS with 40k PEG under $\sigma_{\text{norm}} = 3.6$ GPa versus ϵ_Z of $80.16 \pm 0.1\%$ (from 151.4 ± 24.0 nm to 30.0 ± 4.6 nm) for large isolated AuNS with 40k PEG under a higher $\sigma_{\text{norm}} = 6$ GPa.

[0058] FIG. 36 Tabulated various compressed morphologies of small AuNSs for different initial equilibrium structures of the AuNSs with the corresponding true yield stresses at a compression velocity of 0.005 nm/ps and 0.001 nm/ps. The load is applied along [001] direction at 300K. All snapshots are taken at engineering strain of 38%.

[0059] FIG. 37 A), B) Shape outline drawn along the anisotropic boundary line of the deformed (yellow outlined) small AuNR with 5k PEG (position 13), which was subsequently used for

estimation of the area and ellipse fitting. C), D) Ellipse fitting of the shape outline using ImageJ. All scale bars are A), C) 500 nm, and B), D) 50 nm.

[0060] FIG. 38 A) As-assembled large AuNSs with 5k PEG on Si substrate, B) compressed large AuNSs with 5k PEG on the Si substrate (within the center square area), and C) SAM/top compression Si wafer after the compression process, showing no adhering particles. D) As-assembled large AuNSs with 5k PEG on the Si substrate, E) compressed large AuNS with 5k PEG on the Si substrate (within the center square area), and F) top compression Si wafer with no SAM after the compression process, with significant amounts of adhered particles. AuNSs were transferred onto the top Si wafer (area coverage of ~61% by AuNSs) after compression. Scale bars are 500 μm . Representative images (shown for positions 1, 9, and 5) of the particles remaining on the bottom Si substrate after a significant amount have been picked up by bare top compression Si wafer with no SAM. Scale bars are 10 μm .

[0061] FIG. 39 Schematic of methodology for statistical calculation of AuNP area coverage on the silicon substrate. The left panel shows the boundary area of the as-assembled and compressed region of medium AuNP 5k PEG on silicon substrate. All scale bars are 250 nm.

[0062] FIG. 40 Example area coverage quantification for assembled large AuNS 5k PEG, at position 12. The scale bar is 2 μm . The 20kx magnification SEM image is converted to binary, and the area coverage is calculated to be 19.11%.

[0063] FIG. 41 Schematic representation of a typical brilliant-cut diamond, showing different sides such as table, crown, pavilion, and culet, with a pavilion angle of 40.75° .

[0064] FIG. 42 Nominal pressure estimation from the compressed area. A) 15 GPa compression of medium AuNS on a sapphire sample. B) The red labeled area ($\sim 1245 \mu\text{m}^2$) denotes the compressed area that was in contact with the culet of the diamond. C) The red labeled area ($\sim 2935 \mu\text{m}^2$) denotes the compressed area which is in contact with the culet and the pavilion. Scale bar 100 microns.

[0065] FIG. 43 A) and B) Schematic of the compression of monolayer assembly of AuNS on a sapphire substrate. The diamond indenter compresses the AuNS/sapphire and locally transforms the 0D/1D nanoparticles into anisotropic 2D morphologies. C) and D) AFM topography of as-assembled monolayer of large AuNSs (60 nm) and after 15 GPa compression. The RMS roughness is $6.37 \pm 0.46 \text{ nm}$ and $2.15 \pm 0.23 \text{ nm}$ of as-assembled and after compression large AuNS,

respectively, indicating flattening induced by severe plastic deformation. Inset: the SEM image, exhibiting as-assembled and 15 GPa compressed large AuNS monolayer (Scale bars are 200 nm).

[0066] FIG. 44 Morphology transformation of various sizes of AuNS via solid-state uniaxial compression. As-deposited AuNS of size (i.e., diameter) A) small, B) intermediate, and C) medium. The inset FFT shows partially diffused rings with distinguishable hexagonal spots, which are indicative of a nearly hexagonal close-packed assembly of the AuNSs. Deformed state of AuNS with sizes D) small, E) intermediate, and F) medium. The final anisotropic morphology could be influenced by the crystal facet orientation of the individual AuNSs on the substrate as well as interactions between neighboring AuNSs, thus deforming in different anisotropic shapes. The inset FFTs indicate the lower correlation between AuNSs arrangement. All scale bars are 400 nm.

[0067] FIG. 45 Transformation of small (18 nm) AuNS into anisotropic 2D morphologies with varied interparticle distances. As-deposited (A) short (MW 5k) PEG, (B) long (MW 40k) PEG, and after 15 GPa compressed (C) short (MW 5k) PEG, (D) long (MW 40k) PEG AuNS. As evident, (C) the short PEG had a lower interparticle distance (~3.3 nm) and formed a nearly continuous 2D Au morphology after compression, whereas (D) the long PEG had a lower interparticle distance (~32.1 nm) and still maintains some interparticle separation with anisotropic deformed morphology.

DETAILED DESCRIPTION OF THE INVENTION

[0068] Before the present invention is described in further detail, it is to be understood that the invention is not limited to the particular embodiments described. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting. The scope of the present invention will be limited only by the claims. As used herein, the singular forms “a”, “an”, and “the” include plural embodiments unless the context clearly dictates otherwise.

[0069] It should be apparent to those skilled in the art that many additional modifications beside those already described are possible without departing from the inventive concepts. In interpreting this disclosure, all terms should be interpreted in the broadest possible manner consistent with the context. Variations of the term “comprising”, “including”, or “having” should be interpreted as referring to elements, components, or steps in a non-exclusive manner, so the referenced elements, components, or steps may be combined with other elements, components, or steps that are not

expressly referenced. Embodiments referenced as “comprising”, “including”, or “having” certain elements are also contemplated as “consisting essentially of” and “consisting of” those elements, unless the context clearly dictates otherwise. It should be appreciated that aspects of the disclosure that are described with respect to a system are applicable to the methods, and vice versa, unless the context explicitly dictates otherwise.

[0070] Numeric ranges disclosed herein are inclusive of their endpoints. For example, a numeric range of between 1 and 10 includes the values 1 and 10. When a series of numeric ranges are disclosed for a given value, the present disclosure expressly contemplates ranges including all combinations of the upper and lower bounds of those ranges. For example, a numeric range of between 1 and 10 or between 2 and 9 is intended to include the numeric ranges of between 1 and 9 and between 2 and 10.

[0071] The word “exemplary” is used herein to mean serving as an example, instance, or illustration. Any aspect or design described herein as “exemplary” is not necessarily to be construed as preferred or advantageous over other aspects or designs.

[0072] Furthermore, the disclosed subject matter may be implemented as a system, method, apparatus, or article of manufacture using standard engineering techniques to produce hardware, firmware, software, or any combination thereof to implement aspects detailed herein.

[0073] In some implementations, devices or systems disclosed herein can be utilized, manufactured, or installed using methods embodying aspects of the invention. Correspondingly, any description herein of particular features, capabilities, or intended purposes of a device or system is generally intended to include disclosure of a method of using such devices for the intended purposes, a method of otherwise implementing such capabilities, a method of manufacturing relevant components of such a device or system (or the device or system as a whole), and a method of installing disclosed (or otherwise known) components to support such purposes or capabilities. Similarly, unless otherwise indicated or limited, discussion herein of any method of manufacturing or using for a particular device or system, including installing the device or system, is intended to inherently include disclosure, as embodiments of the invention, of the utilized features and implemented capabilities of such device or system.

[0074] Additionally, unless otherwise specified or limited, the terms “about” and “approximately,” as used herein with respect to a reference value, refer to variations from the reference value of $\pm 15\%$ or less, inclusive of the endpoints of the range. Similarly, the term

“substantially equal” (and the like) as used herein with respect to a reference value refers to variations from the reference value of less than $\pm 30\%$, inclusive. Where specified, “substantially” can indicate in particular a variation in one numerical direction relative to a reference value. For example, “substantially less” than a reference value (and the like) indicates a value that is reduced from the reference value by 30% or more, and “substantially more” than a reference value (and the like) indicates a value that is increased from the reference value by 30% or more.

[0075] The previous description of the disclosed embodiments is provided to enable any person skilled in the art to make or use the invention. Given the benefit of this disclosure, various modifications to these embodiments will be readily apparent to those skilled in the art, and the principles defined herein may be applied to other embodiments without departing from the spirit or scope of the invention. Thus, the invention is not intended to be limited to the embodiments shown herein but is to be accorded the widest scope consistent with the principles and novel features disclosed herein.

[0076] Unless specified or limited otherwise, the terms “connected,” and “coupled” and variations thereof are used broadly and encompass both direct and indirect mountings, connections, supports, and couplings. Further, “connected” and “coupled” are not restricted to physical or mechanical connections or couplings. As used herein, unless expressly stated otherwise, “connected” means that one element/feature is directly or indirectly connected to another element/feature, and not necessarily electrically or mechanically. Likewise, unless expressly stated otherwise, “coupled” means that one element/feature is directly or indirectly coupled to another element/feature, and not necessarily electrically or mechanically.

[0077] As used herein, a “mechanocaloric material” shall refer to a material capable of exhibiting a thermal response when subjected to an external stress and/or strain.

[0078] Gold, as the canonical precious metal with superlative material properties, has been instrumental in shaping the modern world, from microelectronics to (nano)medicine. In nanoscopic form, low dimensional 0D/1D gold nanoparticles exhibit properties different from their “bulk” 3D counterparts, arising from reduced physical dimensionality and confinement effects. Precise control over the size, shape, aspect ratio (AR), surface chemistry, and ligand distribution of nanoparticles in seed-mediated colloidal synthesis has led to the development of innovative methods for forming nanoscale thin films. Due to the minimization of net surface energy, these colloidally-synthesized nanoparticles typically exhibit intrinsic high-symmetry and faceted

crystalline morphologies such as nanospheres, nanorods, nano-polyhedrons, nanocubes, nano-octahedron, nanostars, nano-plates, nanocages, and nanoshells. Modifying these intrinsic symmetries in nanoparticles introduces morphological anisotropy that can induce emergent properties such as localized surface plasmon resonance, catalysis, and magnetism. Conventional bottom-up solution-based techniques, including seed-mediated colloidal synthesis, vapor deposition, electrochemistry, and sonochemistry, can yield morphologically anisotropic AuNPs. Multi-step, seed-mediated techniques allow morphological control with capping layers over nanoparticle shape, sizes, and surface chemistries while achieving scalable synthesis. Kinetically controlled geometric anisotropy can be achieved by optimizing metal precursor concentration, synthesis conditions (temperature, time), structure-directing reducing agents, additives, and surfactants.

[0079] In contrast, top-down, solid-state techniques described herein provide a different, more cost-effective alternative route to achieving morphological control and thus far have mainly entailed lithographic patterning (optical, imprint, focused ion beam, etc.) and compression strategies. However, lithography techniques are often limited by lithographic resolution, scalability, and poor crystallinity. Mechanical-based (i.e., deformation) strategies offer exciting opportunities for control over nanoparticle morphology to induce anisotropy. Conventional top-down compression-based strategies primarily entail hydrostatic compression of nanoparticle superlattices, resulting in omnidirectional sintering-driven 3D mesoporous gold architectures.

[0080] Overall, shape anisotropy in AuNPs induced by uniaxial compression remains underexplored. Further understanding of this severe plastic-deformation process akin to nanoscale system lends insights into the deformation of metal nanoparticles at extreme length scales and the associated parameters. These anisotropic transformations into 2D gold leaf morphologies are investigated experimentally and computationally. The top-down, uniaxial compression-based nanoscale system technique demonstrated here is versatile and generalizable to other metallic, polymeric, or ceramic nanoparticles. The observed plasticity and transformed 2D morphologies depend on the precursor AuNP size (diameter and aspect ratio) and the on-substrate assembly/interparticle separation.

[0081] In one aspect, the present disclosure relates to a method for producing a metal nanostructure, The method comprises applying a uniaxial deformation to a plurality of

nanoparticles comprising a metal, whereby the plurality of nanoparticles is compressed under the uniaxial deformation to produce a metal nanostructure having a thickness of 100 nm or less.

[0082] The term “metal nanostructure” generally refers to a network of a metal material with a nanometer-scale or sub-nanometer-scale thickness. For example, a metal nanostructure can refer to a contiguous thin film having sub-100 nm thickness, which optionally include openings formed therein to allow the chemical or physical properties of the thin film to be tuned to a particular application. The thickness of the metal nanostructure of the present disclosure is typically below 100 nm, for example 50 nm or less, 20 nm or less, 10 nm or less, 5 nm or less, 2 nm or less, 1 nm or less, or 0.5 nm or less. In some cases, the thickness of the metal nanostructure can correspond with a thickness of the atoms of the nanostructure. For example, thin films can be produced that are 1, 2, 3, 4, 5, or more atoms thick. The present metal nanostructure can be in any suitable form with a particular range of thickness, including but not limited to sheet, plate, layer, film, mesh, coating, slab, skin, leaf, and membrane forms as understood in the art. In various embodiments, the present metal nanostructure also may be referred to as nanostructure, nanoplate, nanolayer, nanofilm, nanomesh, nanocoating, nanoslab, nanoskin, nanoleaf, or nanomembrane, etc., depending on its particular form. In some embodiments, the nanostructure as described herein has a sheet-like or thin film form, which can be referred to as nanostructure or nanofilm. The present metal nanostructure (e.g., nanostructure or nanofilm) can have a two-dimensional (2D) morphology (e.g., an anisotropic morphology) with various length and width measurements, uniformity, density, composition, porosity, roughness, thickness, surface area, and other morphological characteristics.

[0083] In addition to the metal, the present metal nanostructure (e.g., nanostructure) can include other chemical agents or material or substrate or encapsulant or passivation (e.g., polymers, surfactants, chelators, etc.) as a structural and/or stabilizing component.

[0084] In some embodiments, the nanoparticles comprise gold, silver, platinum, copper, gallium, cobalt, bismuth, iron, cadmium, manganese, zinc, nickel, palladium, titanium, iridium, aluminum, tin, indium, antimony, magnesium, chromium, molybdenum, tungsten, silicon, arsenic, tellurium, an alloy thereof, or a combination thereof. In some embodiments, the nanoparticles comprise gold. The metal can be in a form of a metal element (e.g., pure metal), a metal compound (e.g., metal oxide, metal halide, organometallic compound, etc.), an alloy, or a combination of different metals. The metal of the nanoparticles can comprise any element that can form stable

nanoparticle precursor in elemental form. The metal can be passivated by a stable shell of its own oxide/nitride, etc., or passivated by polymer (brushes) or other encapsulants.

[0085] The nanoparticles of the present disclosure can be colloiddally synthesized by know processes, including for example the process described in Kimling et al., . Phys. Chem. B 110, 15700–15707 (2006) Vigderman et al., Chem. Mater. 25, 1450–1457 (2013); and Sau et al., Langmuir 20, 6414–6420 (2004), which are incorporated herein by reference in their entireties. These nanoparticles are synthesized by dispersing small clusters of atoms or molecules in a liquid medium, creating a stable colloidal suspension. The process typically involves the reduction of metal salts to form metallic nanoparticles or the precipitation of non-metallic nanoparticles in a solution. Stabilizing agents, such as surfactants or polymers, are often added to the solution to prevent the nanoparticles from aggregating, thereby maintaining their unique properties. Colloidal synthesis allows for precise control over the size, shape, and composition of the nanoparticles, which can significantly influence their optical, electronic, and catalytic properties. The colloiddally-synthesized nanoparticles typically include a variety of materials, including metals, metal oxides, semiconductors, and polymers. In some embodiments, the colloiddally-synthesized nanoparticles are submicroscopic particles made up of atoms or molecules of a metal coated in a polymer.

[0086] The size, shape, and composition of the present nanoparticles can be precisely controlled during the synthesis process, allowing for the creation of spherical, rod-shaped, cubic, or even more complex morphologies. In some embodiments, the nanoparticles are colloiddally-synthesized gold nanoparticles (AuNPs). The present nanoparticles can comprise nanospheres, nanorods, nanocubes, nanostars, nanoshells, nanotubes, or a combination thereof. The nanoparticles can have a size of ones to hundreds of nanometer, such as the diameter of a nanosphere (0D morphology) or the diameter and length of a nanorod (1D morphology). In some embodiments, the nanoparticles comprise gold nanospheres (AuNSs) having a size of about 1 nm to about 150 nm, such as about 10 nm to about 150 nm, about 10 nm to about 100 nm, or about 10 nm to about 80 nm. In some embodiments, the nanoparticles (e.g, AuNSs) have a size of about 5 nm, about 18 nm, about 60 nm, or about 105 nm.

[0087] Average nanoparticle size refers to the average diameter of particles within the nanoscale range, typically between 1 and 1000 nanometers. This measurement includes any coatings or surface modifications present on the nanoparticles. The size of a nanoparticle is a critical parameter that influences its physical, chemical, and biological properties, including

surface area, reactivity, solubility, and interaction with biological systems. Measurement of nanoparticle size can be achieved using various techniques such as dynamic light scattering (DLS), transmission electron microscopy (TEM), or scanning electron microscopy (SEM). Accurate determination of nanoparticle size is essential for the characterization, application, and regulation of nanoparticulate materials in various fields, including medicine, electronics, and materials science. The average particle size can be calculated using different methods depending on the data obtained, such as number average, volume or mass average, and surface average.

[0088] In some embodiments, the nanoparticles further comprise a ceramic coating. Exemplary polymers may include but are not limited to silica coatings, titania coatings, alumina coatings, zirconia coatings, cerium oxide coatings, magnesium oxide coatings, hafnium oxide coatings, yttria coatings, lanthanum oxide coatings, or spinel coatings.

[0089] In some embodiments, the nanoparticles further comprise a polymer. Exemplary polymers may include but are not limited to polyethylene glycol, polyvinyl alcohol, polystyrene sulfonate, chitosan, polyvinylpyrrolidone, polyacrylic acid, polyethyleneimine, polylactic acid, polyglycolic acid, dextran, poly(2-ethyl-2-oxazoline, poly(N-isopropylacrylamide), or a combination thereof. In some embodiments, the polymer is polyethylene glycol. Polyethylene Glycol (PEG) can refer to a polyether compound that includes repeating units of ethylene oxide ($\text{CH}_2\text{CH}_2\text{O}$). PEG can be available in a range of molecular weights, typically from a few hundred to several thousand Daltons, which influences its physical properties such as viscosity, solubility, and melting point. PEG can be hydrophilic (water-attracting), making it soluble in water and various organic solvents.

[0090] The polymer can have a molecular weight of about 1k Da to about 100 kDa, including but not limited to about 5 kDa to about 100 kDa, about 5 kDa to about 80 kDa, about 5 kDa to about about 50 kDa, or about 5 kDa to about 40 kDa. The molecular weight can be, for example, about 5 kDa, about 10 kDa, about 20 kDa, about, 40 kDa, about 60 kDa, or about 80 kDa.

[0091] Polymer crystallinity refers to the degree to which polymer chains are organized into a highly ordered, repeating lattice structure within a material. Crystallinity is an important parameter that affects the physical properties of polymers, including mechanical strength, thermal stability, density, transparency, and chemical resistance. The crystalline regions in a polymer are typically interspersed with amorphous (non-crystalline) regions, and the overall crystallinity is expressed as a percentage, indicating the proportion of the polymer that is crystalline. Measurement of polymer

crystallinity can be achieved through various analytical techniques such as X-ray diffraction (XRD), differential scanning calorimetry (DSC), and infrared spectroscopy. Controlling polymer crystallinity is crucial for tailoring material properties for specific applications in industries such as plastics, textiles, and electronics. In some embodiments, the polymer of the nanoparticles has crystallinity between 30 and 70%.

[0092] The polymer can have a hydrodynamic length of about 10 nm to about 50 nm including but not limited to about 10 nm to about 40 nm, about 10 nm to about 30 nm, about 10 nm to about 20 nm, or about 20 nm to about 30 nm. The molecular weight can be, for example, about 10 nm, about 20 nm, about 30 nm, about 40 nm, or about 50 nm.

[0093] The plurality of nanoparticles can form an assembly of nanoparticles, such as an organized assembly. The plurality of nanoparticles (e.g., an assembly of nanoparticles) can include any crystal structure of the nanoparticles. The nanoparticles can be close-packed and/or non-close packed and/or periodically arranged and/or non-periodically arranged and/or form a layer of nanoparticles on a surface. In some embodiments, the plurality or assembly of nanoparticles is a monolayer of the nanoparticles. For example, the monolayer can be a hexagonal closed packed monolayer formed by depositing colloidal synthesized nanoparticles (e.g., AuNSs) on a surface (e.g., a silicon wafer surface). The size of the nanoparticles can affect the thickness of the assembly (e.g., monolayer). In some embodiments, the plurality or assembly (e.g., monolayer) of nanoparticles has a thickness of less than 1 μm , such as 800 nm or less, 500 nm or less, 200 nm or less, or 100 nm or less. In some embodiments, the monolayer of nanoparticles has a thickness of at least 1 nm, at least 5 nm, at least 10 nm, at least 50 nm, at least 100 nm, such as at least 200 nm, at least 400 nm, or at least 600 nm. In some embodiments, the monolayer of nanoparticles has a thickness of about 10 nm to about 800 nm, such as about 10 nm to about 500 nm or about 10 nm to about 200 nm.

[0094] The plurality or assembly of nanoparticles can be in a dispersed arrangement where the particles are spaced from one another on a plate for compression. For example, the nanoparticles have an interparticle separation (distance between adjacent particles) of about 1 nm to about 200 nm, such as about 5 nm, about 10 nm, about 25 nm, about 50 nm, about 100 nm, or about 200 nm. This is different from conventional bulk material processing where a monolithic mass of material is formed into a single sheet. This is also different from existing nanoscale compression methodologies like a diamond anvil that require the compressed material to be enclosed within a

capsule. As result of being contained in the capsule, the material therein experiences multidimensional compression due to the capsule itself compressing in on the material. By using multiple dispersed particles between plates, each of the particles can more effectively undergo 1D compression. As the particles are compressed, and as described in greater detail below, the particles can merge into one another to form a contiguous thin film. Effectively, the dispersed particles undergo cold welding during compression to form the thin film.

[0095] Turning now to FIGS. 1-5 an example pressing system 100 for forming thin films from dispersed particles is illustrated. In general, as illustrated in FIG. 1, the pressing system 100 includes a plurality of particles 104 (e.g., nanoparticles) arranged on a first pressing member (e.g., a first pressing plate 108) in a dispersed arrangement. In the dispersed arrangement, the individual particles define an average interparticle spacing of about 1 nanometer to 200 nanometers. The average interparticle spacing can be more or less depending on the type of particles, particle material, suspension medium (e.g., for a colloidal solution), or other parameters. As described above, the particles can be any metallic particle or alloy, including for example, gold platinum, silver, copper, iron, steel, or other metal. As described further below, the pressing system 100 may further include a second pressing member (e.g., a second plate 112) configured to engage the first plate 108 to mechanically deform the particles 104 arranged thereon into a film 116 (e.g., a contiguous nanofilm) (as shown in FIG. 3). In the illustrated example, the pressing members are configured as substantially flat plates. In other examples, other types of pressing members can be used, for example, rollers, curved plates, conveyors, etc., or combinations thereof.

[0096] A material property of plates utilized to compress particles can determine factors such as maximum pressure applied to the plates, as well as a smoothness of a surface thereof. Referring to FIG. 1, the first plate 108 and the second plate 112 can comprise any hard material, such as diamond, sapphire, silicon wafers, or another type of material suitable for pressing. The particular material of the plates can be selected in accordance with a type or size of particle being compressed. Additionally, the first plate 108 and the second plate 112 may comprise different materials having different material properties (e.g., different hardness, density, or other material property). It is appreciated that altering a material of the first and second plates 108, 112 may alter factors such as a maximum thickness of the film 116.

[0097] In some examples, a pressing system can utilize a press machine to provide sufficient pressure to mechanically compress the particles 104 into the film 116. For example, as illustrated

in FIG. 1, the pressing system 100 may include a press 120 that is used to compress the first plate 108 against the second plate 112. The first plate 108 and the second plate 112 can be removably attached to form part of the press 120. In this way, different types of plates can be used with the press 120. As illustrated in FIG. 1, the press 120 may be a hydraulic press, however, the press 120 may instead be a pneumatic press, a hand operated press, or a motor operated press.

[0098] In some examples, the press 120 may include an actuator 124 (e.g., an actuator system) that is configured to drive a press plate 128 toward a bed 132. As illustrated in FIG. 1, the press plate 128 and the bed 132 may each be a plate. In some examples, the bed 132 may be the first plate 108 and the press plate 128 may be the second plate 112. However, in other examples, the first plate 108 may be removably secured to the bed 132, and the second plate 112 may be removably secured to the press plate 128, to allow a type of the first or second plate 108, 112 used to create the film 116 to be quickly and easily switched. It is further appreciated that in some examples, both the first plate 108 and the second plate 112 may instead rest or otherwise be removably secured to the bed 132. As described below, different types of the plates 108, 112 can advantageously be used to create the film 116 having various different properties. The bed 132 and press plate 128 are optional and some examples of a press can couple directly with the first plate 108 and the second plate 112.

[0099] The press 120 is configured to move at least one of the pressing members (e.g., the first plate 108 and the second plate 112) to reduce a distance therebetween and effectuate a unidirectional compression on the particles to form a metal nanostructure (e.g., a nanofilm). For example, the actuator 124 may be configured to translate or otherwise move the press plate 128 using a ram 136, which in turn, moves the second plate 112 relative to the first plate 108 along a first direction. The actuator 124 may be a hydraulic actuator, a linear actuator, toggle actuator, magnetic actuator, inductive actuator, pneumatic actuator, or a rotary actuator, configured to extend the ram 136, and thus advance the press plate 128 attached to the ram 136 toward the bed 132. In some examples, the actuator 124 may be commanded by a controller 140. For example, the controller 140 may be configured to actuate the actuator 124 to advance the press plate 128 toward and away from the bed 132. Additionally, as described below, the controller 140 may be utilized to control a distance between the press plate 128 and the bed 132, or between the first plate 108 and the second plate, as well as a pressure therebetween.

[00100] In some examples, the controller 140 may receive feedback regarding an operation of the press 120 via one or more sensors 144. For example, a sensor connected to the controller 140 may be a distance sensor, a proximity sensor, a switch, a hall effect sensor, a load sensor, a pressure sensor, or a force sensor, which can be configured to indicate a stroke length of the ram 136, a hydraulic pressure within the actuator 124 (e.g., within a cylinder or pump of actuator 124), a pressure or distance between the first plate 108 and the second plate 112, or a pressure or distance between the press plate 128 and the bed 132.

[00101] In some examples, the sensors 144 may allow the controller 140 to actuate the press 120 to provide a predetermined pressure on the particles 104, or to provide a predetermined final compression distance between the first plate 108 and the second plate 112, in order to ensure the film 116 is properly formed. Specifically, the sensors 144 or the controller 140 may be configured to generate a signal corresponding to a state or compression (e.g., a full compression) of the particles 104 on the plates 108, 112 based on the distance or pressure data collected by the sensors 144.

[00102] In some examples, a user may control certain functions of a press using a user interface. Specifically, the press 120 may include a user interface 148 that allows a user to control actuation of the actuator 124. For example, input to the user interface 148 may cause the controller to actuate the actuator 124, and thus advance the press plate 128 toward the bed 132. Additionally, the user interface 148 may allow the user to specify a pressure at which the particles 104 are compressed between the first plate 108 and the second plate 112. In other examples, the user interface 148 may allow the user to specify a desired final compression distance between the first plate 108 and the second plate 112, or between the press plate 128 and the bed 132. As described above, the sensors 144 may provide data to the controller 140 that allows the controller 140 to actuate the press 120 (via actuator 124) to provide a predetermined pressure on the particles 104. The controller 140 can control the press 120 to provide a single compression or a series of compressions to the particles 104 to form the nanofilm. When a series of compressions are used, the compressions can increase an applied pressure or a compression distance (e.g., an actuation distance that reduces the spacing between the pressing members).

[00103] In some examples, the pressing system 100 may include a dispensing system 152 configured to dispense the plurality of particles 104 onto the first plate 108 or the second plate 112. Specifically, the dispensing system 152 may include a pump 156 that can be selectively

actuated dispense to a colloidal solution that includes the plurality of particles 104 onto the first plate 108 or the second plate 112. In some examples, the dispensing system 152 may be configured to dispense the particles 104 in a predetermined dispersed arrangement, as described further below.

[00104] Still referring to FIG. 1, in some examples, the particles 104 can be positioned on the first plate 108 and/or the second plate 112 in a dispersed arrangement. Specifically, in the dispersed arrangement the particles 104 may be separated by an average interparticle separation distance 160 of about 1 nm to about 200 nm, such as about 5 nm, about 10 nm, about 25 nm, about 50 nm, about 100 nm, about 200 nm, about 500 nm, or about 1000 nm. It is appreciated that a ratio of the average interparticle distance to particle size can be about 0.006 to about 200, such as about 0.75, about 5, or about 25, or about 100.

[00105] As described above, the pressing system 100 may include the press 120 that is configured advance the second plate 112 toward the first plate 108, or vice versa, to compress the particles 104 dispersed on the first plate 108. As illustrated in FIG. 2, the pressing system 100 may include the first plate 108 and the second plate 112 that are arranged opposed and substantially parallel relative to one another. Specifically, a first engaging surface 164 of the first plate 108 may be arranged opposite and substantially parallel to a second engaging surface 168 of the second plate 112. During the compression process, at least one of the plates 108, 112 can be advanced toward one another along a compression axis 172 that extends substantially perpendicular to the first engaging surface 164 or the second engaging surface 168. In some examples, the compression axis 172 may be a center axis of the ram 136 of the press 120. Properly arranging the first plate 108 parallel to the second plate 112, and translating the plates 108, 112 along the compression axis 172 can ensure uniaxial compression of the particles 104 between the engaging surfaces 164, 168 and therefore between the plates 108, 112.

[00106] Referring to FIGS. 2 and 3, as the plates 108, 112 are translated toward one another along the compression axis 172, the plates 108, 112 may compress the particles 104 arranged thereon. As illustrated in FIG. 3, the uniaxial compression provided by the plates 108, 112 causes the plurality of particles 104 to expand into one another to form the film 116 (e.g., via cold welding or pressure welding), as shown in FIG. 4. In some examples, the particles 104 may expand substantially parallel to the engaging surfaces 164, 168 of the plates 108, 112, or substantially perpendicular to the compression axis 172.

[00107] In some examples, the particles 104 may be compressed between the plates 108, 112 at a predetermined pressure. For example, the predetermined pressure may be 3.6 GPa. Additionally or alternatively, the particles 104 may be compressed between the plates 108, 112 to a predetermined final compression width. For example, as illustrated in FIG. 3, a minimum compression distance 176 between the plates 108, 112, and therefore a final width of the particles 104, may be between 5 nanometers and 2000 nanometers. As a result of compressing the particles 104 at the predetermined pressure, or at the minimum compression distance, the particles 104 may expand and join together to form the film 116. As described above, the film can be an assembly (e.g., monolayer) of the particles 104 having a thickness 180 of less than 1 μm , such as 800 nm or less, 500 nm or less, 200 nm or less, or 100 nm or less. Put another way, the film 116 can be one, two, three, four, five, etc. atoms thick.

[00108] Referring briefly to FIGS. 5 and 6, in some examples it may be advantageous to create a film 116 having a predetermined surface texture. For example, the film 116 may be created to have one or more perforations, one or more embossments, or one or more debossments. The perforations, embossments, and debossments may advantageously alter properties of the film 116 (e.g., mechanical, electrical, or thermal properties).

[00109] In some examples, a surface texture of plates can be transferred to a film formed thereon. For example, at least one of the plates 108, 112 may include protrusions, embossments, or debossments that impart a specific shape or structure to the film 116 formed thereon. The plates 108, 112 may impart a specific shape or structure to the film 116 by selectively controlling an expansion of one or more of the particles 104, or by selectively controlling bonding between sets of the particles 104 that are arranged adjacent to one another. Referring specifically to FIG. 6, in some examples, one or more perforations 184 may be formed in the film 116 by one or more protrusions 188 arranged on the second plate 112 and/or the first plate 108. As illustrated in FIG. 6, the protrusions 188 may extend from the second plate 112 toward the first plate 108. Specifically, the protrusions 188 may extend from the first engaging surface 164 toward the second engaging surface 168. In some examples, a thickness of the protrusions 188 measured substantially parallel to the compression axis 172 may be less than or equal to a thickness of the particles 104 (e.g., the final width thereof), to allow the plates 108, 112 to properly compress the particles 104 without interference.

[00110] Still referring to FIG. 6, during compression the protrusions 188 may selectively prevent adjacent particles 104 from bonding. Specifically, the protrusions 188 may provide a physical barrier between one or more adjacent sets of the particles 104. As illustrated in FIG. 5, the resultant film 116 may include a plurality of perforations 184 resulting from the one or more adjacent particles that were not bonded together. In some examples, the perforations 184 may be arranged in a pattern to form an organized mesh. However, in other examples, the perforations 184 may be dispersed on the film at random. As described below, the pattern of the perforations 184 can be determined by the arrangement of the protrusions on the plates 108, 112. In other examples, the perforation 184 can be the result of the interparticle spacing 160.

[00111] Referring again to FIG. 6, in some examples, the protrusions 188 may be arranged in a regular pattern (e.g., rows and columns, or other known pattern) to create a regular mesh of the perforations 184. However, the protrusions 188 may instead be arranged in an irregular pattern, or may not be arranged in a pattern, to alter an arrangement of the perforations 184 and thus properties of the resultant film 116. In some examples, the protrusions 188 may be pyramidal structures, however the protrusions 188 may instead define any shape, such as spherical, conical, cuboid, or other applicable shape.

[00112] Referring now to FIG. 8, an alternative configuration is illustrated, which includes many of the same components described in the previous figures, albeit with variations in their arrangement. The pressing system 100 remains central to the setup, with the first plate 108 and the second plate 112 still positioned to compress the particles 104 to form the film 116. As before, these plates may be composed of materials such as diamond, sapphire, or silicon wafers, depending on the specific requirements of the experiment.

[00113] Referring now to FIG. 9, an alternative configuration, including a hydraulic press and utilizing a diamond holder for precision compression. As shown, the pressing system 100 has been adapted to accommodate the first plate 108 and/or the second plate 112, which is secured within a diamond holder as the press plate 128. The diamond holder is chosen as the press plate 128 for its exceptional hardness and stability, ensuring that the wafer remains securely positioned during the compression process. The first plate 108 and the second plate 112, previously described as being composed of various hard materials, now work in conjunction with the diamond holder press plate 128 to uniformly compress the plurality of particles 104.

[00114] Referring now to FIG. 10, an alternative example, of the press system 100, in this case, configured as a manual press configured to apply force onto a wafer for the compression of metallic nanocrystals is shown. The press 120 can include a handle to allow a user to manually apply a uniaxial compression to a plurality of particles 104. In this setup, the press system is mounted and is configured to apply a force to compress the plurality of particles 104. The press system includes a drill bit, which is aligned with the first plate 108 and/or the second plate 112. This setup is particularly useful for experiments requiring precise, controlled application of force at a slower rate, as the manual operation allows for careful adjustments. In this configuration, the press system machine 100 offers a simple yet effective means of applying controlled pressure to compress the plurality of particles.

[00115] Referring to FIG. 11, in some examples, the hydraulic press (e.g., press system 100) is combined with an optional thermal element 146 (e.g., a hot plate) for heating. In this configuration, plurality of particles 104 is positioned on the first plate 108 which is on the bed 132 which is a hotplate as the thermal element 146 and provides controlled heating during compression. The hydraulic press 120, equipped with a press plate 128, applies force to the plurality of particles 104 while the bed 132, which in some examples facilitates the thermal-assisted compression of the plurality of particles 104 via combination of the bed 132 equipped with a hot plate as the thermal element 146. This setup allows simultaneous application of pressure and heat, enabling precise control over the formation of the nanoscale film 116.

[00116] Referring to FIG. 12, in some examples, a hydraulic press is utilized in combination with a custom-made conduction thermal element 146 (e.g., a conductive heater block). In this setup, the plurality of particles 104 is placed on the first plate 108 within the thermal element 146 which is a conduction heater block, which provides precise and uniform heating during compression. In other examples, other types of thermal control elements (e.g., a heater or chiller) can be used to modulate and control a temperature of particles during compression. The hydraulic press 120 applies force through the press plate 128, while the conduction heater block ensures effective thermal conduction across the first plate 108. This configuration enables controlled application of both pressure and heat, optimizing the formation of the nanoscale film 116.

[00117] In some examples, the first plate 108 and/or the second plate 112 can include the protrusions 188 that form an embossment or a debossment. Specifically, the plates 108, 112 can be embossed or debossed to form the films 116 with particular patterns or shapes to create

nanowires for use in circuits, sensor, or other types of electronic components. In that regard, at least one of the plates 108, 112 can include embossments or debossments that control (e.g., limit) the expansion of at least some of the particles 104 to provide the resultant film 116 with a desired shape.

[00118] In some examples, the plates 108, 112 can optionally include a removable substrate 190 (see FIG. 1). For example, the substrate 190 may be coupled to at least one of the plates 108, 112 and may be configured to couple to the particles 104 during compression. Specifically, the substrate may adhere or otherwise couple to the film 116 allowing the film 116 to be easily peeled off or otherwise removed from the plates 108, 112 and subsequently applied to a product.

[00119] FIG. 7 illustrates an example method for forming the film 116 from the plurality of particles, according to an example embodiment. Method S100 shown in FIG. 7 presents an embodiment of a method that could be used using the pressing system 100 as shown in FIGS. 1-6. Method S100 may include one or more operations, functions, or actions as illustrated by one or more of the method steps. Also, the various steps may be combined into fewer blocks, divided into additional steps, and/or removed based upon the desired implementation.

[00120] It should be understood that for this and other processes and methods disclosed herein, flowcharts show functionality and operation of one possible implementation of present embodiments. Alternative implementations are included within the scope of the example embodiments of the present disclosure in which functions may be executed out of order from that shown or discussed, including substantially concurrent or in reverse order, depending on the functionality involved, as would be understood by those skilled in the art.

[00121] At step S104, the method S100 may include arranging a first pressing member and a second pressing member on a press. At step S108 the method S100 may include coupling or otherwise arranging a substrate on the first pressing member and/or on the second pressing member. At step S112 the method S100 may include depositing a colloid solution containing a plurality of particles between the first pressing member and the second pressing. At step S116 the method S100 may include arranging the plurality of nanoparticles in a dispersed configuration to define an average interparticle distance. At step S120 the method S100 may include advancing one or more of the first pressing member and the second pressing member toward one another to achieve a predetermined distance or pressure therebetween. At step S124 the method S100 may include uniaxially compressing the plurality of particles so that the plurality of particles expand in a

direction substantially perpendicular to a direction of the uniaxial compression, the plurality of particles expanding to couple to one another to form a film. At step S128 the method S100 may include forming a plurality of perforations, embossments, or debossments on or in the film. At step S132 the method S100 may include coupling the film to the substrate. At step S136 the method S100 may include removing the film from the first pressing member or the second pressing member.

[00122] In some embodiments, the method comprises depositing the plurality of nanoparticles onto a bottom substrate, thereby forming the assembly of nanoparticles on the bottom substrate; placing a top substrate over the assembly of nanoparticles, such that the assembly of nanoparticles is between the top substrate and the bottom substrate; and reducing the physical spacing between the top substrate and the bottom substrate, whereby the assembly of nanoparticles is deformed under the uniaxial compression. In some embodiments, the bottom substrate comprises a silicon wafer surface, onto which the nanoparticles are deposited. In some embodiments, the bottom substrate comprises a silicon wafer surface, onto which the nanoparticles are deposited.

[00123] The method may comprise applying a uniaxial deformation by applying a uniaxial pressure to the plurality or assembly of nanoparticles. The uniaxial pressure can be, for example, about 2.0 GPa to about 10.0 GPa. For example, the uniaxial pressure can simply be the pressure from the weight of the top substrate itself. The uniaxial pressure can be at least 0.5 GPa, at least 1 GPa, at least 2 GPa, at least 5 GPa, or at least 10 GPa. In some embodiments, the uniaxial pressure is about 2.0 GPa to about 5.0 GPa.

[00124] Typically, the colloiddally grown gold nanoparticles can be single crystals with a few bicrystals and agglomerated single crystals. In some embodiments, amorphous metallic-glass or nanocrystalline metal nanoparticles can also be used for the present method, which can be produced through colloidal or non-colloidal means.

[00125] The thickness of the metal nanostructure produced by the present method can be well below 10 nm, such as 5 nm or less, 2 nm or less, 1 nm or less, or 0.5 nm or less. In some embodiments, the metal nanostructure produced by the present method has a thickness of 1 nm or less.

[00126] The uniaxial deformation (e.g., by application of uniaxial pressure) can result in an increase of the surface area of the plurality or assembly of nanoparticles. In some embodiments, the deformation is largely elastic and the nanoparticles “bounce back” completely, resulting in

essentially no increase of the surface area. The upper limit could be much larger than 100%, where the most extreme example would be In some embodiment, the nanoparticles with a large volume to surface area ratio (e.g., nanospheres) are compressed entirely to a monolayer or even sub-monolayer with all atoms exposed as “surface,” which results in many folds of increase of the surface area (e.g., 10-fold or more). In some embodiments, the compression under the uniaxial deformation (e.g., by application of uniaxial pressure) causes an increase of the surface area by about 25% to about 50%.

[00127] The present disclosure also provides a metal nanostructure produced by the methods disclosed herein.

[00128] In another aspect, the present disclosure provides a metal nanostructure comprising a plurality of nanoparticles, wherein the plurality of nanoparticles comprise a metal, and wherein the metal nanostructure has a thickness of 10 nm or less. In some embodiments, the plurality of nanoparticles have an average particle size between about 1 nanometer and about 500 nanometers. In some embodiments, the plurality of nanoparticles have an average particle size of at least 1 nm, at least 5 nm, at least 20 nm, or at least 50 nm. In some embodiments, the nanoparticles comprise gold.

[00129] In some embodiments, the nanostructure as described herein has a two-dimensional anisotropic morphology. The nanostructure shape may be round, hexagonal, octagonal, square, rectangular, triangular, ribbon, or irregular.

[00130] Ribbon-shaped nanoparticles are elongated nanostructures with a flat, thin morphology resembling a ribbon. These nanoparticles have one dimension significantly larger than the other two, typically with widths ranging from 1 to 100 nanometers and lengths that may extend to several micrometers. The unique shape of ribbon-shaped nanoparticles imparts distinct physical and chemical properties, such as anisotropic conductivity, optical characteristics, and mechanical strength.

[00131] The Schmid factor (m) is defined as the product of the cosine of the angle between the applied stress direction and the slip direction (ϕ) and the cosine of the angle between the normal to the slip plane and the stress direction (λ):

$$m = \cos(\phi) \cdot \cos(\lambda)$$

[00132] The Schmid factor indicates how much of the applied stress is resolved along the slip direction, thus contributing to the shear stress on a particular slip system. The Schmid factor of the nanostructure (e.g., a nanosheet or nanofilm) can be at least 0.05, at least 0.10, at least 0.15, at least 0.25, at least 0.35, at least 0.50, at least 0.75, or at least 0.90. In some embodiments, the nanostructure has a Schmid factor about 0.25 to about 0.50.

[00133] A “unit cell” in this context refers to the smallest repeating structural unit within a crystal lattice of the nanostructure (e.g., nanosheet or nanofilm). It is the fundamental building block that, when stacked in three-dimensional space, forms the entire crystal structure. The height of the unit cell can vary depending on the specific material and its crystallographic properties.

[00134] For the nanostructure (e.g., nanosheet or nanofilm) described herein, the height of a single unit cell can vary depending on the material. This implies that the compression-induced vertical deformation could range from a minimal displacement equivalent to the height of a single unit cell, up to a deformation corresponding to the thickness of 1000 unit cells.

[00135] In another aspect, the present disclosure provides an article or device comprising the metal nanostructure as described herein. As nonlimiting example, the metal nanostructure as described herein (e.g., gold nanostructure) can be used in articles and devices such as decorations, tools, household appliances, coatings, sensors, electrical contacts, interconnects, separation membrane, filter membrane, photonics, microelectronics, and microchips.

[00136] The disclosure also provides a system for producing a metal nanostructure. The system comprises a bottom substrate configured to receive nanoparticles, thereby forming assembly of nanoparticles on the bottom substrate; a top substrate configured to contact the assembly of nanoparticles on the bottom substrate; and a controller configured to apply a uniaxial pressure to the top substrate, whereby the assembly of nanoparticles is compressed under the uniaxial pressure.

[00137] As nonlimiting examples, the present disclosure includes preparation of 0D AuNS and 1D AuNR. Small gold nanospheres (AuNSs) (~18 nm) were prepared via the Turkevich method. One hundred milliliters of nanopure H₂O and 250 μ L of 100 mM HAuCl₄ were added to a 125-mL flask. The solution was stirred at 600 rpm and brought to a rapid boil before adding 7 mL of 1% sodium citrate (m/v). The solution was then stirred for 30 min at just below boiling. An additional 2.5 mL of 1% sodium citrate (m/v) was added, and the reaction was stirred while heating for 10 min. The heat was then turned off, and the particles were cooled to near-room temperature

with continued stirring (60 min). The solution was centrifuged at 9,000 RCF for 20 min, the supernatant was removed, and the pellet was resuspended in 10 mL nanopure H₂O.

[00138] Medium (~59 nm) and large (~103 nm) AuNSs were prepared via the seed-mediated synthesis by Chan et al. As outlined above, small Au seeds (14 nm) were prepared by the Turkevich method, with 60 mL nanopure H₂O, 0.1524 mL of 100 mM HAuCl₄, and 1.8 mL of 1% sodium citrate (m/v). The reaction was stirred for 10 min just below boiling, and the second sodium citrate addition was omitted. After cooling the particles to near-room temperature, the solution was centrifuged at 11,000 RCF for 20 min, the supernatant was removed, and the pellet was resuspended in 10 mL nanopure H₂O. For the growth of the 59 and 103 nm AuNSs, 480 mL nanopure H₂O and 1.27 mL of 100 mM HAuCl₄ were added to two 500-mL flasks. While stirring at 800 rpm, Au seed solution was added to each flask to reach a final seed concentration of 0.0353 nM (for 59 nm AuNS) and 0.0127 nM (for 103 nm AuNS). 1.1 mL 1% sodium citrate (m/v) was added to each flask. The reactions were stirred 5 s, followed by rapidly adding 5 mL of 30 mM hydroquinone. The reactions were stirred at 800 rpm at 25°C for 60 min. Particles were then centrifuged at 4,000 RCF (59 nm AuNS) and 2,000 RCF (103 nm AuNS) for 15 min, supernatants were removed, and pellets were resuspended in 10 mL nanopure H₂O.

[00139] Short AuNRs (47 × 16 nm, AR 3) were prepared via our previously reported method. Single-crystal cetyltrimethylammonium bromide (CTAB)-capped seeds were prepared by rapid injection of ice-cold 10 mM aqueous sodium borohydride into a rapidly stirring solution of 10 mL aqueous 100 mM CTAB and 0.25 mM HAuCl₄. The reaction was stirred rapidly for 10 min and then left still for 1 h. For NR growth, 475 mL 100 mM aqueous CTAB, 1.25 mL 100 mM aqueous AgNO₃, and 25 mL 10 mM HAuCl₄ were added to a 1-L flask. Next, 2.75 mL 0.1 M ascorbic acid was added, which caused the solution to turn colorless. Finally, 600 µL of the Au seed solution was added, and after thorough mixing, the reaction was kept still at 27°C overnight. The solution was centrifuged at 4,500 RCF for 15 min, and the particles were washed twice in 1 mM aqueous CTAB.

[00140] Long AuNRs (99 × 14 nm, AR 7) were prepared via the synthesis method of Vigdeman and Zubarev et al. Single-crystal CTAB-capped seeds were prepared by rapid injection of 460 µL ice-cold 10 mM sodium borohydride in 10 mM aqueous NaOH into a rapidly stirring solution of 10 mL aqueous 100 mM CTAB and 0.50 mM HAuCl₄. The reaction was stirred rapidly for 10 min and then left still for 1 h. For NR growth, 475 mL 100 mM aqueous CTAB, 1.5 mL 100 mM

aqueous AgNO₃, and 25 mL 10 mM HAuCl₄ were added to a 1-L flask. Next, 25 mL of 100 mM hydroquinone was added, which caused the solution to turn colorless. Finally, 8 mL of the Au seed solution was added, and after thorough mixing, the reaction was kept still at 27°C overnight. The solution was centrifuged at 4,500 RCF for 15 min, and the particles were washed twice in 1 mM aqueous CTAB.

[00141] All particles were functionalized with mPEG-SH to reduce NP aggregation upon deposition. Particles were diluted to 1 nM in 0.2 mM mPEG-SH MW 5k (shorter) PEG or 0.1 mM mPEG-SH MW 40k (longer) PEG. Excess capping ligands were removed from the particles by washing them six times with nanopure water, followed by dispersion in nanopure water to the target particle concentration.

[00142] As nonlimiting examples, the present disclosure includes AuNS and AuNR assembly on silicon substrate. Polished silicon wafers (prime grade, UniversityWafer, Inc.) were used for assembling AuNS and AuNR. The silicon wafers were diced into 2 mm × 2 mm square substrates and cleaned using deionized (DI) water, acetone, and isopropyl alcohol (IPA) via ultrasonication, followed by piranha cleaning (3:1 sulfuric acid and 30% hydrogen peroxide) and DI water rinsing. Silicon substrates were further undergone through O₂ plasma to increase hydrophilicity. The concentration and volume of the colloidal AuNP solutions were tailored to the desired as-assembled area coverage and then drop-casted onto the silicon wafers and left to dry slowly to ensure monolayer assembly of the AuNPs. The as-assembled AuNP/Si was characterized via SEM and AFM to statistically quantify the area of coverage and confirm monolayer closed-packed assembly.

[00143] As nonlimiting examples, the present disclosure includes compression of AuNP. Uniaxial compression was applied to the AuNPs via a custom-built hydraulic press setup ensuring solid-state, hard-contact compression. This study uses this custom technique to ensure displacive motion-mediated structural transformation, in contrast to in situ deformation within transmission electron microscopy (TEM) setups, which is often dominated by diffusion-mediated structural reconstruction due to electron beam-induced sample heating and atomic diffusion. Silicon wafers prepared in the same manner as the AuNP assembly substrate were diced into 1 mm × 1 mm squares as top compression surfaces. To prevent the top compression surface from picking up the AuNPs (i.e., to keep the AuNPs on the silicon substrate), a self-assembled monolayer (SAM) was deposited onto the top compression surfaces by exposing them to trichloro(1H,1H,2H,2H-

perfluorooctyl)silane vapor in a vacuum desiccator (shown in Fig. 38). The compression force was measured using a flat membrane box load cell sensor. The duration of the compression transformation process is ~ 10 s. Our solid-state uniaxial compression was performed at a loading rate of 0.58–1.86 nm/s (i.e., strain rate of 0.03–0.19/s), with the compressive force held stable for ~ 10 s before unloading.

[00144] As nonlimiting examples, the present disclosure includes estimation of the nominal compression stress and normalized compression stress. The custom-made solid-state compression setup consists of a top compression silicon wafer of $1\text{ mm} \times 1\text{ mm}$ and a bottom substrate silicon wafer of $2\text{ mm} \times 2\text{ mm}$. Colloidal AuNP solution is deposited on the bottom substrate silicon wafer and then compressed with the top compression silicon wafer. The applied nominal stress (σ_{nom}) is calculated by considering the nominal force (F_{nom}) applied over the total nominal contact area (A_{nom}) between the top compression silicon wafer and the bottom substrate silicon wafer ($A_{\text{nom}} = \sim 1\text{ mm}^2$). The applied normalized stress (σ_{norm}) is calculated by considering the nominal force (F_{nom}) acting on the area covered by the as-assembled AuNPs on the substrate (shown in Figs. 39 and 40). Therefore, $\sigma_{\text{norm}} = (\sigma_{\text{nom}}/\text{area coverage of AuNP}) = (F_{\text{nom}})/(A_{\text{nom}} \times \text{area coverage of AuNP})$. Evenly spaced, 13 positions (with polar symmetry) are statistically sampled across each of the as-assembled AuNP/Si wafers to determine the area coverage of AuNP. The as-assembled samples with uniform coverage (with a statistical coefficient of variation [COV] of less than 30%) are used for compression to ensure uniform compressive stress distribution.

[00145] EXAMPLES

[00146] Gold nanospheres (AuNSs) and gold nanorods (AuNRs) were colloidal synthesized and subsequently functionalized with thiolated methoxyl polyethylene glycol (mPEG-SH). The hydrophilic capping polymer brushes improve AuNP colloidal stability and reduce agglomeration in solution via steric isolation, thus improving deposition and assembly uniformity on the substrate for the compression process (see Materials and Methods for details). The AuNS and AuNR colloidal solutions were drop-casted and assembled in (sub)monolayers onto polished silicon substrates ($2 \times 2\text{ mm}^2$). A custom-built hard-contact compression setup was used to apply uniaxial compressive stress via direct contact between the top silicon wafer surface and the assembled AuNP on the bottom silicon substrate (AuNP/Si) (Fig. 13A). The degree of compression is quantified from the applied *nominal* stress (σ_{nom}) and applied *normalized* stress (σ_{norm}) (see Materials and Methods for details).

[00147] To determine the appropriate amount of stress to apply and induce severe plastic deformation and 2D transformation of the AuNPs, the strengths of gold micro/nano-crystals documented in the existing literature was considered. Significant disparities of reported yield strength exist in the literature, mainly due to the difference of particle size, shape, loading conditions and etc. Therefore, considering higher stiffness (59) and higher compression resistance, and lower density of structural defects in the present colloidally synthesized AuNPs compared to bulk gold, it was estimated that for the small AuNPs (~18 nm diameter), an applied *normalized* stress of ~3.6 GPa would sufficiently initiate dislocation nucleation and induce severe plastic deformation to study the anisotropic 2D morphological transformation. The empirical results indeed show that AuNPs of different sizes, morphologies, and assemblies all exhibit significant plastic deformation under ~3.6 Gpa applied uniaxial *normalized* compressive stress. Three different sizes (average diameter) of AuNSs, small (~18 nm), medium (~59 nm), and large (~103 nm), were studied to understand the effect of uniaxial compressive stress on different-sized AuNSs and their resultant solid-state transformation to 2D morphology. These AuNSs were coated with 5k Da PEG (also denoted as ‘shorter PEG’) capping layer to provide a steric hindrance to maintain interparticle separation and stability in the monolayer assembly, which is estimated as $\sim 4.5 \pm 4.7$ nm (small AuNSs), $\sim 7.9 \pm 11.9$ nm (medium AuNSs), and $\sim 7.7 \pm 12.7$ nm (large AuNSs) (Fig. 18, and Table 1). The as-assembled morphology of the small, medium, and large AuNSs with 5k PEG on the substrate form monolayer hexagonal closed packed (HCP) assemblies, verified via atomic force microscopy (AFM) and scanning electron microscope (SEM) (Fig. 14A-C). The AuNSs undergo severe plastic deformation due to applied uniaxial *normalized* compressive stress, with anisotropic expansion on the substrate in the lateral in-plane directions and concomitant thickness reduction in the vertical out-of-plane direction. As a result, the AuNSs deform into various disk-like, oblong, and oval shapes due to compressive stress-induced dislocation nucleation and mobility (Figs. 13B and 13C). The induced severe plastic deformation phenomenon is evident from the flattened 2D leaf-like morphology, which is attributable to the unique malleability of gold extending down even to the single-digit nanometer scale (Figs. 13D and 13E).

Table 1. Tabulated data for the calculated IPS for the different sizes of AuNS with different PEG lengths.

AuNP Type	Centroid to centroid distance (nm)	Particle diameter (nm)	IPS (nm)
Small AuNS 5k PEG	27.8 ± 2.8	23.3 ± 3.8	4.5 ± 4.7
Medium AuNS 5k PEG	59.1 ± 5.0	51.2 ± 10.8	7.9 ± 11.9
Large AuNS 5k PEG	99.1 ± 6.9	91.4 ± 10.7	7.7 ± 12.7
Small AuNS 40k PEG	154.6 ± 65.4	28.4 ± 3.4	126.2 ± 65.5

[00148] The deformation of bulk (polycrystalline) gold is dictated by the dislocation mobility, dislocation hindrance, dislocation entanglement, dislocation bowing (Orowan strengthening), dislocation pile-up (Hall-Petch mechanism), etc. At the nanoscale regime in AuNPs, dislocation nucleation, migration towards interfaces, and starvation (less probability of multiplication) dominate the deformation behavior. During compression of the AuNSs, elastic deformation is followed by a plastic deformation regime where dislocations initiate at the contact interfaces and propagate through multiple possible slip planes within the particle. Experimentally, different possible compression directions coexist due to the stochastic crystallographic orientations of the individual AuNSs (Schmid factor ranges from 0.37 to 0.49) (Table 2).

Table 2. Tabulated Schmid factor for compressive stress at different compression directions on the AuNP facets, considering the slip plane and slip direction as {111} and {101}, respectively. The Schmid factor ranges from 0.37 to 0.49.

Compression direction	Slip plane	Slip direction	Angle between compression direction and normal to slip plane, $\phi(^{\circ})$	Angle between compression direction and slip direction, $\lambda(^{\circ})$	Schmid Factor
001	111	101	54.7	45	0.408
110	111	101	35.26	60	0.408
100	111	101	54.7	45	0.408
311	111	101	29.5	64.76	0.37
210	111	101	39.23	50.77	0.49

[00149] The dislocation nucleation and movement are evident from the *post-mortem* SEM images where shear bands are prominent (Figs. 19-20). Owing to the intrinsic high surface-to-

volume ratio of AuNSs, many free facets of AuNSs act as sources and sinks for these dislocations. The transformed morphologies of the compressed AuNSs exhibit anisotropic morphologies with significant expansion of the nanoparticle lateral sizes and reduction of the interparticle spacing (Figs. 14D-F). The transformed 2D morphologies from the 0D AuNSs may result from dislocation escape towards the free surfaces of AuNSs upon compression. Eventually, the lateral in-plane expansion causes adjacent AuNSs to narrow the gap of initial interparticle separation and could also introduce sintering via atomic migration at the AuNSs boundary edge. The resultant fast Fourier transform (FFT) pattern of the deformed AuNSs no longer shows distinguishable spots, but rather a diffused ring, indicative of a lowering of the nanoparticles' ordering (lower correlation length) and higher distribution of interparticle centroid-to-centroid distances (inset of Figs. 14D-F).

[00150] To understand the effect of crystal orientations of the as-assembled AuNSs on the anisotropic transformation process and the resultant 2D morphology, we analyzed the crystallographic evolution of the AuNSs via electron backscatter diffraction (EBSD). While the characterization of the relatively smaller AuNSs was elusive due to limitations in imaging resolution, the crystallographic orientation of the large AuNSs was resolvable both in their as-assembled and compressed 2D morphologies (Figs. 21A-F). The facet orientations of the as-assembled AuNSs appear to be fairly random, with some minor texturing of (212) facets aligned with the (substrate) nominal z-direction (Fig. 21C). After compression, the 2D morphology appears to feature predominantly (101) facets aligned with the (substrate) nominal z-direction (Fig. 21D). This direct observation of the crystallographic evolution is further evidence of the severe plastic deformation and 2D transformation experienced by the AuNSs. A complex dependency could exist between the transformed 2D morphology, nanostructure, and crystallographic texture stemming from the individual's initial faceting and crystallographic orientation as-assembled AuNSs and their mutual interactions, which calls for further in-depth exploration beyond the scope of this work.

[00151] The morphological evolution and induced z-strain (ϵ_z) of different-sized AuNSs are statistically quantified from AFM mapping by comparing the thicknesses of initial as-assembled ($t_{\text{as-assembled}}$) versus the compressed nanoparticles ($t_{\text{compressed}}$) (Fig. 22). Here, the vertical out-of-plane z-strain is defined as $\epsilon_z = (t_{\text{as-assembled}} - t_{\text{compressed}})/t_{\text{as-assembled}}$. The effective thicknesses of the as-assembled AuNSs are determined to be 18.8 ± 0.4 nm (small AuNS), 51.6 ± 0.6 nm (medium

AuNS), and 83.6 ± 0.7 nm (large AuNS) (Table 3). In comparison, the thickness of the compressed anisotropic 2D AuNSs is much thinner than the dimensions of the as-synthesized and the thickness of the as-assembled AuNSs. The thicknesses of the compressed AuNSs are 11.6 ± 0.8 nm (small AuNS), 22.1 ± 2.9 nm (medium AuNS), and 37.0 ± 1.7 nm (large AuNS) (Table 3). This reduction in vertical dimension translates to a compression-induced vertical strain (ϵ_z) of $38.12 \pm 0.1\%$ for small AuNS, $57.06 \pm 0.1\%$ for medium AuNS, and $55.71 \pm 0.1\%$ for large AuNS. Given the same applied *normalized* stress for all three AuNS sizes, the smaller AuNSs appear to be relatively less compressible.

Table 3. AFM-extracted metrology data for as-assembled and compressed: small, medium, and large AuNSs with 5k PEG at different positions.

	As-is (nm)	Compressed (nm)	As-is (nm)	Compressed (nm)	As-is (nm)	Compressed (nm)
Position 1	18.06	10.64	51.05	23.47	83.54	34.82
Position 2	18.69	12.67	51.91	20.79	83.1	35.15
Position 3	18.84	11.82	50.32	19.87	84.19	36.24
Position 4	19.4	13.14	51.35	20.23	84.69	34.76
Position 5	18.97	11.44	52.54	21.54	83.05	38.37
Position 6	18.28	11.88	51.68	18.16	82.69	37.47
Position 7	19.12	12.01	51.7	21.62	83.49	36.51
Position 8	18.9	10.61	51.53	21.38	83.26	39.47
Position 9	18.61	10.55	51.62	27.9	83.4	38.85
Position 10	18.67	11.61	51.98	26.47	84.77	38.74
Average	18.75	0.83	51.57	22.14	83.62	37.04
SD	0.37	7.18	0.56	2.85	0.67	1.69
COV	1.97	7.18	1.09	12.89	0.79	4.57
ϵ_z		38.12%		57.06%		55.71%

[00152] In addition to the nanoparticle size, the as-assembled interparticle separation and adjacent nanoparticle interactions also affect the transformed 2D morphology. More significant interparticle separation can be achieved by 1) reducing the drop-casted AuNS colloidal

concentration and/or solution volume and 2) attaching PEG capping layers of different (longer) lengths. However, just lowering the deposited colloidal concentration and/or solution volume alone is insufficient to effectively modulate the as-assembled interparticle separation, as it yields sparse but agglomerated (closed-packed) patches of AuNSs on the substrate surface. Therefore, the length of the PEG brushes grafted is varied for this study: shorter PEG – molecular weight (MW) 5k Da with a hydrodynamic length of $\sim 10\text{--}18$ nm and longer PEG - MW 40k Da with a hydrodynamic length of $\sim 34\text{--}39$ nm (Fig. 23). Along with tuning the colloidal concentration, the varied PEG length modulates the steric hindrance between nanoparticles during the drop-casting and assembly process while providing control over the interparticle separation of the as-assembled AuNSs. Small AuNSs (20 nm) were selected to study the influence of interparticle separation on the 2D morphological transformation of AuNSs (close-packed assembly vs. isolated particles). The small AuNSs are suitable for this investigation due to their higher grafting surface density and their relatively larger PEG length to AuNS size ratio, making the effect of interparticle separation more pronounced. After the deposition, the average as-assembled interparticle separation of small AuNS with 40k PEG ($\sim 126.2 \pm 65.5$ nm) was found to be higher compared to those with 5k PEG ($\sim 4.5 \pm 4.7$ nm) (Figs. 15A, 15B, and Table 1).

[00153] The small AuNSs with 5k PEG mostly remained in close-packed and monolayer arrangement, forming a mesoscopic networked pattern. Any particular AuNSs in this networked structure can have a range of neighboring AuNSs depending on its location: interior AuNSs have six adjacent AuNSs, and edge or corner AuNSs have one to five adjacent AuNSs, which results in varying degrees of lateral resistance under the same applied compression in the z-direction (Figs. 15A and 15C). In comparison, the isolated small AuNSs with 40k PEG have larger interparticle separation without lateral resistance from adjacent AuNSs and the same applied compression induces a higher degree of 2D transformation (Figs. 15B, 15D), transforming the isolated small AuNSs with 40k PEG into oval, disk-like 2D morphologies (Fig. 15D). Statistical analysis of SEM images shows that isolated small AuNSs with 40k PEG exhibit ~ 1.9 times larger lateral area expansion due to significantly larger plastic deformation compared to the close-packed small AuNSs with 5k PEG (Fig. 24). In addition, AFM measurements indicate a much larger ϵ_z for isolated small AuNSs with 40k PEG ($64.88 \pm 0.1\%$) compared to the closed-packed small AuNSs with 5k PEG ($38.12 \pm 0.1\%$) (Fig. 15E,). This larger deformation of the isolated small AuNSs with 40k PEG in comparison to the closed-packed small AuNSs with 5k PEG is in part attributable to

their differing lateral resistance from neighboring AuNSs. Similarly, a higher degree of 2D transformation was observed for isolated large AuNSs with 40k PEG compared to close-packed large AuNSs with 5k PEG (Figs. 25-26). AFM measurements corroborate the larger ϵ_z for isolated large AuNSs with 40k PEG ($75.54 \pm 0.1\%$) (Figs. 27-29) compared to the closed-packed large AuNSs with 5k PEG ($55.71 \pm 0.1\%$).

[00154] Moreover, the 2D transformation of AuNP was also found to be influenced by the magnitude of the applied normalized compressive stress, σ_{norm} . Close-packed AuNSs with 5k PEG can be progressively compressed to ever-thinner 2D morphologies by applying progressively larger normalized compressive stress (i.e., nanoscale systems) (Fig. 30). In addition, a much larger applied normalized compressive stress ($\sigma_{\text{norm}} = 6$ GPa) induces a higher degree of 2D transformation and z-strain to the isolated AuNSs. Here, a higher ϵ_z for isolated large AuNSs with 40k PEG ($80.16 \pm 0.1\%$) was observed under $\sigma_{\text{norm}} = 6$ GPa compared to $\epsilon_z = 75.54 \pm 0.01\%$ under $\sigma_{\text{norm}} = 3.6$ GPa (Figs. 31-35). It was observed that the relationship between the induced z-strain and the applied compressive stress is non-linear.

[00155] To understand the atomistic deformation mechanisms of AuNSs under solid-state uniaxial compression, classical MD simulations were adopted to simulate the compression of isolated spherical AuNSs (Fig. 16A) at room temperature (300 K). The compression force is applied along the [001] direction of the AuNS with a velocity of 0.001 nm/ps. The compressive stress within the AuNS was evaluated using two metrics (Fig. 16C). The *true* stress is calculated based on the instantaneous contact surface area (shown in Fig. 16D) of the compressing AuNS. The *engineering* stress is calculated based on the initial (maximum, equatorial) cross-sectional area of the AuNS, similar to the empirical applied *normalized* compressive stress defined earlier. When compression starts, the isolated AuNS presents a linear elastic behavior (Fig. 16C) with zero dislocation density and a constant contact surface area (Fig. 16D). When the engineering strain reaches $\sim 2.9\%$ at a compression depth of 0.6 nm, yielding occurs and the dislocation density starts to increase. The true yield stress is 4.9 GPa, and the corresponding engineering yield stress is 0.18 GPa. The mechanical properties of metal nanoparticles (such as Cu, Au, Al, and Ag) have been reported to be sensitive to particle size, shape, temperature, orientation (55, 67–72), etc. Therefore, the true yield stress (4.9 GPa) and engineering yield stress (0.18 GPa) predicted in our MD simulations reflect reasonable upper and lower limits of the compressive stress for an individual

AuNP to initiate the plastic deformation process, which is consistent with the applied *normalized* compressive stress 3.6 GPa we adopted in the empirical solid-state compression process.

[00156] As the deformation continues, the top and bottom contact surfaces act as stress concentrators, causing glissile Shockley partial dislocations to form at these contact surfaces on the [111] slip planes as the compression depth reaches 0.6 nm, resulting in a huge increment in dislocation density (Fig. 16D). These glissile dislocations formed on [111] slip planes move inward of the AuNP. As the topmost layer of atoms becomes compressed into the second topmost layer, the Shockley partials symmetrically formed on the {111} planes react with each other, leading to the formation of pyramid hillock structures. Similar pyramid hillock structures have been reported in other FCC (face centered cubic) spherical monocrystals (Cu and Al) at low temperatures (10 K) through MD simulations. The topmost contact area progresses into the second topmost layer of AuNS, causing the sharp decrease of the true stress after yielding. Then the true stress climbs again before new dislocations are nucleated. The critical resolved shear stress (CRSS) is calculated to be 2.3 GPa, which falls in a similar range to previously published results. The deformed AuNS appears to have an oblong oval shape at 38% strain, with dislocation nucleation on {111} slip planes (Fig. 16B). Multiple MD simulations were conducted at two different loading rates (0.005 nm/ps and 0.001 nm/ps). Different deformed shapes were observed due to dynamic evolution of dislocations at 300 K (the selected deformed shapes at 38% strain are listed in Fig. 36). The variety of deformed AuNS shapes obtained from MD simulations are consistent with the polydispersity of empirically observed anisotropic 2D morphologies (Fig. 15D).

[00157] Solid-state nanoscale systems enables morphological transformation not just of 0D AuNS precursors but also of other metal nanoparticles shapes such as nanorods, nano-polyhedrons, nanostars, nanocages, etc. In particular, AuNRs (gold nanorods), as canonical anisotropic 1D metal nanocrystals, have well-established synthesis protocols with precise control over crystallinity, dimensionality (i.e., aspect ratio, $AR = \text{length}/\text{width}$), and their dependent properties. To demonstrate the generalizability of nanoscale systems, two different-sized AuNRs were transformed into 2D morphologies: Short AuNR (60x20 nm, “AR 3”, with 5k PEG) and Long AuNR (99x14 nm, “AR 7”, with 5k PEG). The as-assembled short AuNRs (Fig. 17A) and long AuNRs (Fig. 17B) were both subjected to applied uniaxial *normalized* compressive stress. The transformed 2D morphologies of both the short (Fig. 17D) and long AuNRs (Fig. 17E) exhibit severe plastic deformation and lateral elongation, transforming from a prismatic morphology into

a more flattened, oblong, ellipsoidal morphology with non-straight edges along the axial direction and in some cases bent rod ends. Regardless of the precursor AuNR size, significant deformation is evident in the transformed 2D morphology, along with the presence of shear bands (Fig. 20).

[00158] Statistical metrology analysis of individual AuNRs was performed to gain further insight into the morphological transformation. The projected lateral areas for the as-assembled and compressed AuNRs were quantified from SEM images (Figs. 37A-B). Metrological analysis of the lateral elongation along the AuNRs axial length and radial width quantifies the in-plane (i.e., substrate plane) anisotropic deformation. However, characterizing the nominal length and width will generate erroneous conclusions due to the non-uniform boundary edges of the compressed AuNR morphology. Therefore, the closest approximation of the as-assembled and compressed AuNRs shape is performed by ellipse fitting and extracting the major (length) and minor (width) axis information (Figs. 37C-D). Each AuNR was analyzed via ellipse fitting by equating their enclosed area and equating their second-order central moment of area.

[00159] The aforementioned statistical metrology analysis of the average lateral area indicated that the short AuNRs were expanded by 80% (from $1162.4 \pm 41.0 \text{ nm}^2$ to $2093.2 \pm 98.0 \text{ nm}^2$) as a result of compression (Fig. 17C), whereas the long AuNRs experienced an average lateral area increase of 37.68% (from $2155.0 \pm 28.7 \text{ nm}^2$ to $2967.0 \pm 38.9 \text{ nm}^2$) (Fig. 17F). Due to severe plastic deformation, the short AuNRs length (major axis) expanded from $57.9 \pm 0.7 \text{ nm}$ to $85.8 \pm 1.9 \text{ nm}$, and the width (minor axis) expanded from $25.2 \pm 0.3 \text{ nm}$ to $29.9 \pm 0.7 \text{ nm}$ (Fig. 17G). Similarly, after compression, the long AuNRs length (major axis) increased from $117.6 \pm 0.9 \text{ nm}$ to $139.6 \pm 1.6 \text{ nm}$, and the width (minor axis) expanded from $23.1 \pm 0.2 \text{ nm}$ to $26.8 \pm 0.3 \text{ nm}$ (Fig. 17G).

[00160] The vertical z-strain for transformed AuNRs was statistically derived from AFM height maps. The thicknesses of the as-assembled and compressed short AuNRs indicate an induced z-strain, $\epsilon_{Z, \text{ short AuNR}}$ of $49.33 \pm 0.1\%$ (from $\sim 18.1 \pm 2.4 \text{ nm}$ to $\sim 9.2 \pm 0.7 \text{ nm}$) (Fig. 17H), whereas the long AuNRs exhibited a slightly smaller $\epsilon_{Z, \text{ long AuNR}}$ of $42.1 \pm 0.1\%$ (from $14.4 \pm 1.2 \text{ nm}$ to $8.4 \pm 0.6 \text{ nm}$) (Fig. 17H). Considering both the thickness reduction (z-strain) and the average lateral area expansion, the more slender, long AuNRs appear to be relatively less compressible compared to the girthier, short AuNRs under the same applied *normalized* compressive stress, suggested by earlier studies. Previous computational and experimental efforts on similar gold nanocrystals (i.e., nanowires) have primarily focused on axial tensile or nanoscale bending tests. These observed

dependencies of mechanical properties on the size of metallic nanowires generally exhibited trends of smaller nanowires having higher strength. Our results here provide a different perspective to the existing literature by studying the deformation of nanorods in the radial direction, which warrants further investigations to gain a better understanding of the mechanisms underlying metallic nanocrystal deformation. Overall, it is evident that our solid-state 2D transformation technique is extendable to study the deformation and transformation of other nanocrystals beyond 0D AuNSs and 1D AuNRs.

[00161] In conclusion, nanoscale compression systems have been extended by several orders of magnitude down to the single-digit nanometer scale via solid-state, uniaxial compression of 0D gold nanospheres and 1D gold nanorods, transforming them into anisotropic 2D gold leaf morphologies. The resultant 2D morphologies are found to be influenced by the precursor gold nanocrystal morphology, dimensions (diameter, aspect ratio), and interparticle interactions. In addition, the ability to induce additional nanoparticle shape anisotropy enables control of the leaf-like 2D gold's shape, lateral size, thickness, and crystallinity. We postulate that this nanoscale systems process is potentially compatible with nano-imprinting or nano-embossing techniques to induce various hierarchical morphologies. Such versatility and generalizability of this solid-state compression methodology could open new pathways to investigate interesting morphological transformations and strain-induced emergent phenomena across a broad palette of nanocrystals.

[00162] Molecular dynamics simulation

[00163] The LAMMPS package was adopted to perform the classical molecular dynamics simulations. Spherical AuNSs of diameter 20 nm were carved out from a perfect FCC Au crystal structure (Fig. 16A). The lattice constant is 0.408 nm. The simulation box size is 40.4 nm × 32.23 nm × 59.99 nm with a xy tilt of 18.6 nm. The vacuum space within the simulation box keeps AuNS isolated from interactions and allows AuNS to deform freely under compression. The embedded atom method (EAM) potential was adopted to describe the pairwise interactions of Au atoms. The AuNS was first equilibrated at 300 K under an NVT ensemble for structure relaxation. The center of mass and momentum of AuNS is confined to eliminate the rigid body translation and rigid body rotation motions. After relaxation at 300 K, the AuNS was placed between two virtual planar compression surfaces. The planar surfaces are presented by two repulsive force fields moving toward the center of AuNS with a constant velocity of 0.001 nm/ps. The uniaxial compression is along the z-direction aligned with the [001] crystallographic orientation of the Au crystal. The

loading speed is faster than the experimental setup but appears to have a minimum impact on the deformation mechanism of AuNS during the compression. The stiffness of the force field was defined as $1,000 \text{ eV/\AA}^{-3}$, equivalent to rigid body compression. The time step size is 1 fs. During compression, the force applied on AuNS was calculated by the reaction force exerted on the planar compression surface. The compressed contact surface area was calculated using Delaunay triangulation. The dislocation density was evaluated through the visualization software OVITO.

[00164] EBSD

[00165] EBSD mapping was performed using an FEI Helios G4 PFIB equipped with an EDAX Velocity EBSD camera, a 10-kV beam voltage, a beam current of 6.4 nA, and a nominal working distance of approximately 6 mm. All EBSD data sets (maps) were collected using EDAX TEAM software with a 6-nm step size, the “Medium-Large” Hough mask setting, 8×8 EBSD pattern binning, and the “Enhanced” EBSD pattern digital processing setting. The EBSD pattern at each point in the map was simultaneously recorded during the collection of the map data set. Subsequently, EDAX OIM 8 software was used to generate the inverse pole figure maps and pole figures for each data set. Finally, neighbor pattern averaging and reindexing was performed to improve indexing accuracy using the acquired EBSD patterns for each map data set.

[00166] Interparticle separation (IPS) calculation

[00167] The interparticle separation (IPS) of the as-assembled AuNSs is calculated by analyzing SEM images. The SEM images are obtained of AuNSs at 100kx and processed using ImageJ software to perform binary conversions. A Fast Fourier transformation (FFT) pattern of the binary images is obtained. Subsequently, six distinguished FFT spots were used to estimate the centroid to centroid distance for the as-assembled AuNSs (Fig. 18). The average centroid-to-centroid distance (d_{cc}) was calculated statistically by averaging data from SEM images from thirteen spots across the “central region”. We denote the particle diameter as d_p , so $IPS = d_{cc} - d_p$. The average particle diameter is estimated from the nominal particle projection area from SEM images for each sized AuNS. The IPS data for different-sized AuNS with shorter (5k) and longer (40k) PEG are all tabulated in Table 1.

[00168] The as-assembled small AuNSs with 40k PEG are spaced far from each other. After performing the same image analysis, the generated FFT pattern does not show any distinguishable pattern to quantify the centroid-to-centroid distances. Therefore, for as-assembled small AuNS

with 40k PEG, the IPS is calculated from SEM images by manually determining the centroid-to-centroid distance between 100 pairs of AuNSs using ImageJ.

[00169] The deformation-induced shear bands in AuNSs and AuNRs

[00170] The compression-induced plastic deformation causes dislocation nucleation and movement in the AuNPs (AuNSs and AuNRs). The solid-state deformation process is performed in ambient conditions and is likely dominated by displacement-mediated structural transformation over diffusion-mediated structural transformation. In the *post-mortem* SEM images, we observed prominent shear bands in the compressed AuNSs (Fig 14) and AuNRs (Fig 15), suggesting the dislocation nucleation and movement and displacement-mediated nature of the transformation.

[00171] Crystallographic evolution of AuNS

[00172] The crystallographic orientation of the as-assembled and compressed AuNS was evaluated using electron backscatter diffraction (EBSD) (FEI Helios G4 PFIB) (Fig. 21).

[00173] Characterization of AuNS 5k PEG Morphology and Its 2D Transformation

[00174] The morphology of AuNSs (especially in the z-direction) is characterized via Atomic Force Microscopy (AFM) mapping. For statistical analysis of the thickness evolution and understanding of the uniformity of the compression, ten AFM datasets across the sample are acquired for each as-assembled and compressed sample (Fig. 22A and Table 3). All AFM measurements are acquired via a Veeco Dimension 3000.

[00175] Each AFM map is statistically analyzed to estimate the thickness of the as-assembled AuNSs or the compressed 2D morphology. The AFM images are post-processed, with height histogram information extracted, and fitted with Gaussian distributions.

$$y = y_0 + \left(\frac{A}{w \times \sqrt{\frac{\pi}{2}}} \right) \times e^{(-2 \times \left(\frac{x-x_c}{w} \right)^2)} \quad (1)$$

[00176] The histogram is fitted with two independent Gaussians, corresponding to the pixel sampling of the bare silicon substrate and those of the (as-assembled or compressed) AuNSs. The thickness is calculated from the difference between two fitted means, which corresponds to the difference between the bare substrate and the average height of the as-assembled or compressed AuNSs (Figs. 22B and 22C).

[00177] Metrology analysis of small AuNS with 40k PEG

[00178] Metrology analysis of individual as-assembled and 3.6 GPa (applied normalized stress) compressed small AuNS with 40k PEG was performed by measuring the in-plane lateral projected 2D area. The goal of the metrology analysis of small AuNS 40k PEG is to understand the induced lateral anisotropy on the nanoparticles when they undergo deformation in isolation from other nanoparticles. Four positions near the central compressed region (positions 10, 11, 12, and 13) were chosen, and SEM images of the positions were analyzed. A shape line was drawn along the boundary edges of the as-assembled and compressed AuNSs. Subsequently, the associated AuNS area were measured using ImageJ. Only freely deformed AuNSs were included in the area calculation, while the AuNSs touching the adjacent ones were avoided. The area of the as-assembled and compressed AuNS is $702.5 \pm 24.7 \text{ nm}^2$ and $1337.9 \pm 74.6 \text{ nm}^2$, respectively, indicating ~ 1.9 times lateral area increment due to compression (Fig. 24).

[00179] Transformation of close-packed AuNSs with progressively larger compressive stresses: nanoscale systems.

[00180] The applied normalized stress dictates the post-compression morphology of the AuNSs. We demonstrate that close-packed AuNSs can be compressed repeatedly with progressively higher applied normalized stresses. Figure 30 shows the morphological evolution of close-packed large AuNSs with 5k PEG from as-assembled, then after applied normalized stress of $\sigma_{\text{norm } 1} = 1 \text{ GPa}$, and then again after a larger applied normalized stress of $\sigma_{\text{norm } 2} = 2.15 \text{ GPa}$.

[00181] Molecular Dynamics Simulation of AuNS

[00182] To study the role of the compression velocity of the top compression surface in the deformation behavior of the AuNS, we also selected compression velocity to be $v=0.005 \text{ nm/ps}$, a higher velocity, and run a few more cases with different initial equilibrium configurations. The true yield stress is listed in Fig. 36. The true yield stress evaluated in the MD simulation relates to the compression velocity selections. Even with a higher compression velocity of 0.005 nm/ps , it was found that the average yield stress was within 3% of the yield stress calculated at a low strain rate. However, it was found that the variation in yield stress with a slower compression velocity was less compared to a higher velocity. Therefore in this study, a slower velocity of 0.001 nm/s was adopted. Even though the activated slipping directions are different based on thermal vibrations, all the deformed AuNSs appear to have morphology consistent with the deformed AuNSs in the SEM images shown in Fig. 15. Top view of the compressed AuNS at $\sim 38\%$ strain.

The atoms are colored using dislocation analysis (DXA) in OVITO. Yellow represents the FCC structure, red represents the HCP structure, and surface atoms are removed for better visualization.

[00183] Metrology analysis of AuNR

[00184] The plastic deformation-driven metrology of the AuNR was characterized by analyzing the as-assembled and post-compression morphology. The area of the AuNRs was estimated by drawing a shape outline meticulously along the AuNR boundary using ImageJ (Fig. 37A-B). 100 as-assembled and compressed AuNRs, each, were analyzed across the sample from position 1 to 13.

[00185] Evident from the SEM images, the compression of the short and long AuNRs results in anisotropic 2D morphology with nonuniform edges in the lateral direction. As such, an end-to-end measurement of the dimensions (i.e., length and width) may result in erroneous estimation. We resort to the ellipse fitting of these non-uniform shapes to estimate the metrological evolution (length - major axis and width - minor axis) during the compression process because the AuNR shape can be closely approximated to be elliptical. While acknowledging that this could result in overestimating the dimensions, we aim to estimate the dimensional change by the ellipse fitting of both as-assembled and compressed AuNRs.

[00186] Here, the image analysis of individual AuNRs was performed by fitting an ellipse using ImageJ. An arbitrarily constructed shape with an enclosed profile contains a two-dimensional distribution of data points, which can be fitted by the best representative ellipse using ImageJ. During this attempt toward the elliptical fitting, the area is kept similar (maximum deviation of 4%), while the second-order central moment of both shapes is kept equal. A shape outline is drawn along the boundary edge of the AuNRs to assume their anisotropic shape with a closed profile; subsequently, processing of the image with the best-fitted ellipse was performed to find the length (major axis) and width (minor axis) of the as-assembled and compressed AuNR morphology (Fig. 37D). SEM images for all the positions (1 to 13) across the samples were used to characterize the as-assembled and compressed AuNRs. Only individual AuNRs were characterized, while the sintered AuNRs were avoided during the analysis. This metrology analysis provides statistical information regarding the change of the length (major axis) and width (minor axis) before and after compression.

[00187] Morphological anisotropy characterization and evolution of AuNR

[00188] The morphological characterization of the AuNRs in the z-direction was characterized by methods similar to the AuNSs. For statistical analysis of the thickness evolution and understanding of the uniformity of the compression technique, ten AFM datasets across the sample were acquired and analyzed for each as-compressed and compressed AuNR sample.

[00189] Effect of SAM on the top compression Si wafer

[00190] Both the top Si wafer and bottom Si substrate are of the same bulk material and crystalline orientation. Therefore, the relative surface energy determines the relative binding of AuNPs to either surface after compression. The same cleaning processes were applied to both top and bottom Si wafers, including solvent cleaning, oxygen plasma cleaning, and piranha cleaning, all of which increase the surface energy of the native oxide surface and increase the interaction between the Si wafer and AuNPs during compression. With the bare native oxide surface, we found that a relatively high proportion of AuNPs become attached to the top Si wafer surface after compression, with the AuNP area coverage on the top Si wafer increasing from null to ~61% (Figs. 38 D, E, and F). To prevent this from occurring and to maintain the compressed nanoparticles on the bottom Si substrate, surface modification was performed to the top Si wafer surfaces with self-assembled monolayers (SAM) (trichloro (1H,1H,2H,2H perfluorooctyl), which reduces the surface energy significantly. For example, Wang et al. showed that the surface energy of oxide surfaces on Si wafers can be modified by using SAM which increases the water contact angle from 71.1° to 105.2°. Using this surface modification, the tendency of AuNPs to attach to the top Si wafer surface after compression is drastically reduced (close to null) (Figs. 38 A, B, and C). Consequently, nearly all the compressed AuNPs remain on the bottom Si substrate which facilitates the millimeter-scale uniformity of the compressed AuNP morphology and enables statistical characterization at distributed positions to quantify such uniformity.

[00191] Area coverage calculation

[00192] The area coverages of the AuNPs on the silicon substrates are statistically determined. The deposition parameters, such as nanoparticle concentration, deposition volume, and drying time, are optimized to achieve a deterministic and uniform area coverage of AuNP assembly on the silicon wafer. The area coverages of AuNPs are determined statistically by sampling thirteen positions distributed across the substrate within the central region (within the 0.6 mm × 0.6 mm area), as indicated by the black dots in Fig. 39. For each position, an SEM image is taken (at 20kx magnification with a field of view of ~28 μm^2) and processed using ImageJ software to perform

binary conversion and area coverage calculations (Fig. 40). Considering all thirteen positions, the average area coverage, standard deviation (SD), and coefficient of variation (COV) for each sample are determined (Table 4). The uniform deposition of AuNPs on silicon substrate is confirmed when a sample has less than 30% COV.

Table 4. Tabulated data for the calculated average area coverage of AuNP assembled on silicon substrates.

AuNP Type	Average-Area Coverage (%)
Small AuNS 5k PEG	17.05 ± 1.62
Medium AuNS 5k PEG	21.54 ± 3.35
Large AuNS 5k PEG	18.76 ± 3.69 and 7.89 ± 1.42
Small AuNS 40k PEG	2.77 ± 0.37
Large AuNS 40k PEG	0.26 ± 0.074 and 0.26 ± 0.075
Short AuNR 5k PEG	1.82 ± 0.49
Long AuNR 5k PEG	2.61 ± 0.51

[00193] Nanoscale Systems via Diamond Anvil Cell (DAC)

[00194] In addition to the wafer-to-wafer compression setup, we have utilized nanoscale systems via DAC to glean insight into the nanoscale metallic deformation and possibly understand the effect of the compression surface on the shape anisotropy during 2D transformation. The DAC setup was operated without any pressure transmitting media, facilitating a non-hydrostatic, uniaxial high-pressure compression regime. Lab-grown brilliant-cut diamond (0.15 ct) was utilized to make the indenter for a high-pressure compression experiment. Figure 41 demonstrates the nomenclatures of various diamond facets, namely the table, crown, pavilion, culet, crown angle (34.5°), and pavilion angle (40.75°), respectively. The diamond culet is appropriately milled and shaped using Gallium ion in FIB Quanta 200 3D. First, the gold-palladium was sputter coated on the diamond culet to make it conducive to SEM imaging. Subsequently, the diamond culet was carefully aligned parallel with respect to the ion gun and milled via various ion beam currents. The milling voltage and current (from 30 kV, 20 nA to 15 kV, 1nA) were gradually lowered to achieve a culet with lower surface roughness, although, the culet surface remained visibly rough (with needle-like protrusions) after FIB milling. Subsequently, the diamond culet was further polished using 3M Trizact Hookit 3000, 5000, and 8000 grit foam polishing discs while carefully keeping the culet parallel to the polishing surface. Finally, the rough terrace-like morphology was polished into a smooth diamond culet which was used for the 2D transformation of the nanoparticles.

[00195] It was observed that the Si wafer is not suitable for use (i.e., as a substrate for AuNS assembly) in a non-hydrostatic DAC as the Si wafer tends to fracture and generates Si debris, rendering experimentation and characterization difficult. Therefore, polished sapphires (sapphire) were chosen for the deposition of AuNS due to their excellent hardness, stiffness, and atomic smoothness.

[00196] Pressure Estimation

[00197] As sapphire is electrically insulative in nature, a comprehensive statistical characterization was not performed, thus we have used the applied nominal stress for this portion of the study. Typically, the diamond indenter contacts the sapphire substrate, the AuNS starts to deform with an increase in force and the compression experiment leaves a contact mark on the sapphire substrate. Consequently, the pavilion also contacts the substrate during the compression process (Figure 42A). Aiming to an appropriate nominal pressure calculation, the projected contact area has been considered. Figure 42B and Figure 42C show the area A1 denoting the contact area with the indenter culet, and A2 denoting the contact area with the indenter culet and the pavilion.

[00198] Similar to the previous methodology, the applied nominal stress (σ_{nom}) is calculated by considering the nominal force (F_{nom}) applied over the total nominal contact area (A_{nom}). Here, we have selected a nominal compressive stress of 15 ± 0.75 GPa throughout the study (with the nominal force maintained at 5313 ± 30 g, within a 6% error). Compression of the AuNS on sapphire induces severe plastic deformation and generates a flattened 2D morphology (Figure 43A, B). Figure 43 indicates a decrease in surface roughness from 6.37 ± 0.46 nm to a flattened 2.15 ± 0.23 nm morphology.

[00199] Three different sizes (average diameter) of AuNS with 5k PEG: small (18 nm), intermediate (40 nm), and medium (59 nm) were studied to understand the effect of nanosphere size on the uniaxial compression and their resulting solid-state transformation. The shorter PEG provides a steric hindrance-based interparticle separation in the (sub)monolayer morphology, which is 3.52 nm (small), 9.46 nm (intermediate), and 4.41 nm (medium).

[00200] Figure 44 shows the SEM images of as-assembled and compressed 2D Au morphology of the small, intermediate, and medium AuNS with 5k PEG. The AuNS/sapphire samples were coated with gold-palladium to make them conducive to SEM imaging, therefore, the shear bands are not prominently visible. The transformed 2D Au has predominantly anisotropic disk-like, oval morphology, which could be generated due to the precursor AuNSs' initial shape and crystallinity

which is inherited during synthesis. We believe the deformation mechanism and dislocation movement are very similar to the wafer-to-wafer compression phenomena discussed earlier in this chapter. Herein, a vertical out-of-plane z stress of ϵ_z of 48.15%, 66.96%, and 73.28% is observed for small, intermediate, and medium AuNS, respectively, indicating a similar phenomenon of smaller is less compressible. The deformed AuNSs also exhibit strong interparticle boundary interaction, therefore forming a nanoporous film-like morphology. In addition, we were able to obtain ~2-3 nm 2D Au film-like morphology after applying a high nominal compressive stress (~30 GPa) on the small AuNSs with 5k PEG.

[00201] Moreover, the effect of IPS was evaluated by investigating the deformed state of the isolated AuNS. The isolation of AuNSs was achieved on the sapphire wafer by varying the PEG molecular weight (5k vs 40k) to modulate the interparticle separation from 3.3 nm (closed packed) to 32.1 nm (isolated). As can be seen from Figure 45, the absence of neighboring AuNSs (local coordination number being 0) renders the AuNSs free of lateral resistance and compressible, with prominent anisotropy in all three (x , y , and z) directions.

[00202] In addition, we have investigated and obtained preliminary evidence of the possible influence PEG ligands have on the compressibility of the AuNSs. Oxygen plasma treatment has been shown to affect the morphology of the gold nanoparticle array, morphology, and the organic ligand coating grafted around the nanoparticle.⁹⁰ Here, we have utilized low-power oxygen plasma at a relatively higher pressure to modify the PEG ligands while making sure the AuNS cores are not significantly affected during the process. An applied low-power oxygen plasma (50 W, 1000 mTorr, 10 min) on intermediate (40 nm) AuNS 5k PEG resulted in no visible de-wetting or morphological change of the AuNS array. Upon compression and 2D transformation, higher compressibility was observed for the plasma-treated AuNS under lower applied nominal stress, generating nanofilm with no visible nanopores compared to untreated AuNS array, which could be in part from the physical and chemical modification and oxidation of the PEG during the plasma treatment.

[00203] The thickness evolution of the nanoparticle assembly and induced vertical out-of-plane z -strain was evaluated for the small AuNS with 40k PEG to understand the effect of plasma on the compressibility of the AuNSs and collect evidence on the thin 2D Au. Upon oxygen plasma treatment, it was observed that the thickness of small AuNS was lowered from 20.8 ± 2.8 nm to 18.5 ± 1.88 nm, indicating altered morphology of the PEG ligands around the AuNS along with

the removal of PEG under applied plasma treatment. Subsequently, upon applying nominal compressive stress of 15 GPa, it was observed that the plasma-treated small AuNS experienced ϵ_Z of 78.32% compared to ϵ_Z of 51.40% for untreated small AuNS. While these preliminary data provide evidence of the PEG ligand's influence on the compressibility of AuNS, further in-depth analysis is required to understand the role of many associated parameters such as the isotropic and anisotropic PEG density and length on various sized AuNS, the effect of other species of plasma, plasma power, time, pressure, etc.

[00204] For reasons of completeness, various aspects of the invention are set out in the following numbered clauses:

[00205] Clause 1. A method for producing metal nanostructure, the method comprising:

applying a uniaxial deformation to a plurality of nanoparticles comprising a metal, whereby the plurality of nanoparticles is compressed under the uniaxial deformation to produce a metal nanostructure having a thickness of 100 nm or less.

[00206] Clause 2. The method of clause 1, wherein the nanoparticles comprise gold, silver, platinum, copper, gallium, cobalt, bismuth, iron, cadmium, manganese, zinc, nickel, palladium, titanium, iridium, aluminum, tin, indium, antimony, magnesium, chromium, molybdenum, tungsten, silicon, arsenic, tellurium, an alloy thereof, or a combination thereof.

[00207] Clause 3. The method of any one of clauses 1-2, wherein the nanoparticles comprise gold.

[00208] Clause 4. The method of any one of clauses 1-3, wherein the nanoparticles are colloiddally synthesized nanoparticles.

[00209] Clause 5. The method of any one of clauses 1-4, wherein the nanoparticles further comprise a polymer, or wherein the nanoparticles further comprise a ceramic coating.

[00210] Clause 6. The method of clause 5, wherein the polymer comprises polyethylene glycol, polyvinyl alcohol, polystyrene sulfonate, chitosan, polyvinylpyrrolidone, polyacrylic acid, polyethyleneimine, polylactic acid, polyglycolic acid, dextran, poly(2-ethyl-2-oxazoline, poly(N-isopropylacrylamide), or a combination thereof.

[00211] Clause 7. The method of any one of clauses 5-6, wherein the polymer is polyethylene glycol.

[00212] Clause 8. The method of any one of clauses 1-7, wherein the nanoparticle has a size of about 1 nm to about 150 nm.

[00213] Clause 9. The method of any one of clauses 5-8, wherein polymer has a molecular weight of about 1 kDa to about 100 kDa.

[00214] Clause 10. The method of any one of clauses 5-9, wherein the polymer has a hydrodynamic length of about 10 nm to about 50 nm.

[00215] Clause 11. The method of any one of clauses 5-10, wherein the polymer in the nanoparticles has crystallinity between 30 and 70%.

[00216] Clause 12. The method of any one of clauses 1-11, wherein the plurality of nanoparticles is a monolayer and/or sub-monolayer and/or multilayer of the nanoparticles having a thickness of less than 1 μm .

[00217] Clause 13. The method of any one of clauses 1-12, comprising
depositing the plurality of nanoparticles onto a bottom substrate, thereby forming an assembly of nanoparticles on the bottom substrate;

placing a top substrate over the assembly of nanoparticles, such that the assembly of nanoparticles is between the top substrate and the bottom substrate; and

reducing the physical spacing between the top substrate and the bottom substrate, whereby the assembly of nanoparticles is deformed under the uniaxial compression.

[00218] Clause 14. The method of clause 13, wherein the bottom substrate comprises a silicon wafer surface, onto which the nanoparticles are deposited.

[00219] Clause 15. The method of any one of clauses 1-14, wherein the uniaxial deformation is applied by applying a uniaxial pressure to the plurality of nanoparticles, optionally wherein the uniaxial pressure is about 2.0 GPa to 5.0 GPa.

[00220] Clause 16. The method of any one of clauses 1-15, wherein the metal nanostructure has a thickness of 1 nm or less.

[00221] Clause 17. The method of any one of clauses 1-16, wherein the plurality of nanoparticles has a surface area, and wherein the compression under the uniaxial deformation causes an increase of the surface area by about 25% to about 50%.

[00222] Clause 18. A metal nanostructure produced by the method of any one of clauses 1-17.

[00223] Clause 19. A metal nanostructure comprising a plurality of nanoparticles, wherein the plurality of nanoparticles comprise a metal, and wherein the metal nanostructure has a thickness of 10 nm or less.

[00224] Clause 20. The metal nanostructure of clause 19, wherein the nanoparticles comprise gold.

[00225] Clause 21. The metal nanostructure of any one of clauses 18-20, having a two-dimensional anisotropic morphology.

[00226] Clause 22. The metal nanostructure of any one of clauses 18-21, wherein the nanostructure has a shape, which is round, hexagonal, octagonal, square, rectangular, triangular, ribbon, or irregular.

[00227] Clauses 23. The metal nanostructure of any one of clauses 18-22, wherein the nanostructure has a Schmid factor about 0.25 to about 0.50.

[00228] Clause 24. The metal nanostructure of any one of clauses 18-23, wherein the nanostructure has a compression-induced vertical deformation between 1 unit cell and 1000 unit cells thick.

[00229] Clause 25. An article or device comprising the metal nanostructure of any one of clauses 18-24.

[00230] Clause 26. A pressing system for producing a contiguous nanofilm, the pressing system comprising:

- a first pressing member configured to receive a plurality of dispersed nanoparticles;
- a second pressing member in an opposed configuration with the first pressing member;
- an actuator configured to move at least one of the first pressing member and the second pressing member to apply a uniaxial compression to the plurality of nanoparticles between the first pressing member and the second pressing member, the uniaxial compression causing the plurality of nanoparticles to expand into one another to form the contiguous nanofilm.

[00231] Clause 27. The pressing system of clause 26, wherein the plurality of nanoparticles have an average particle size between about 1 nanometers and about 50 nanometers.

[00232] Clause 28. The pressing system of clause 26, wherein the plurality of nanoparticles has an average interparticle distance of between 1 nanometer and 1000 nanometers.

[00233] Clause 29. The pressing system of clause 26, wherein a ratio of an average particle size of the plurality of nanoparticles and an average interparticle distance is between about 0.006 and 200.

[00234] Clause 30. The pressing system of clause 26, wherein at least one of the first pressing member and the second pressing member is moved so that a shortest distance between the first pressing member and the second pressing member is less than about 1000 nanometers.

[00235] Clause 31. The pressing system of clause 26, wherein a ratio of a shortest distance between the first pressing member and the second pressing member and an average particle size of the plurality of nanoparticles is between about 0.01 and about 1.

[00236] Clause 32. The pressing system of clause 26, wherein a substrate is positioned between the first pressing member and the second pressing member.

[00237] Clause 33. The pressing system of clause 32, wherein the substrate is coupled to at least one of the first pressing member and the second pressing member, and wherein the substrate optionally fixedly couples to the plurality of nanoparticles as the uniaxial compression is applied.

[00238] Clause 34. The pressing system of clause 26, wherein at least one of the first pressing member and the second pressing member includes a surface texture that is transferred to the contiguous nanofilm.

[00239] Clause 35. The pressing system of clause 34, wherein at least one of the first pressing member and the second pressing member includes a projection to form a perforation in the contiguous nanofilm.

[00240] Clause 36. The pressing system of clause 35, wherein the projection is one of a plurality of projections so that the contiguous nanofilm has a mesh structure.

[00241] Clause 37. The pressing system of clause 26, wherein at least one of the first pressing member and the second pressing member is configured to control (lateral) expansion of at least some of the plurality of nanoparticles during the uniaxial compression.

[00242] Clause 38. The pressing system of clause 26, wherein the actuator system includes at least one of a hydraulic actuator, a linear actuator, toggle actuator, magnetic actuator, inductive actuator, pneumatic actuator, and a rotary actuator.

[00243] Clause 39. The pressing system of clause 26, further comprising an electronic controller configured to operate the actuator system.

[00244] Clause 40. The pressing system of clause 39, further comprising a sensor in communication with the controller, the sensor configured to generate a signal corresponding to the state of compression of the plurality of nanoparticles.

[00245] Clause 41. The pressing system of clause 40, wherein the sensor includes at least one of a distance sensor, a proximity sensor, a switch, a hall effect sensor, a load sensor, a pressure sensor, and a force sensor.

[00246] Clause 42. The pressing system of clause 26, wherein the actuator system moves at least one of the first pressing member and the second pressing member along a first direction to control a distance between the first pressing member and the second pressing member in the first direction.

[00247] Clause 43. The pressing system of clause 26, wherein at least one of the first pressing member and the second pressing member is configured as a plate.

[00248] Clause 44. The pressing system of clause 26, further comprising a dispensing system configured to dispense the plurality of nanoparticles onto the first pressing member.

[00249] Clause 45. The pressing system of clause 44, wherein the dispensing system includes a pump configured to pump a colloidal solution that includes the plurality of nanoparticles.

[00250] Clause 46. A method of making a nanofilm, the method comprising:

depositing a plurality of nanoparticles between a first pressing member and a second pressing member, the plurality of nanoparticles being a dispersed configuration to define an average interparticle distance;

moving at least one of the first pressing member and the second pressing member to apply a uniaxial compression to the plurality of nanoparticles so that the plurality of nanoparticles expand in a direction substantially perpendicular to a direction of the uniaxial compression, the plurality of nanoparticles expanding to couple to one another to form the nanofilm.

CLAIMS

We claim:

1. A method for producing metal nanostructure, the method comprising:
applying a uniaxial deformation to a plurality of nanoparticles comprising a metal, whereby the plurality of nanoparticles is compressed under the uniaxial deformation to produce a metal nanostructure having a thickness of 100 nm or less.
2. The method of claim 1, wherein the nanoparticles comprise gold, silver, platinum, copper, gallium, cobalt, bismuth, iron, cadmium, manganese, zinc, nickel, palladium, titanium, iridium, aluminum, tin, indium, antimony, magnesium, chromium, molybdenum, tungsten, silicon, arsenic, tellurium, an alloy thereof, or a combination thereof.
3. The method of any one of claims 1-2, wherein the nanoparticles comprise gold.
4. The method of any one of claims 1-3, wherein the nanoparticles are colloiddally synthesized nanoparticles.
5. The method of any one of claims 1-4, wherein the nanoparticles further comprise a polymer, or wherein the nanoparticles further comprise a ceramic coating.
6. The method of claim 5, wherein the polymer comprises polyethylene glycol, polyvinyl alcohol, polystyrene sulfonate, chitosan, polyvinylpyrrolidone, polyacrylic acid, polyethyleneimine, polylactic acid, polyglycolic acid, dextran, poly(2-ethyl-2-oxazoline, poly(N-isopropylacrylamide), or a combination thereof.
7. The method of any one of claims 5-6, wherein the polymer is polyethylene glycol.
8. The method of any one of claims 1-7, wherein the nanoparticle has a size of about 1 nm to about 150 nm.

9. The method of any one of claims 5-8, wherein polymer has a molecular weight of about 1 kDa to about 100 kDa.
10. The method of any one of claims 5-9, wherein the polymer has a hydrodynamic length of about 10 nm to about 50 nm.
11. The method of any one of claims 5-10, wherein the polymer in the nanoparticles has crystallinity between 30 and 70%.
12. The method of any one of claims 1-11, wherein the plurality of nanoparticles is a monolayer and/or sub-monolayer and/or multilayer of the nanoparticles having a thickness of less than 1 μm .
13. The method of any one of claims 1-12, comprising
depositing the plurality of nanoparticles onto a bottom substrate, thereby forming an assembly of nanoparticles on the bottom substrate;
placing a top substrate over the assembly of nanoparticles, such that the assembly of nanoparticles is between the top substrate and the bottom substrate; and
reducing the physical spacing between the top substrate and the bottom substrate, whereby the assembly of nanoparticles is deformed under the uniaxial compression.
14. The method of claim 13, wherein the bottom substrate comprises a silicon wafer surface, onto which the nanoparticles are deposited.
15. The method of any one of claims 1-14, wherein the uniaxial deformation is applied by applying a uniaxial pressure to the plurality of nanoparticles, optionally wherein the uniaxial pressure is about 2.0 GPa to 5.0 GPa.
16. The method of any one of claims 1-15, wherein the metal nanostructure has a thickness of 1 nm or less.

17. The method of any one of claims 1-16, wherein the plurality of nanoparticles has a surface area, and wherein the compression under the uniaxial deformation causes an increase of the surface area by about 25% to about 50%.
18. A metal nanostructure produced by the method of any one of claims 1-17.
19. A metal nanostructure comprising a plurality of nanoparticles, wherein the plurality of nanoparticles comprise a metal, and wherein the metal nanostructure has a thickness of 10 nm or less.
20. The metal nanostructure of claim 19, wherein the nanoparticles comprise gold.
21. The metal nanostructure of any one of claims 18-20, having a two-dimensional anisotropic morphology.
22. The metal nanostructure of any one of claims 18-21, wherein the nanostructure has a shape, which is round, hexagonal, octagonal, square, rectangular, triangular, ribbon, or irregular.
23. The metal nanostructure of any one of claims 18-22, wherein the nanostructure has a Schmid factor about 0.25 to about 0.50.
24. The metal nanostructure of any one of claims 18-23, wherein the nanostructure has a compression-induced vertical deformation between 1 unit cell and 1000 unit cells thick.
25. An article or device comprising the metal nanostructure of any one of claims 18-24.
26. A pressing system for producing a contiguous nanofilm, the pressing system comprising:
 - a first pressing member configured to receive a plurality of dispersed nanoparticles;
 - a second pressing member in an opposed configuration with the first pressing member;
 - an actuator configured to move at least one of the first pressing member and the second pressing member to apply a uniaxial compression to the plurality of nanoparticles between the first

pressing member and the second pressing member, the uniaxial compression causing the plurality of nanoparticles to expand into one another to form the contiguous nanofilm.

27. The pressing system of claim 26, wherein the plurality of nanoparticles have an average particle size between about 1 nanometers and about 50 nanometers.

28. The pressing system of claim 26, wherein the plurality of nanoparticles has an average interparticle distance of between 1 nanometer and 1000 nanometers.

29. The pressing system of claim 26, wherein a ratio of an average particle size of the plurality of nanoparticles and an average interparticle distance is between about 0.006 and 200.

30. The pressing system of claim 26, wherein at least one of the first pressing member and the second pressing member is moved so that a shortest distance between the first pressing member and the second pressing member is less than about 1000 nanometers.

31. The pressing system of claim 26, wherein a ratio of a shortest distance between the first pressing member and the second pressing member and an average particle size of the plurality of nanoparticles is between about 0.01 and about 1.

32. The pressing system of claim 26, wherein a substrate is positioned between the first pressing member and the second pressing member.

33. The pressing system of claim 32, wherein the substrate is coupled to at least one of the first pressing member and the second pressing member, and wherein the substrate optionally fixedly couples to the plurality of nanoparticles as the uniaxial compression is applied.

34. The pressing system of claim 26, wherein at least one of the first pressing member and the second pressing member includes a surface texture that is transferred to the contiguous nanofilm.

35. The pressing system of claim 34, wherein the at least one of the first pressing member and the second pressing member includes a projection to form a perforation in the contiguous nanofilm.
36. The pressing system of claim 35, wherein the projection is one of a plurality of projections so that the contiguous nanofilm has a mesh structure.
37. The pressing system of claim 26, wherein at least one of the first pressing member and the second pressing member is configured to control (lateral) expansion of at least some of the plurality of nanoparticles during the uniaxial compression.
38. The pressing system of claim 26, wherein the actuator system includes at least one of a hydraulic actuator, a linear actuator, toggle actuator, magnetic actuator, inductive actuator, pneumatic actuator, and a rotary actuator.
39. The pressing system of claim 26, further comprising an electronic controller configured to operate the actuator system.
40. The pressing system of claim 39, further comprising a sensor in communication with the controller, the sensor configured to generate a signal corresponding to the state of compression of the plurality of nanoparticles.
41. The pressing system of claim 40, wherein the sensor includes at least one of a distance sensor, a proximity sensor, a switch, a hall effect sensor, a load sensor, a pressure sensor, and a force sensor.
42. The pressing system of claim 26, wherein the actuator system moves at least one of the first pressing member and the second pressing member along a first direction to control a distance between the first pressing member and the second pressing member in the first direction.
43. The pressing system of claim 26, wherein at least one of the first pressing member and the second pressing member is configured as a plate.

44. The pressing system of claim 26, further comprising a dispensing system configured to dispense the plurality of nanoparticles onto the first pressing member.

45. The pressing system of claim 44, wherein the dispensing system includes a pump configured to pump a colloidal solution that includes the plurality of nanoparticles.

46. A method of making a nanofilm, the method comprising:

depositing a plurality of nanoparticles between a first pressing member and a second pressing, the plurality of nanoparticles being a dispersed configuration to define an average interparticle distance;

moving at least one of the first pressing member and the second pressing member to apply a uniaxial compression to the plurality of nanoparticles so that the plurality of nanoparticles expand in a direction substantially perpendicular to a direction of the uniaxial compression, the plurality of nanoparticles expanding to couple to one another to form the nanofilm.

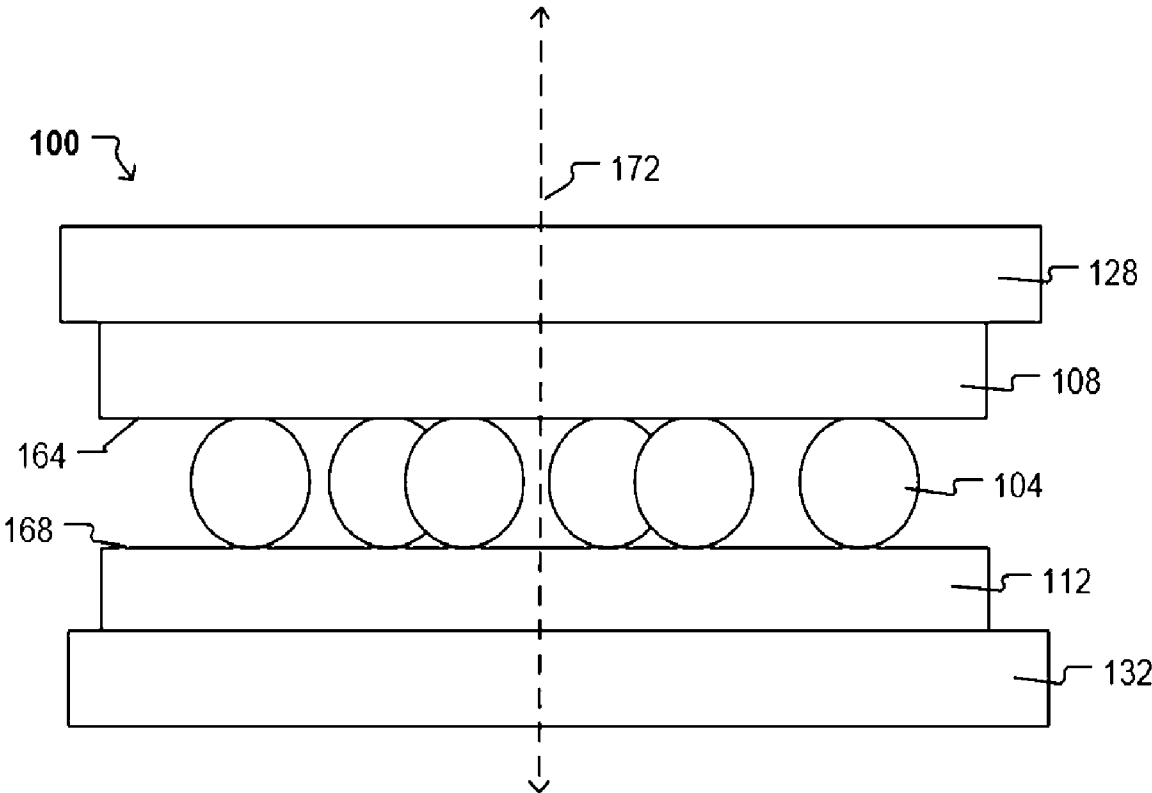


FIG. 2

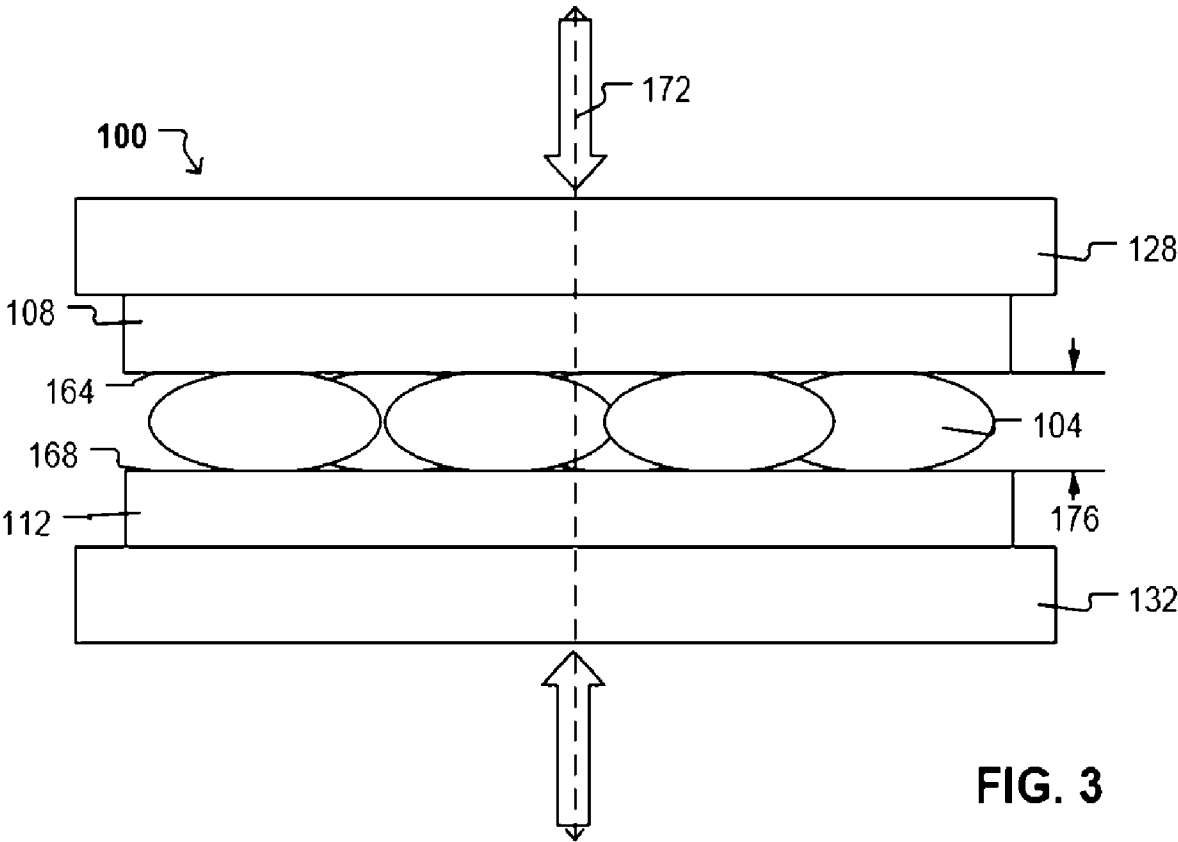


FIG. 3

FIG. 4

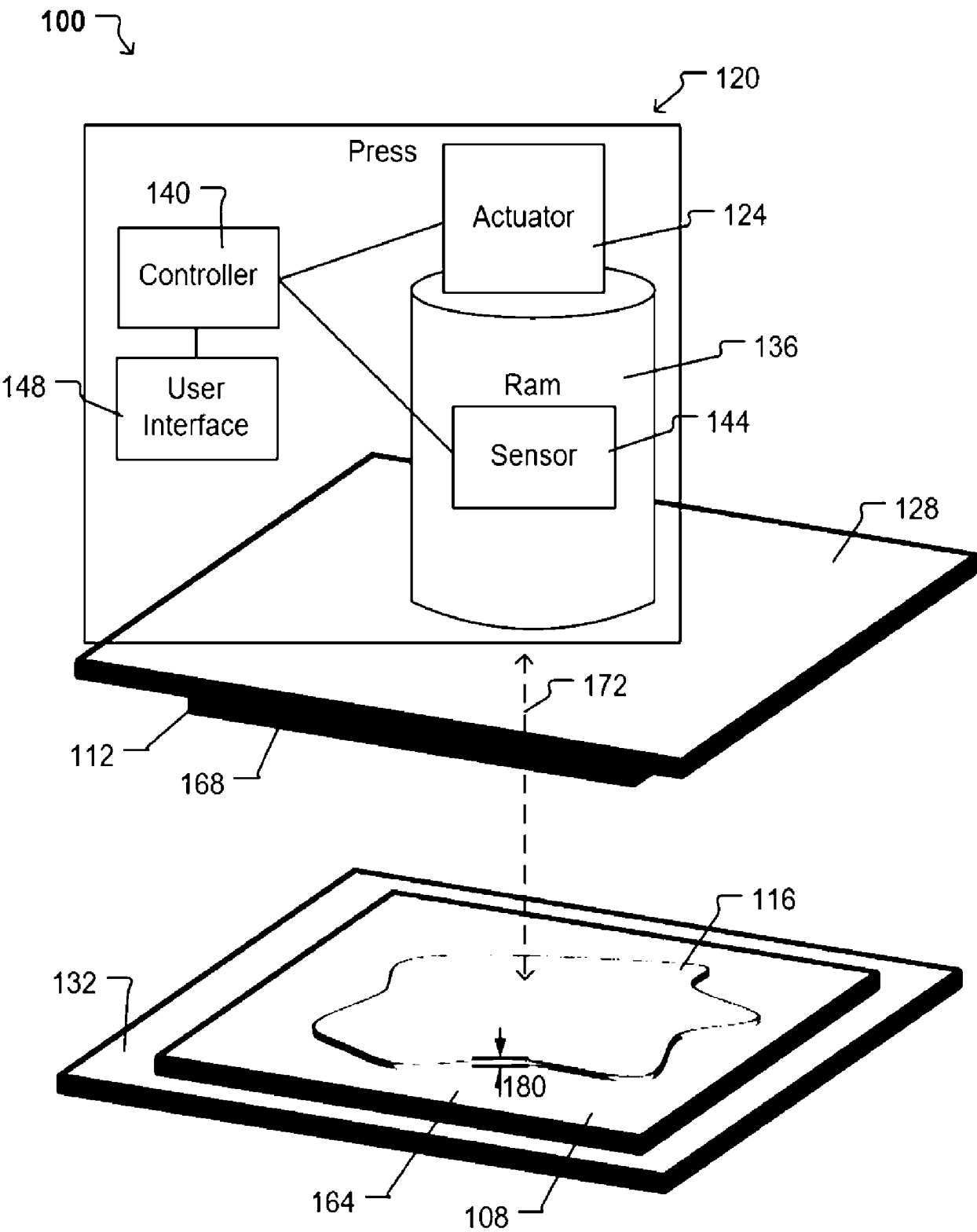


FIG. 5

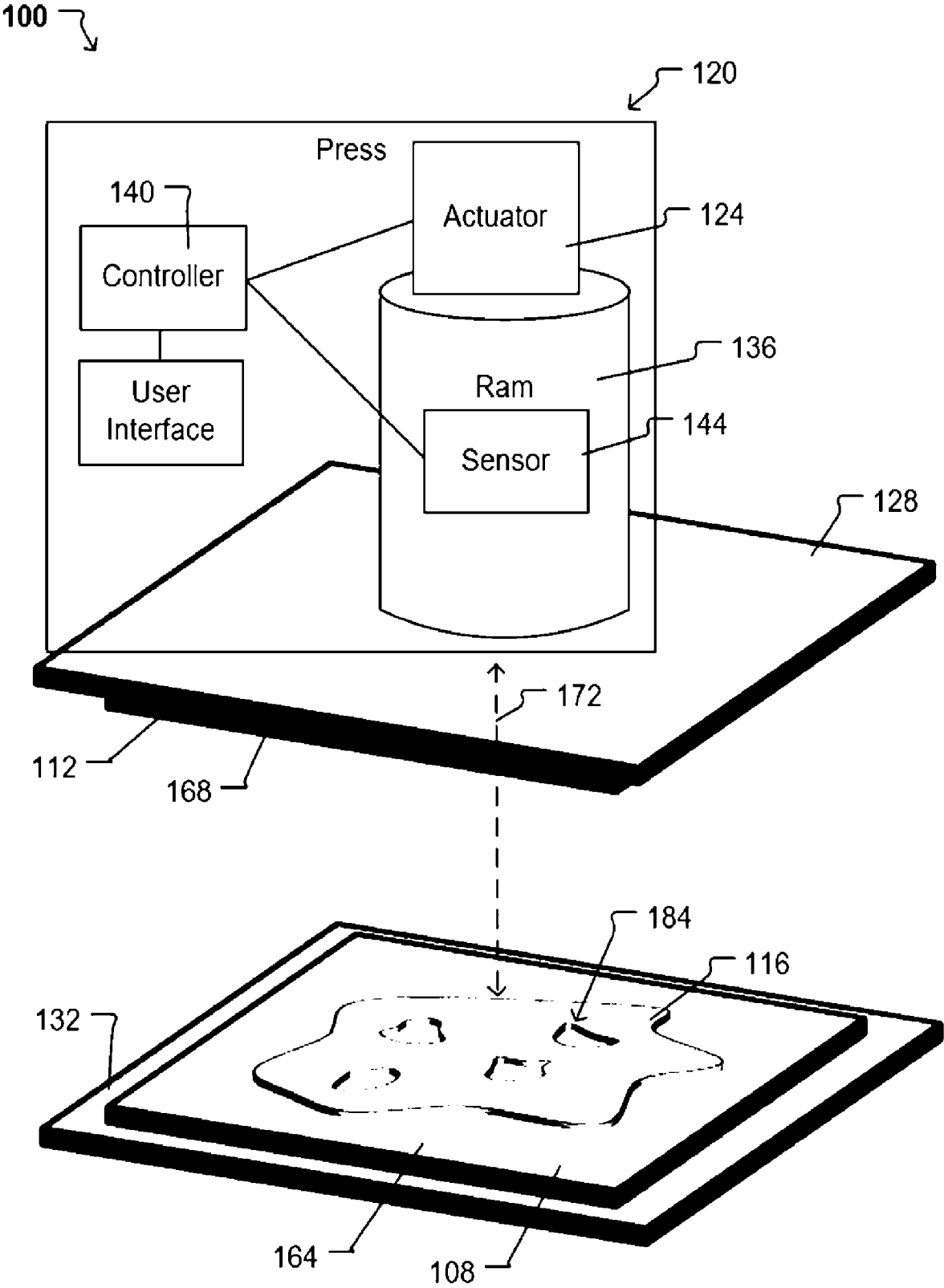


FIG. 6

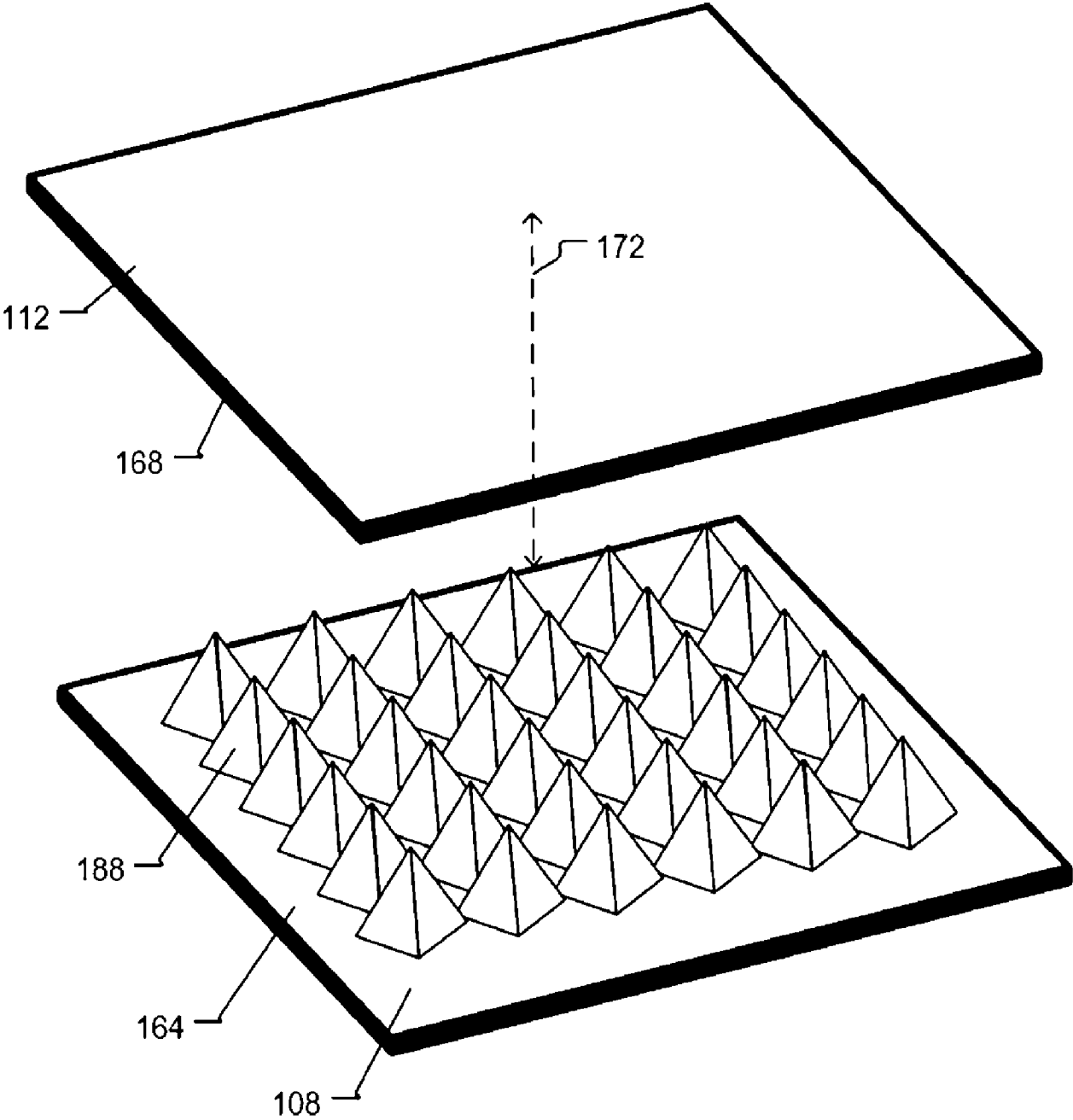


FIG. 7

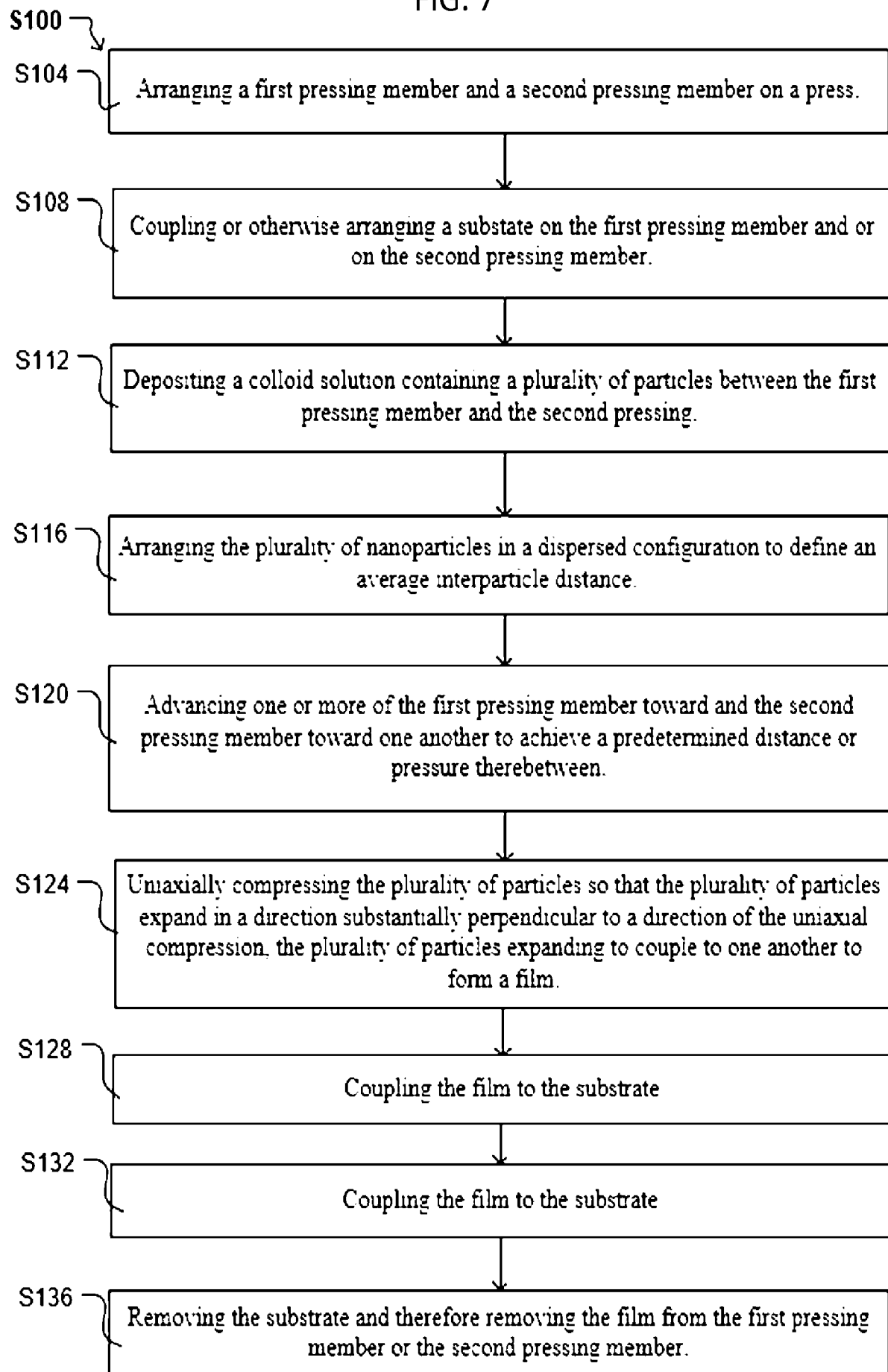


FIG. 8

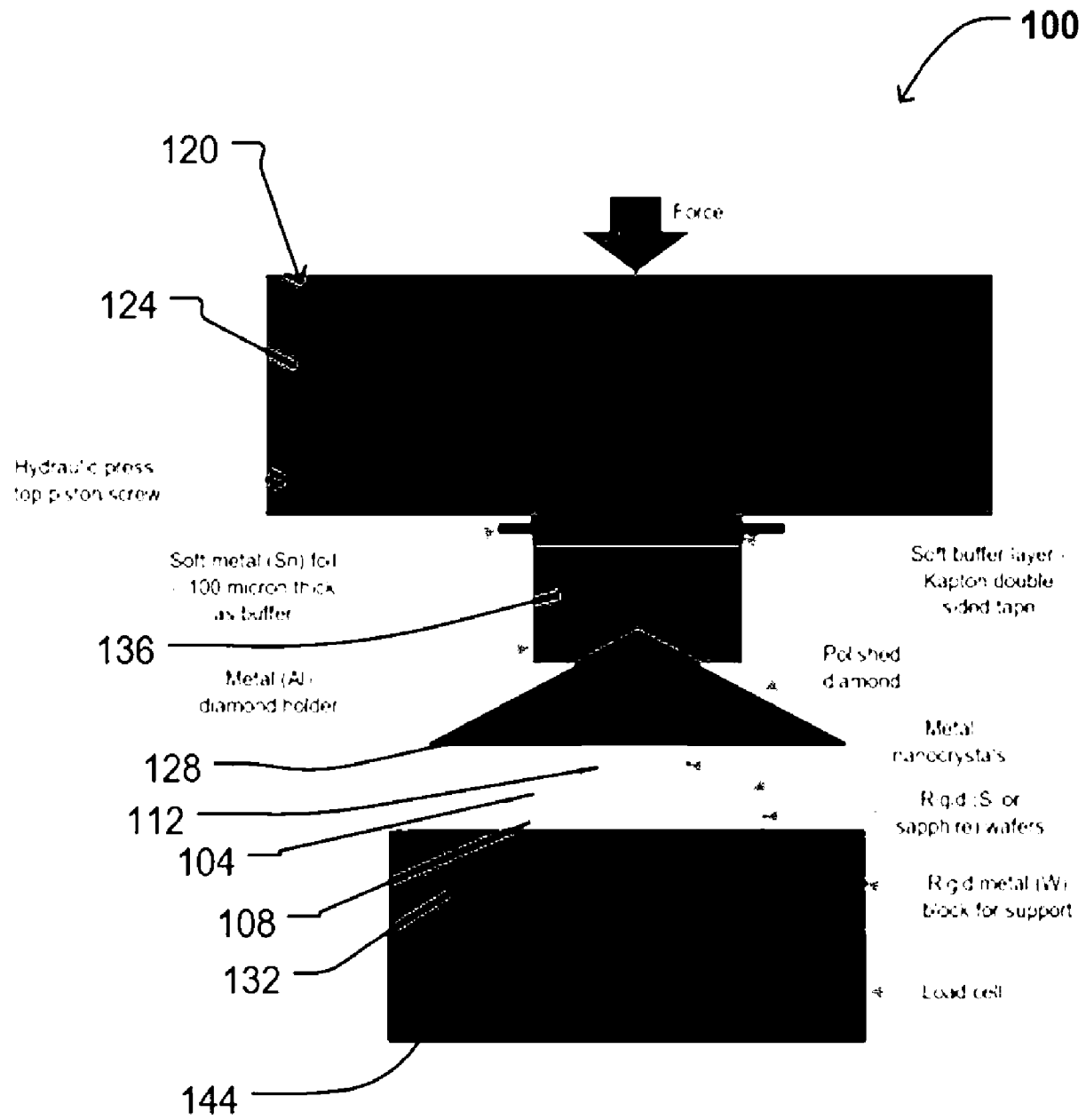


FIG. 9

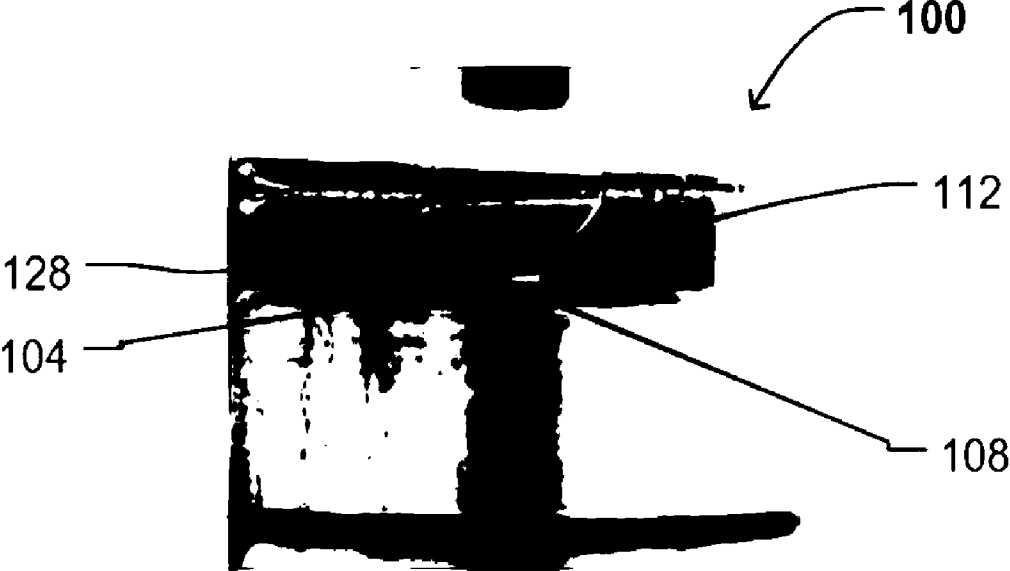


FIG. 10

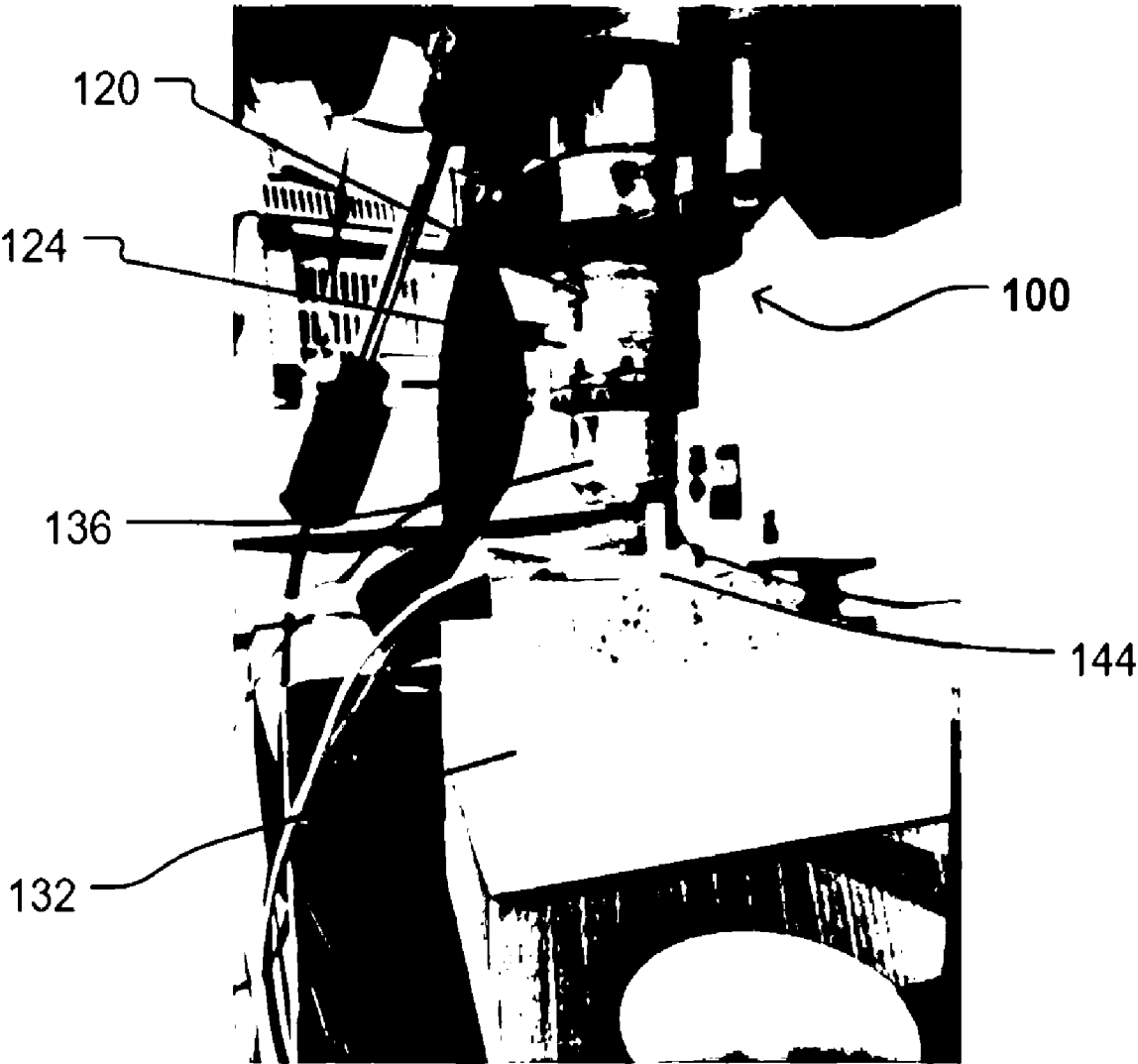


FIG. 11

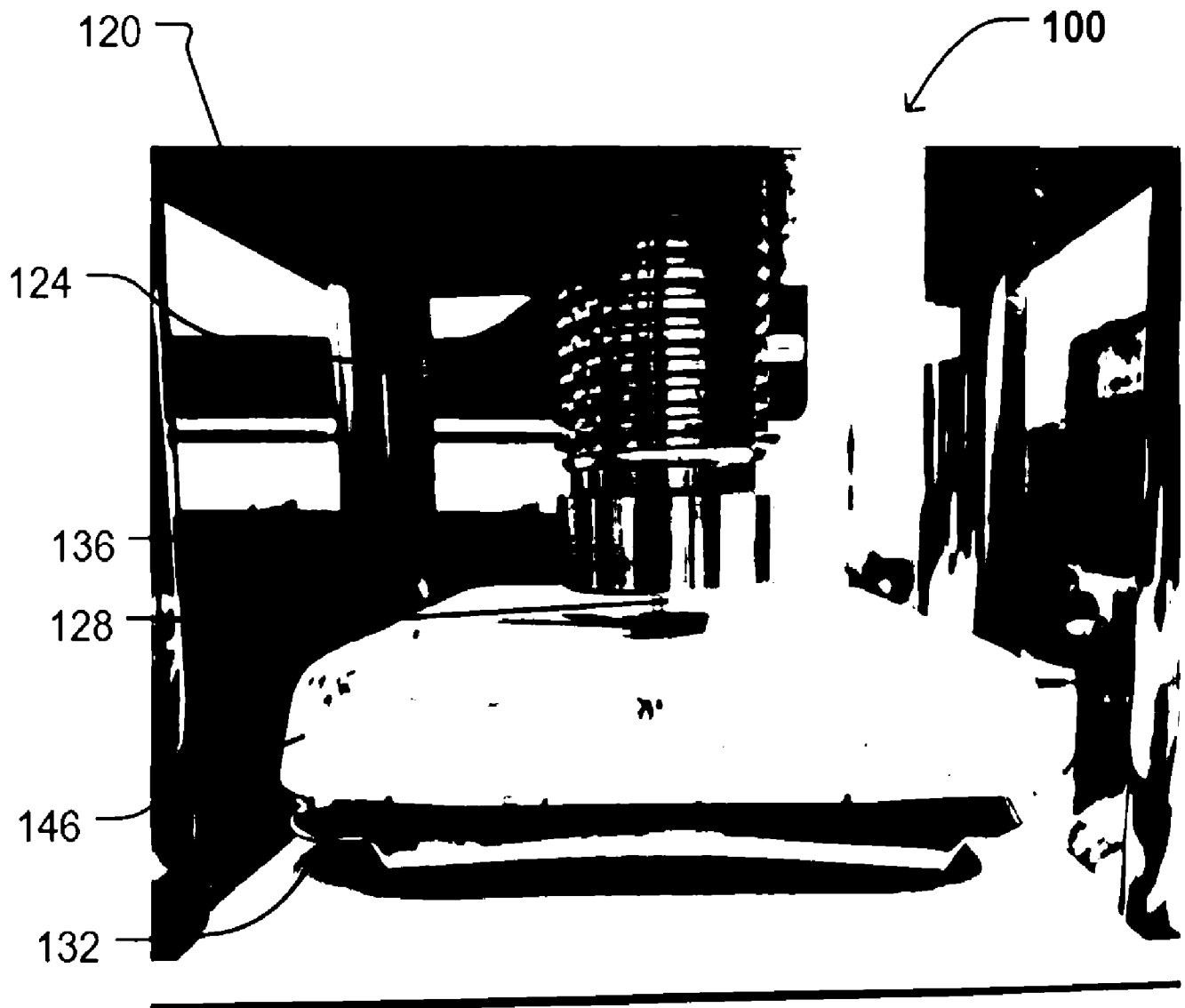


FIG. 12

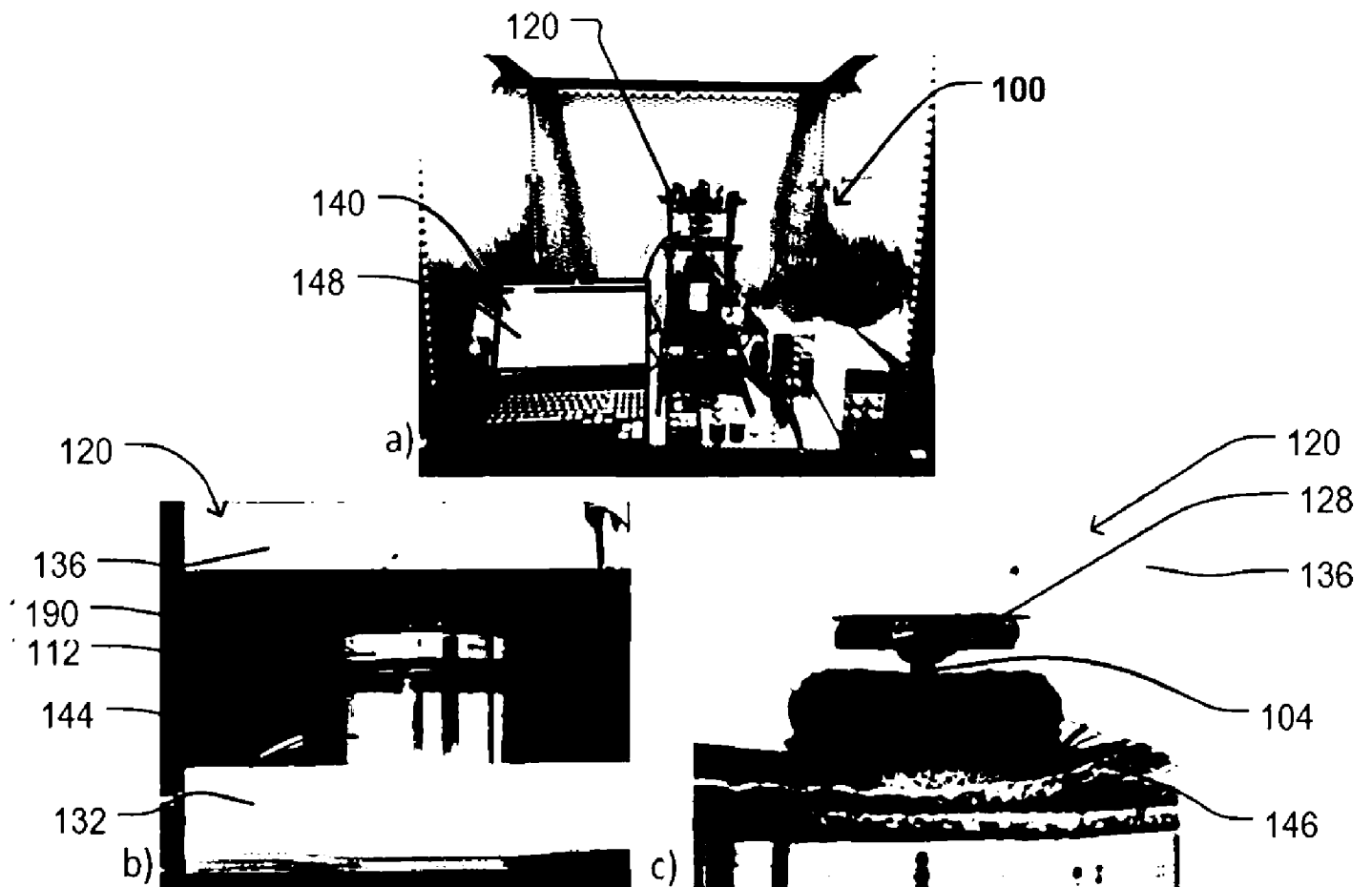


FIG. 13

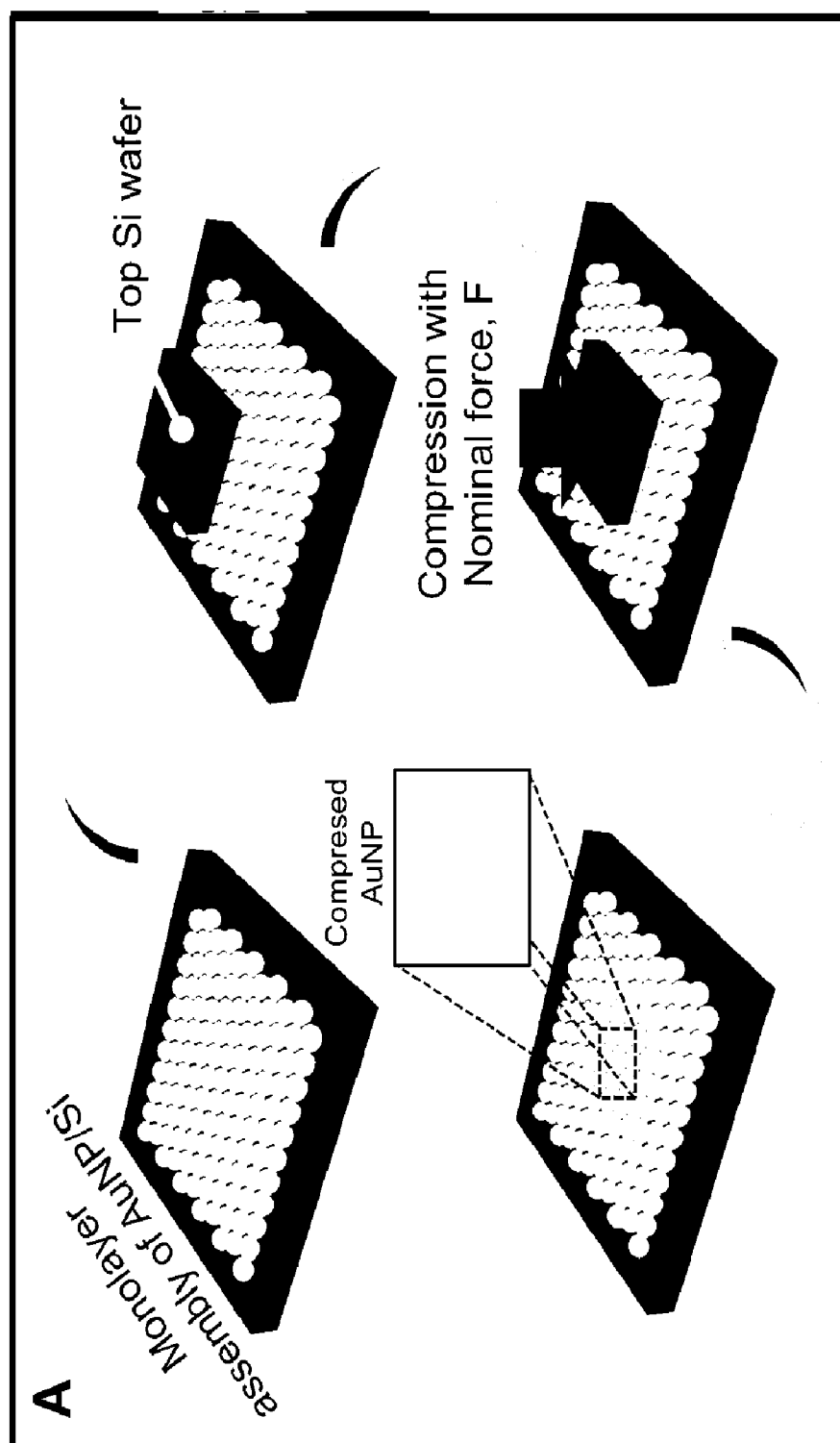


FIG. 13 cont.

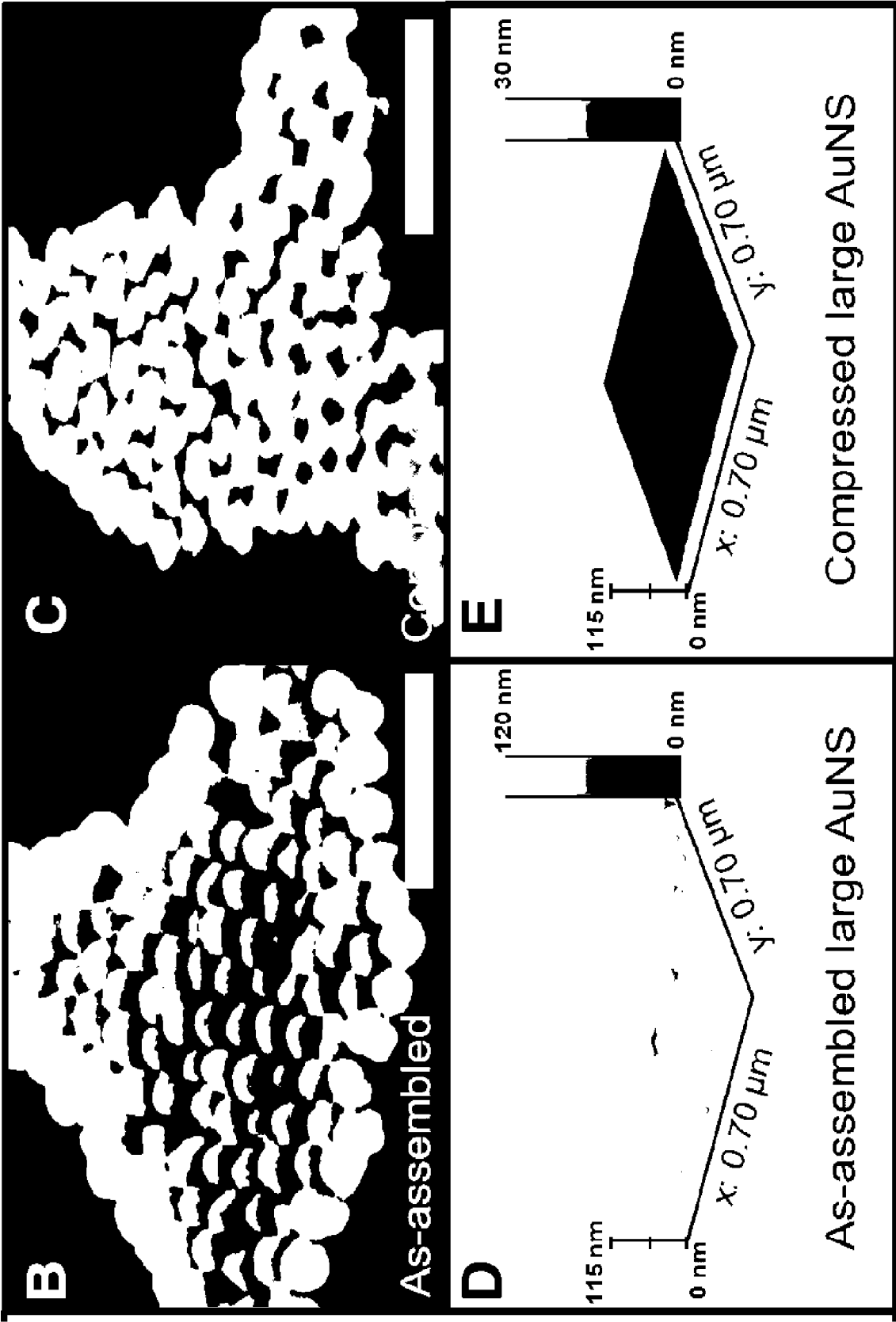


FIG. 14

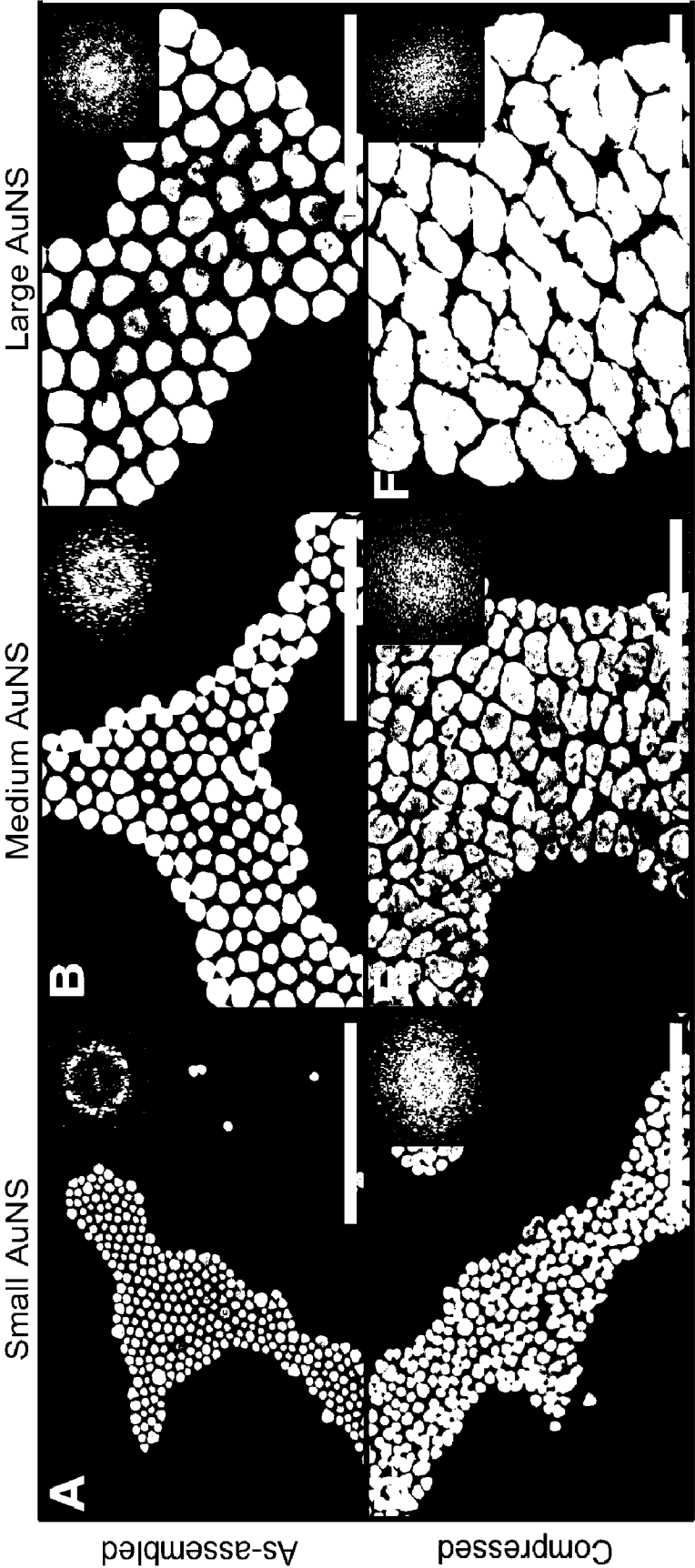


FIG. 14 cont.

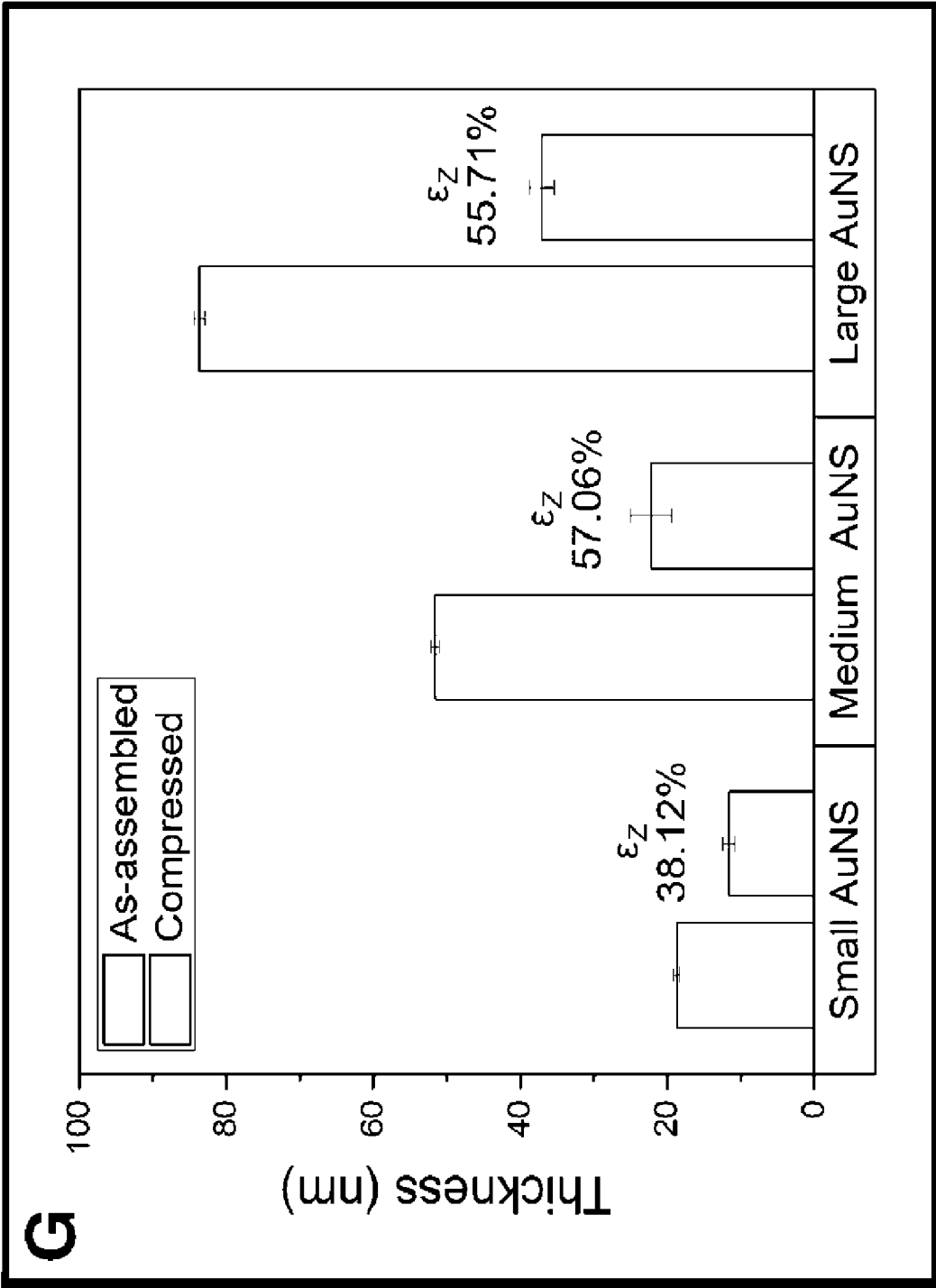


FIG. 15

Shorter (5K) PEG

Longer (40K) PEG

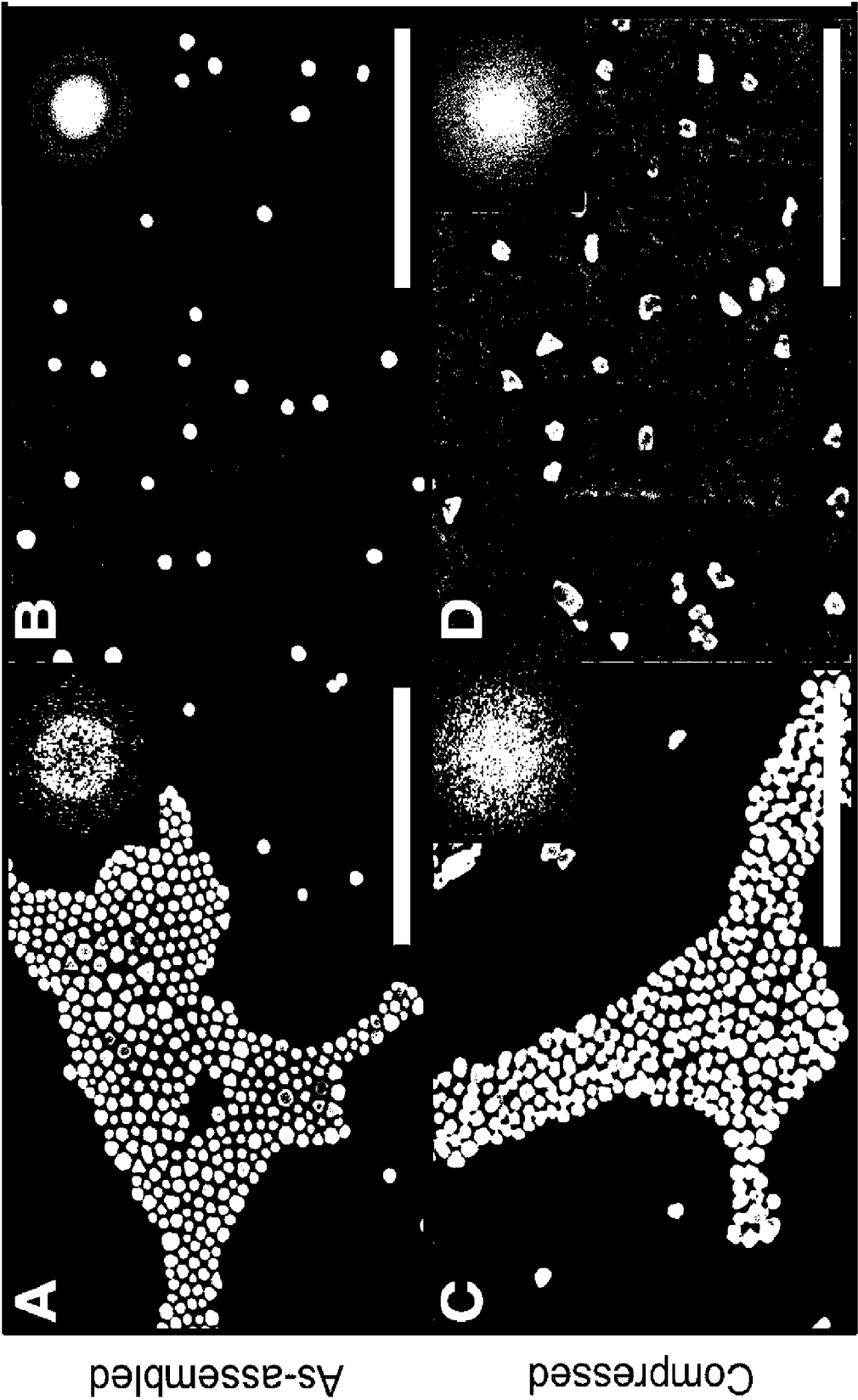


FIG. 15 cont.

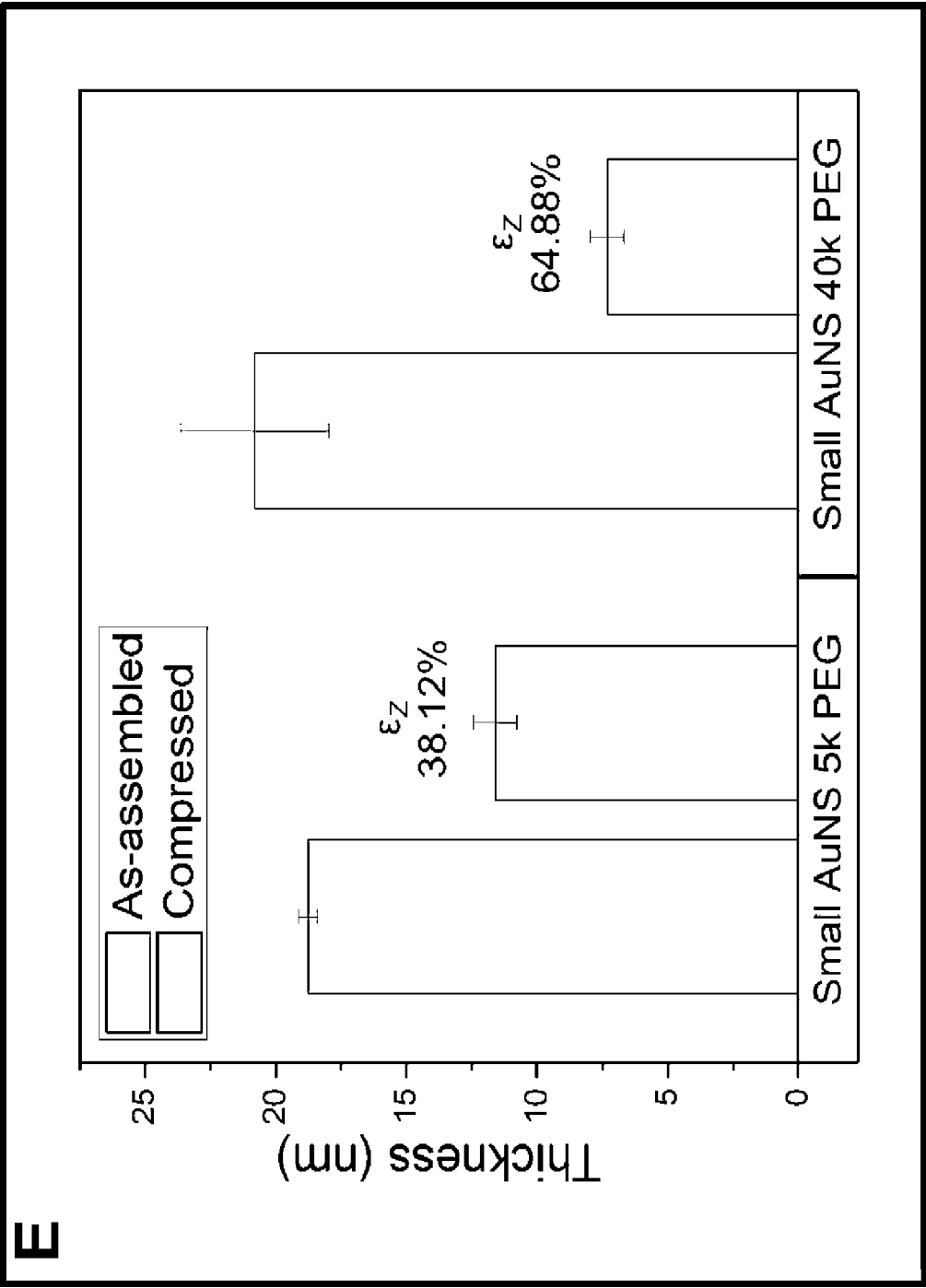


FIG. 16

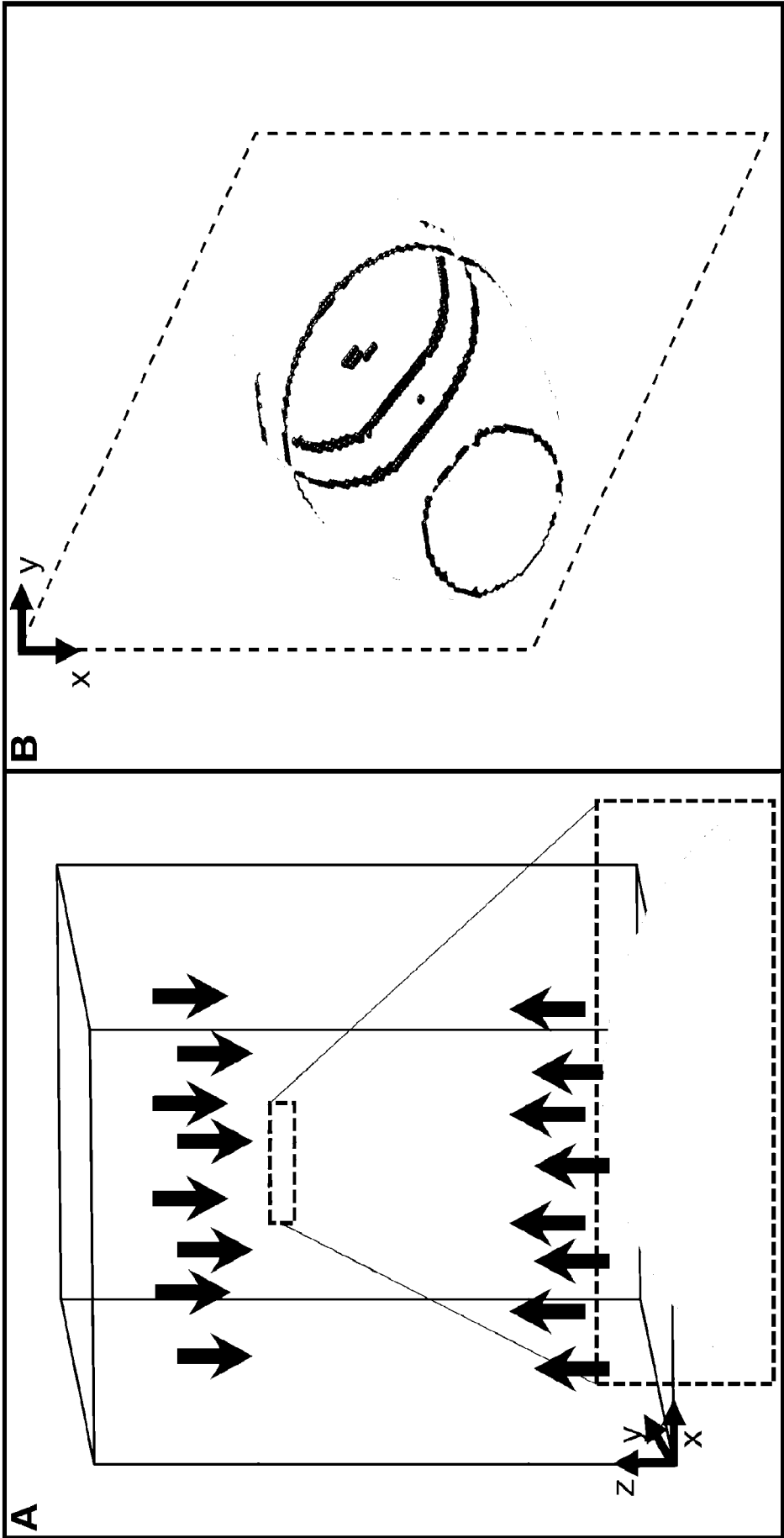


FIG. 16 cont.

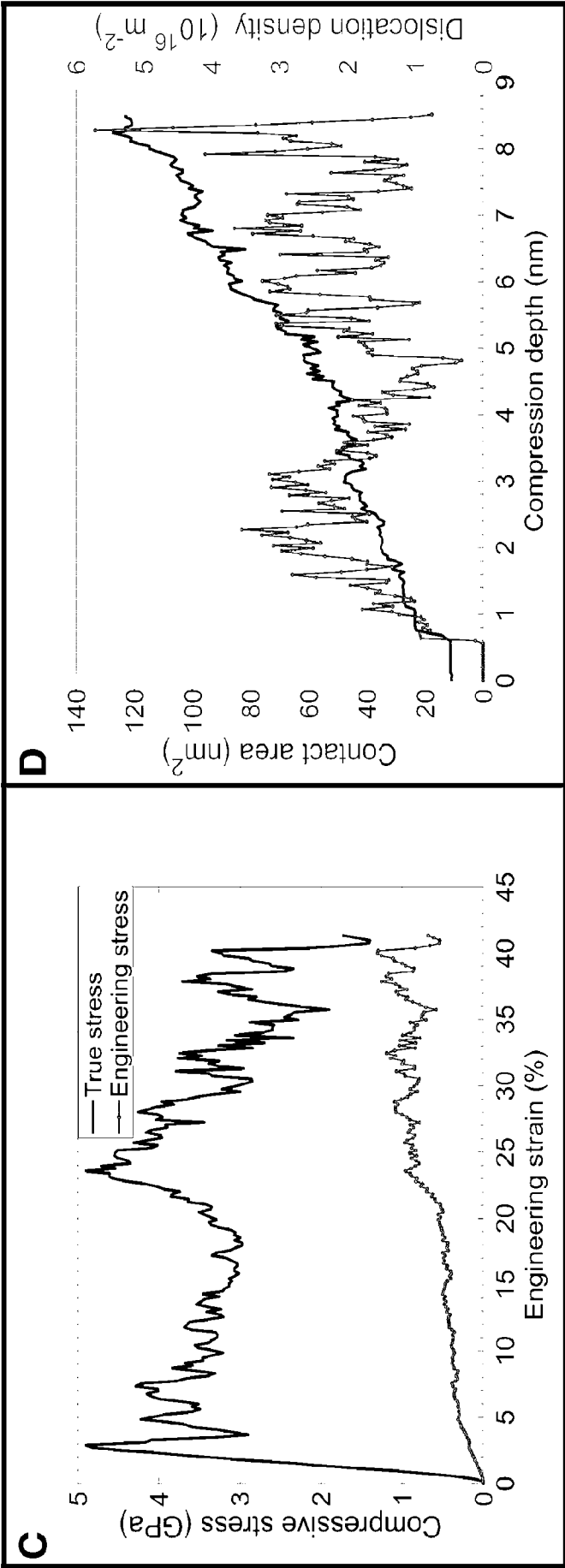


FIG. 17

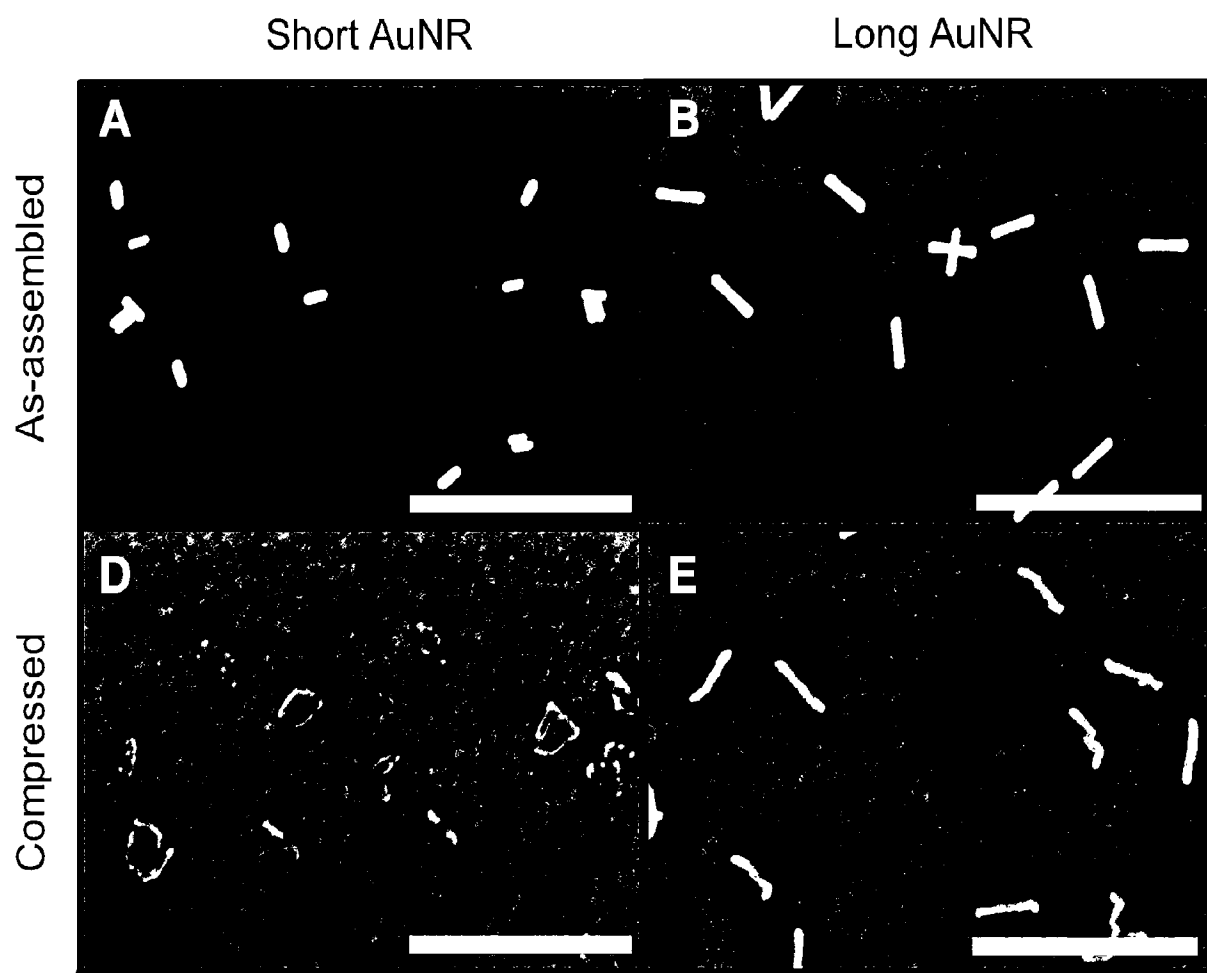


FIG. 17 cont.

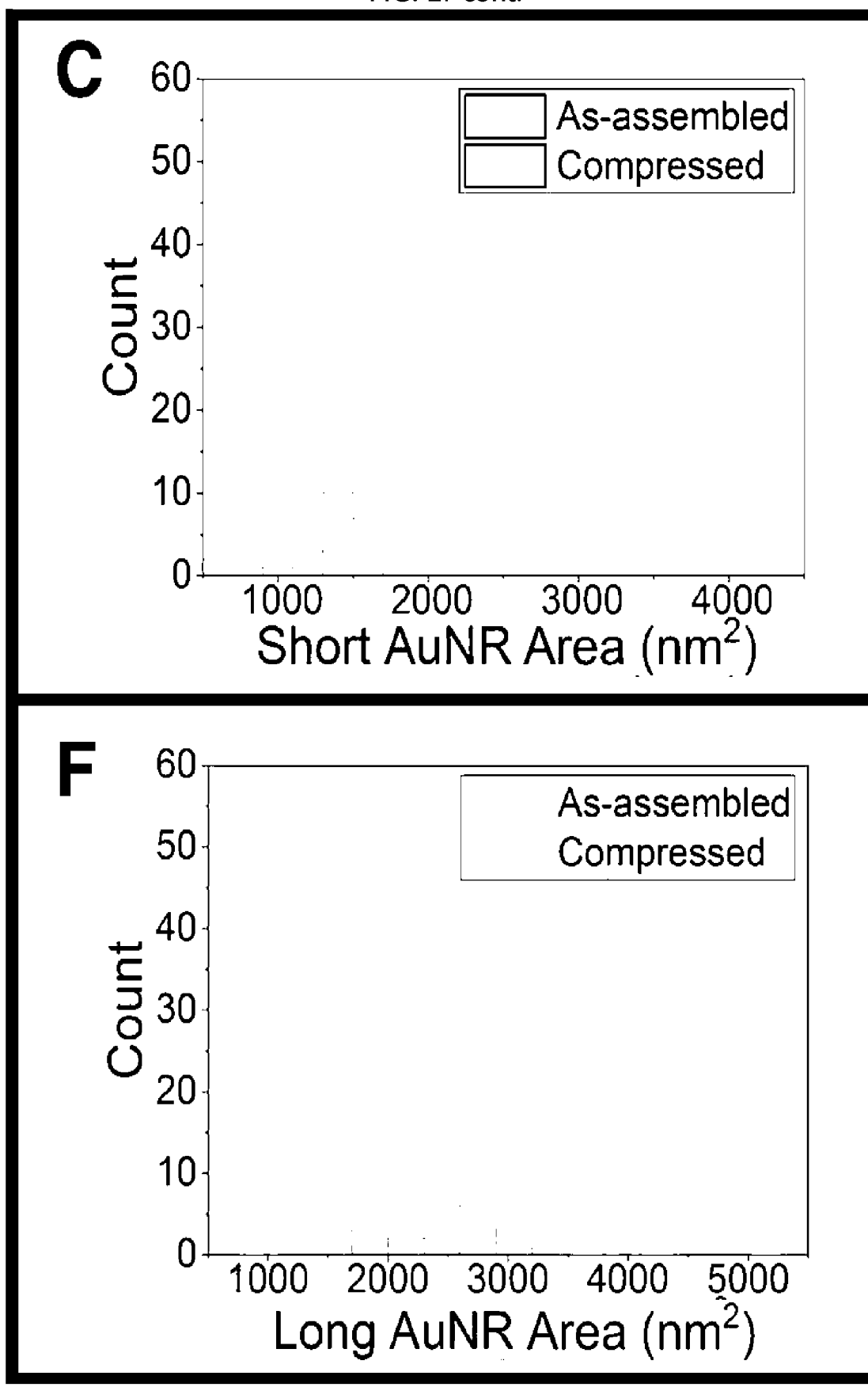


FIG. 17 cont.

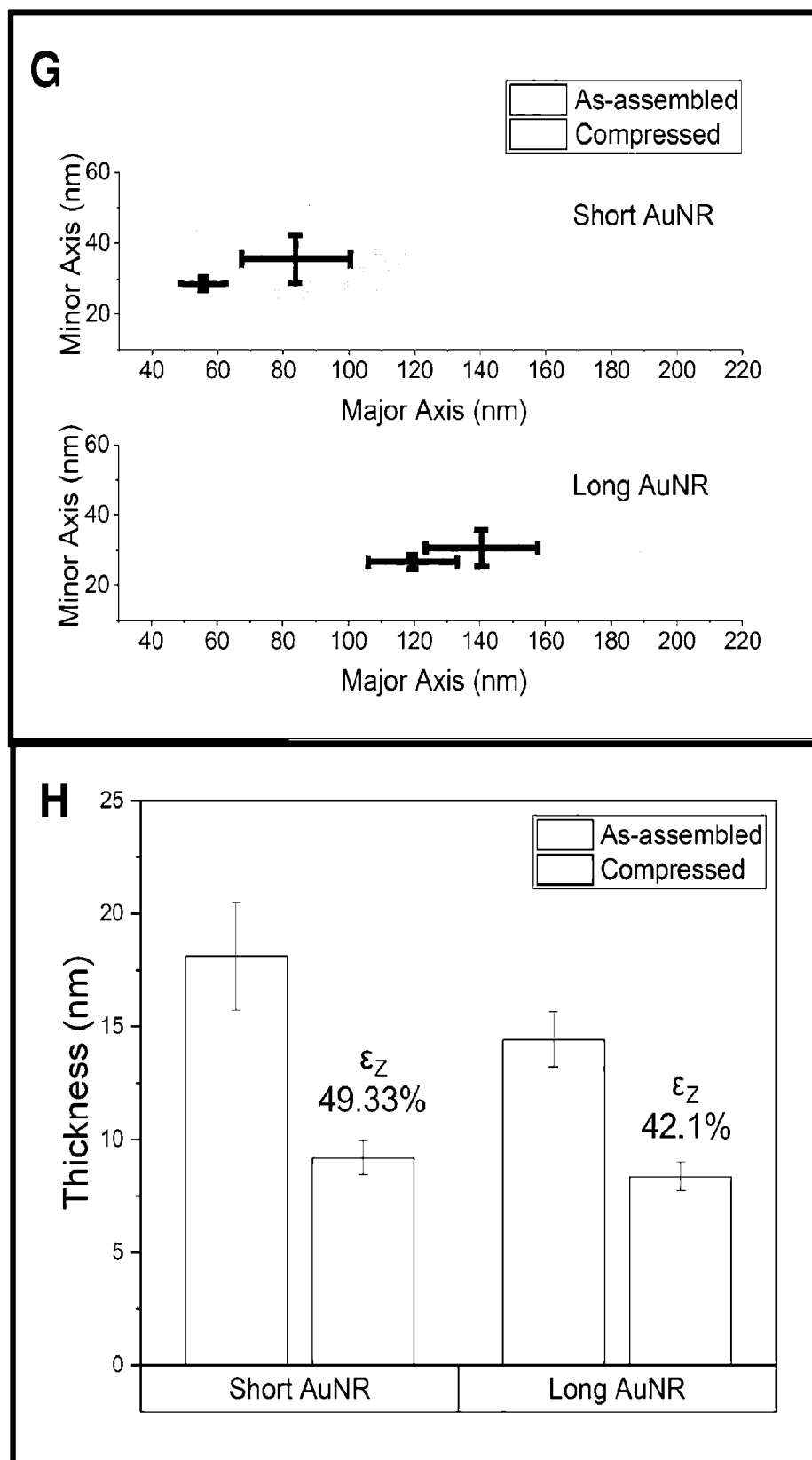


FIG. 18

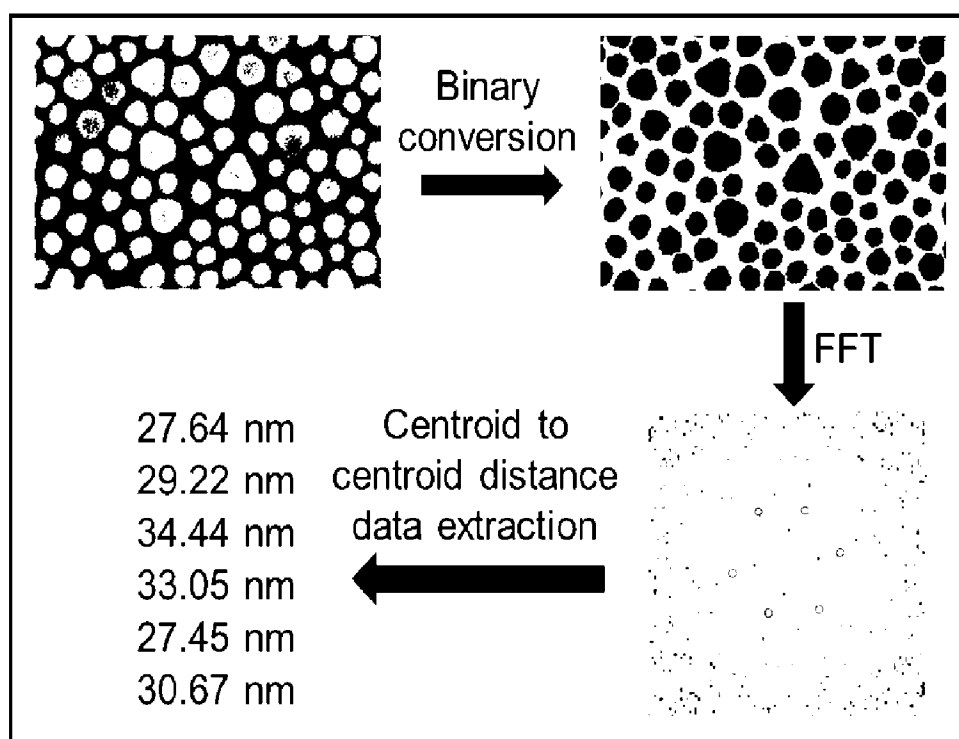


FIG. 19

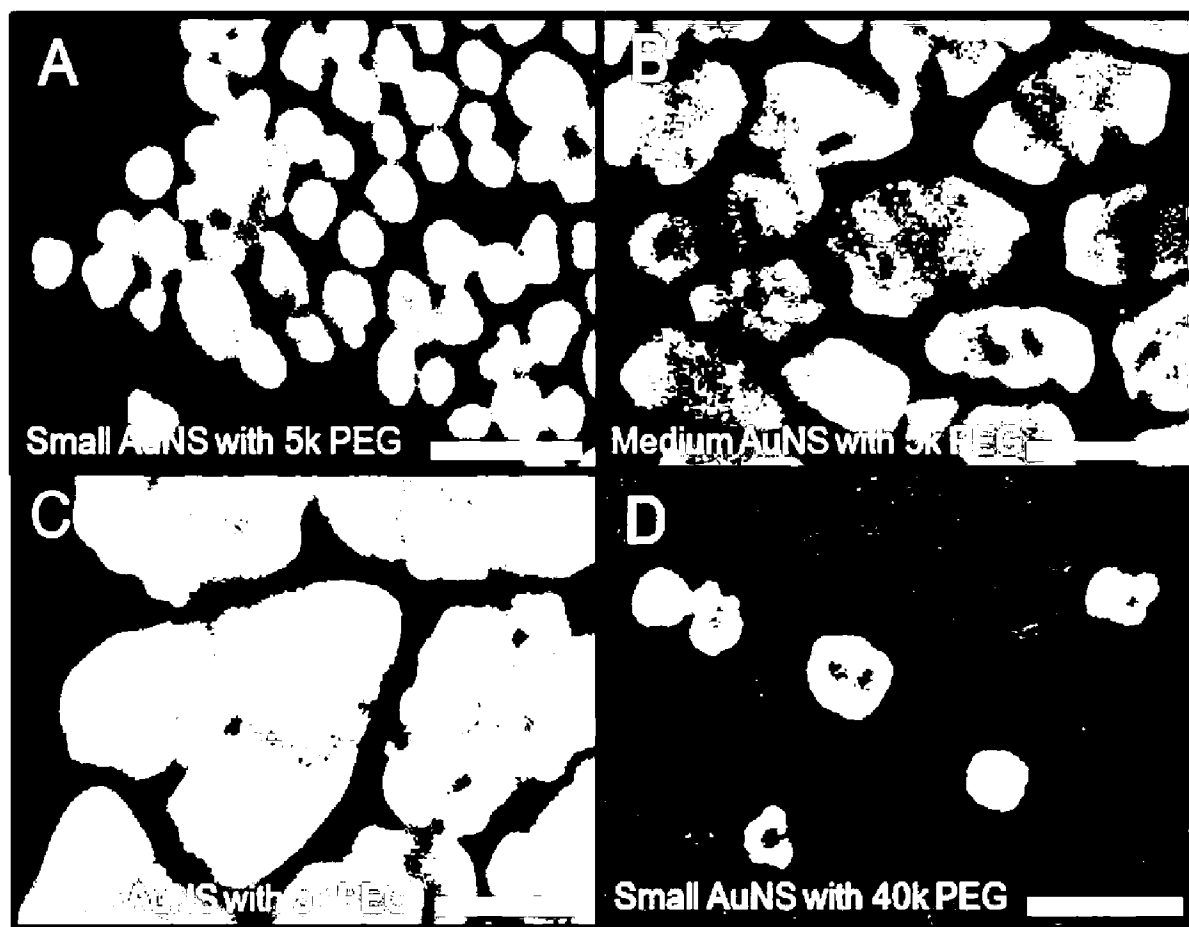


FIG. 20



FIG. 21

As-assembled

Compressed

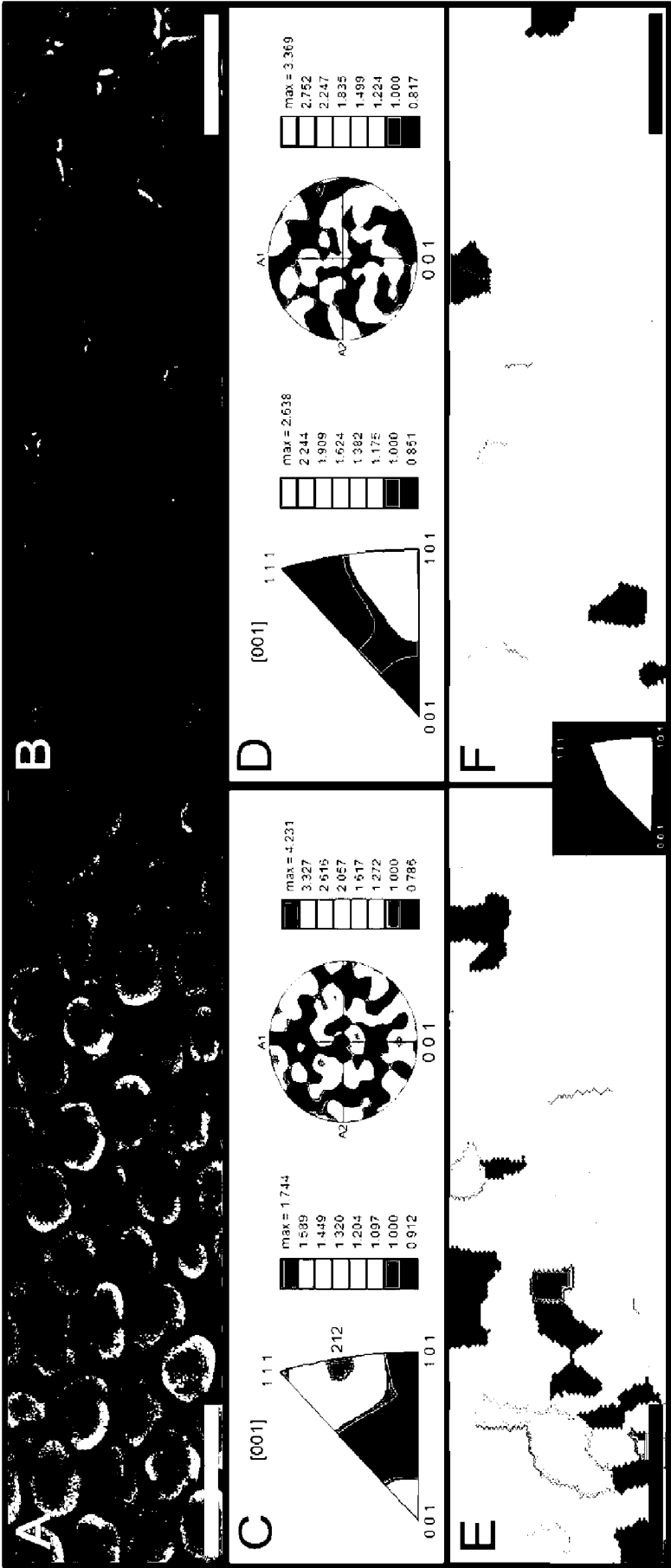


FIG. 22

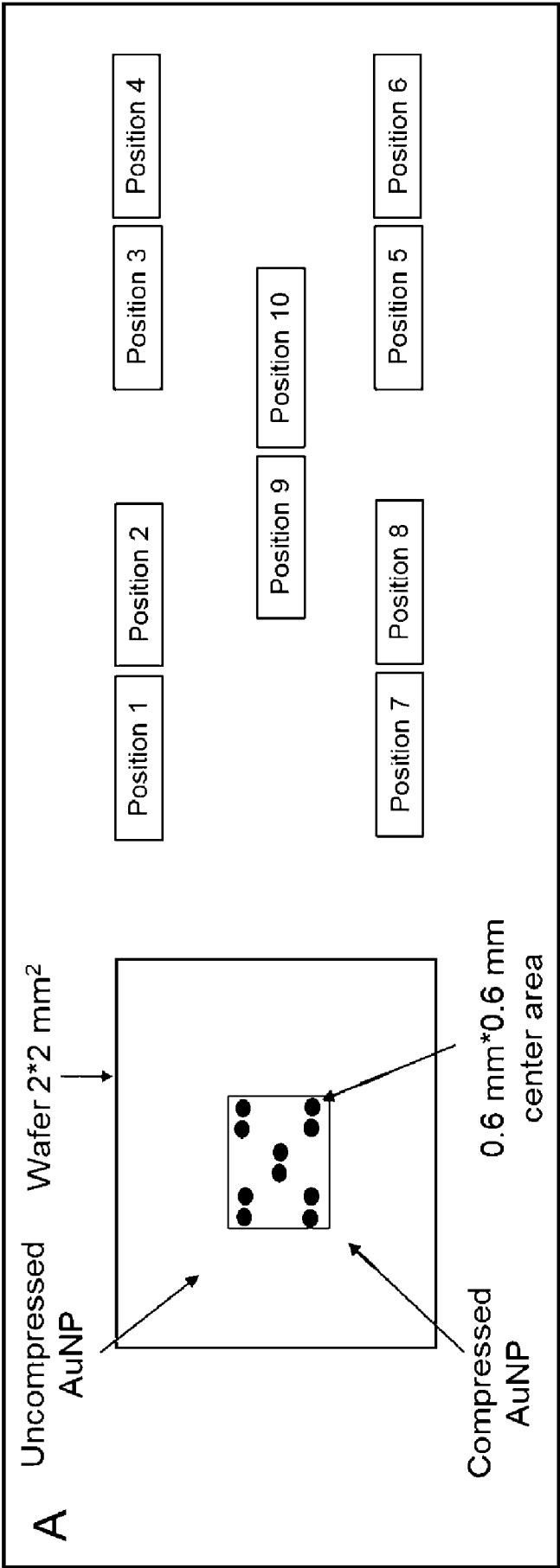


FIG. 22 cont.

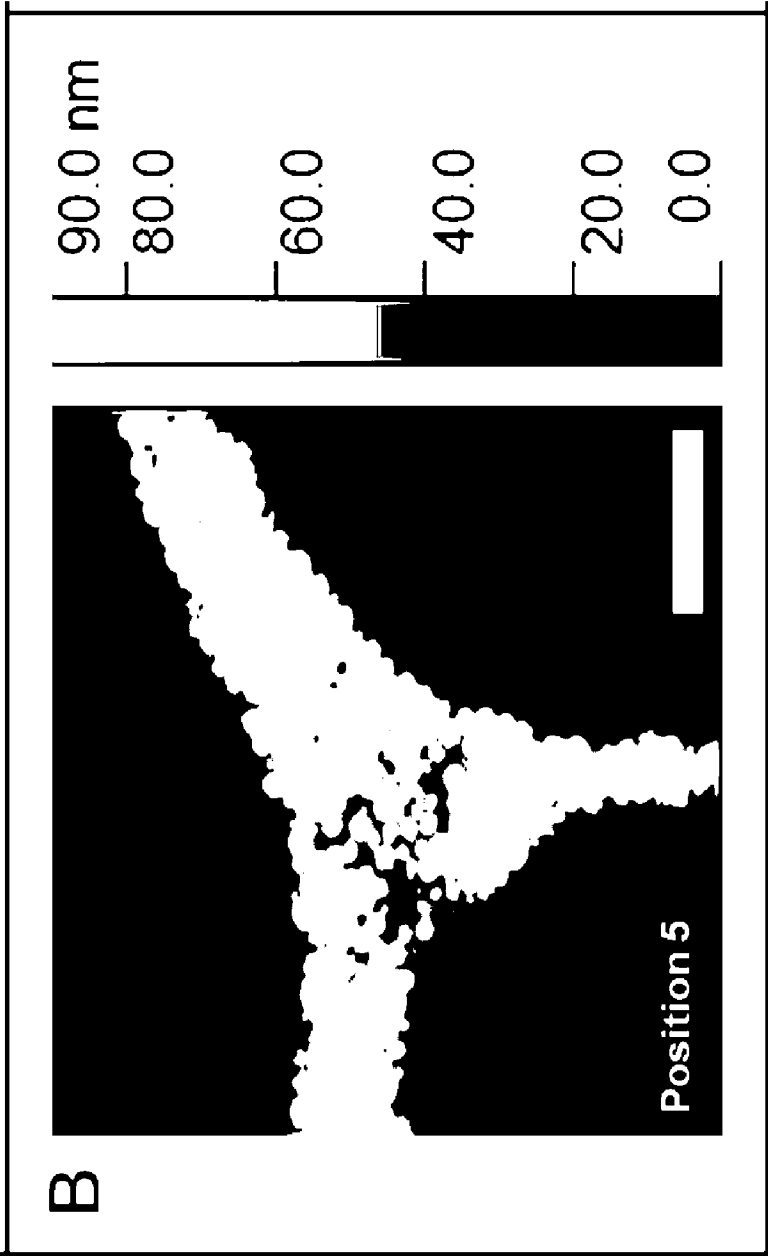


FIG. 22 cont.

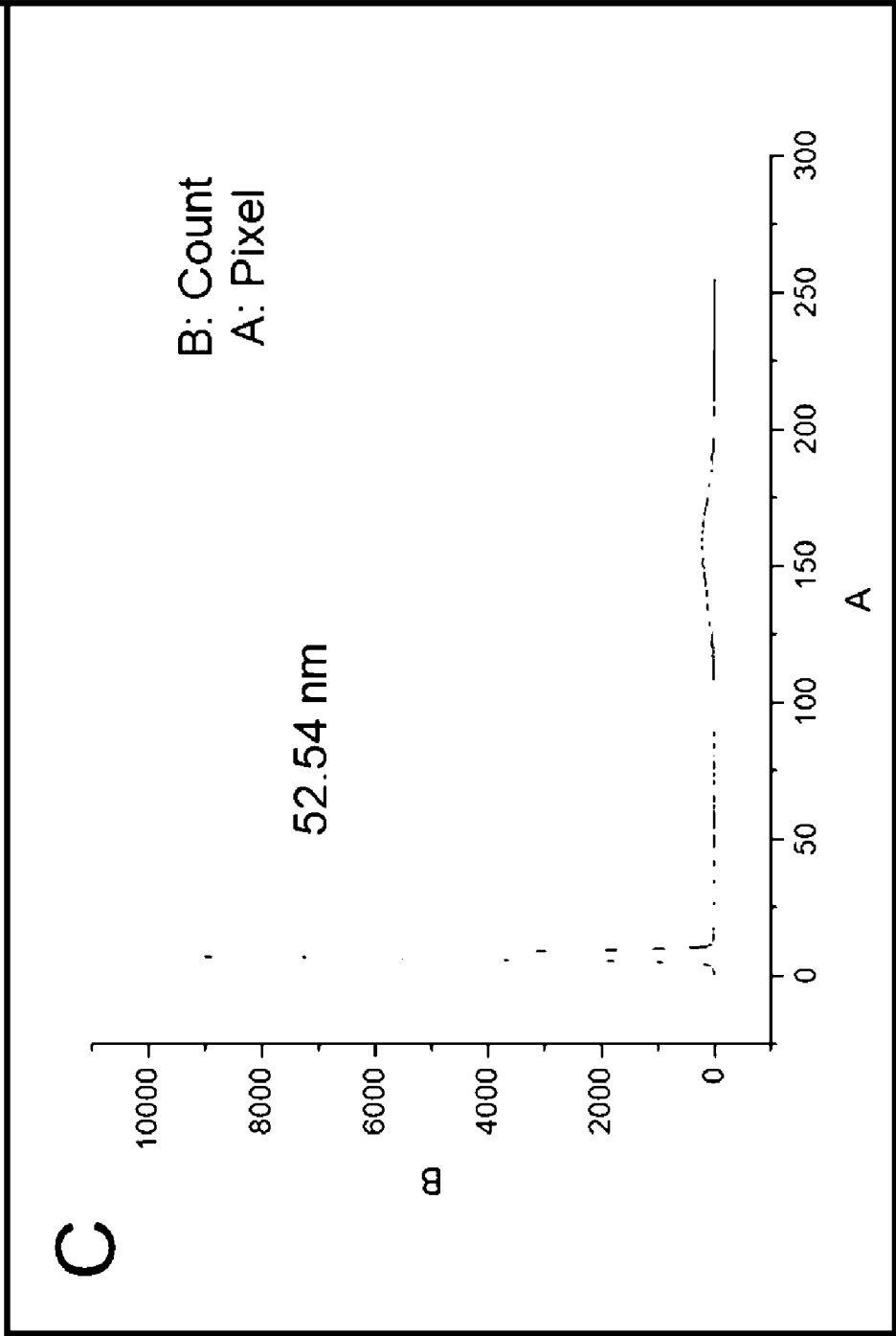


FIG. 23

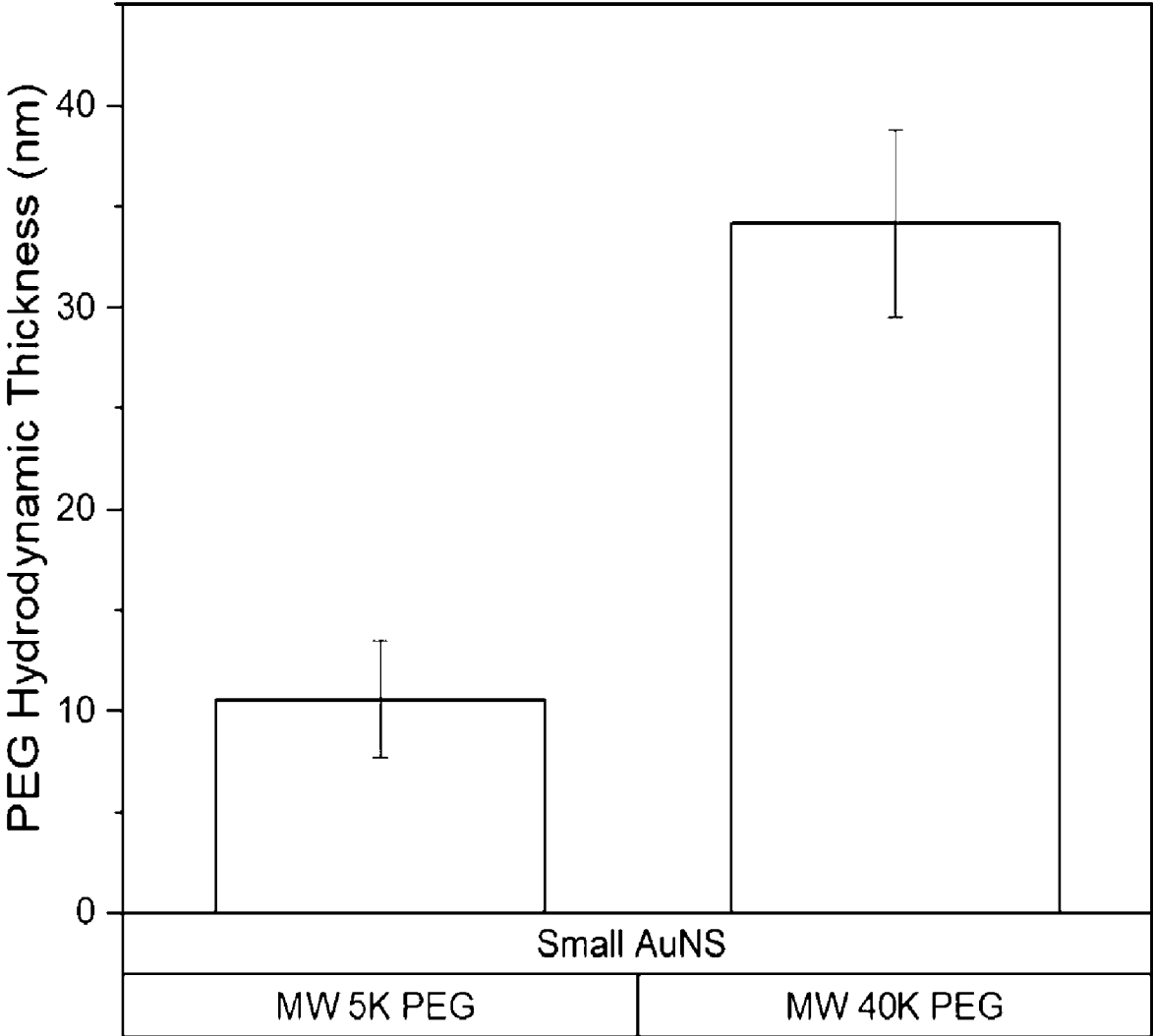


FIG. 24

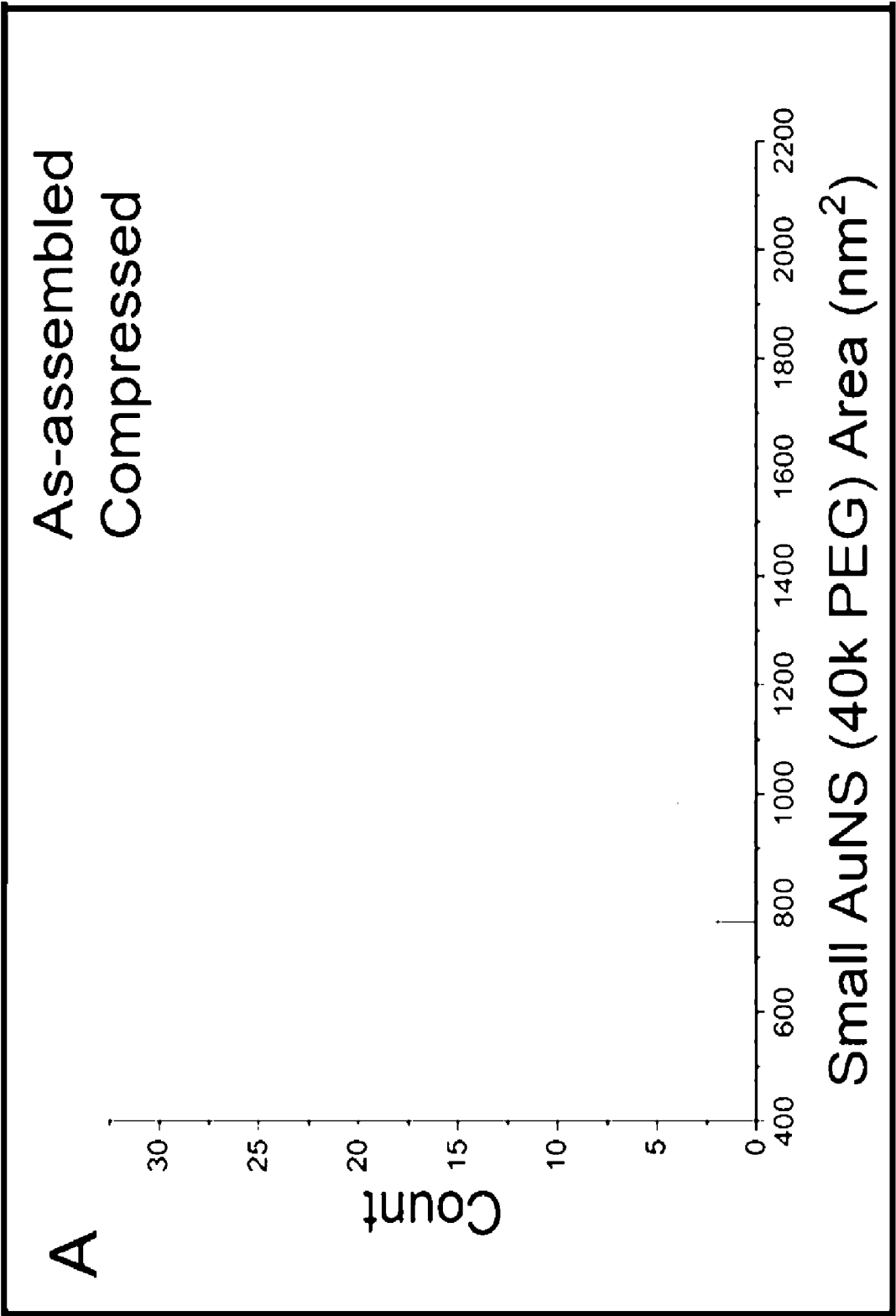


FIG. 24 cont.

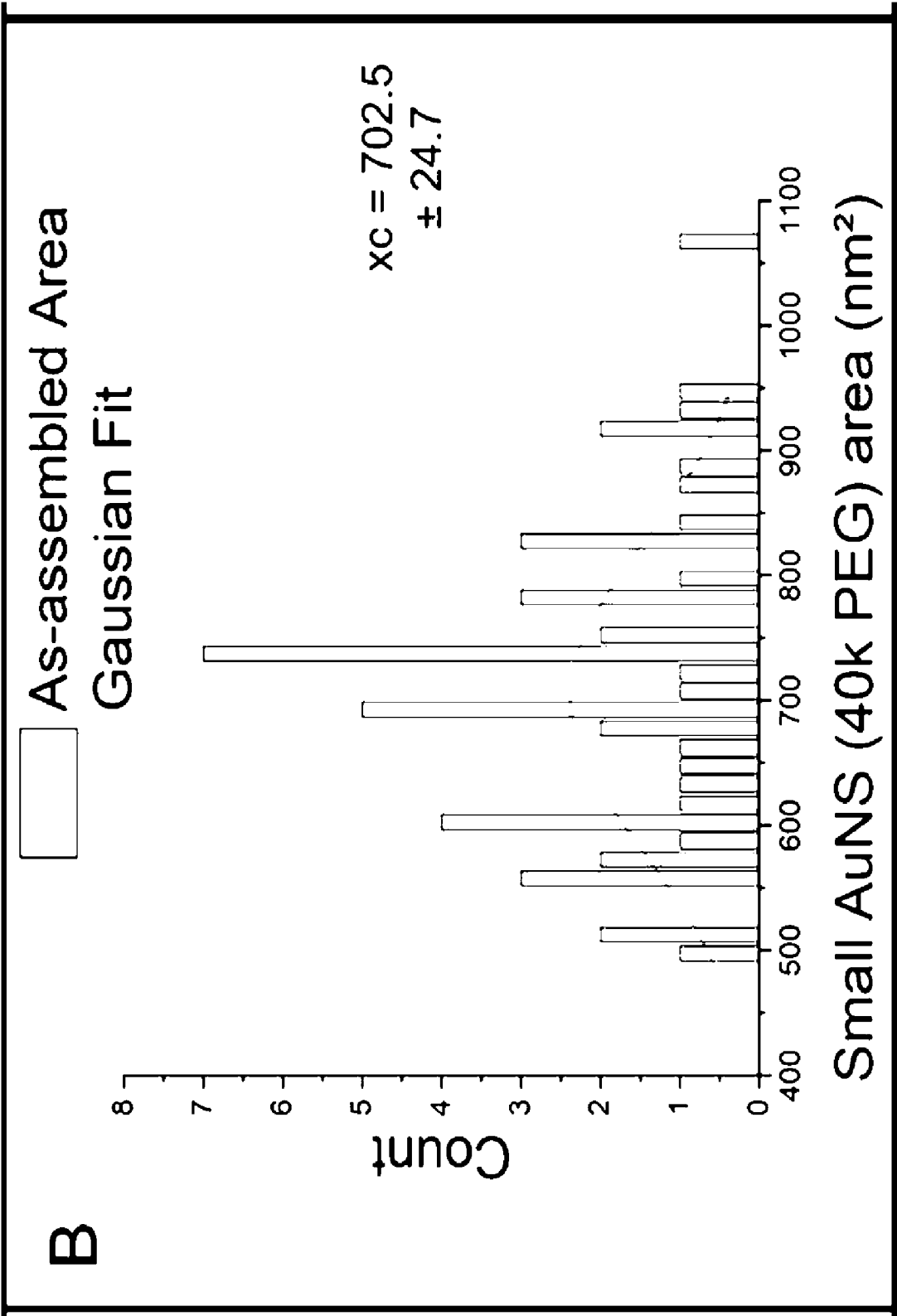


FIG. 24 cont.

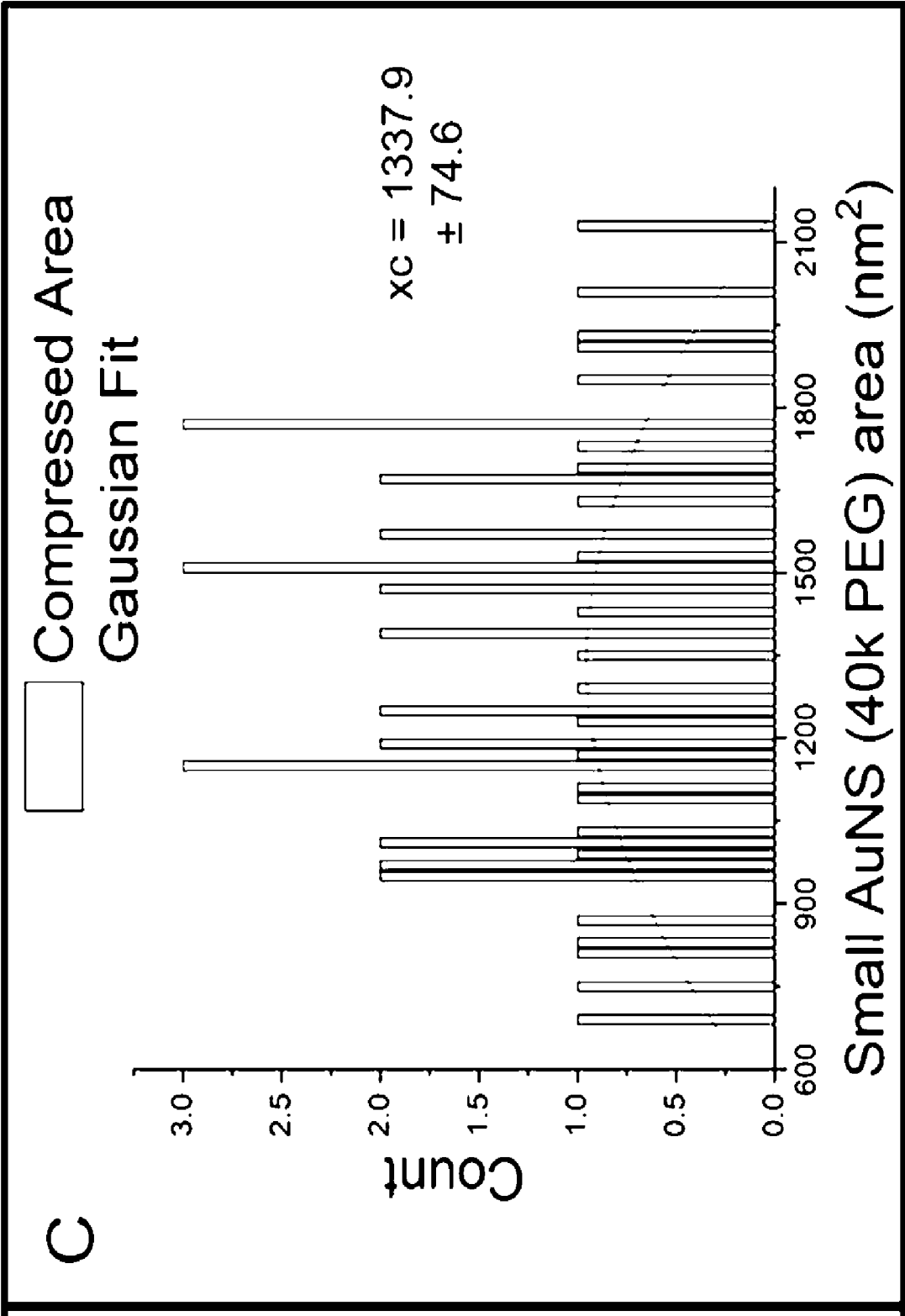


FIG. 25

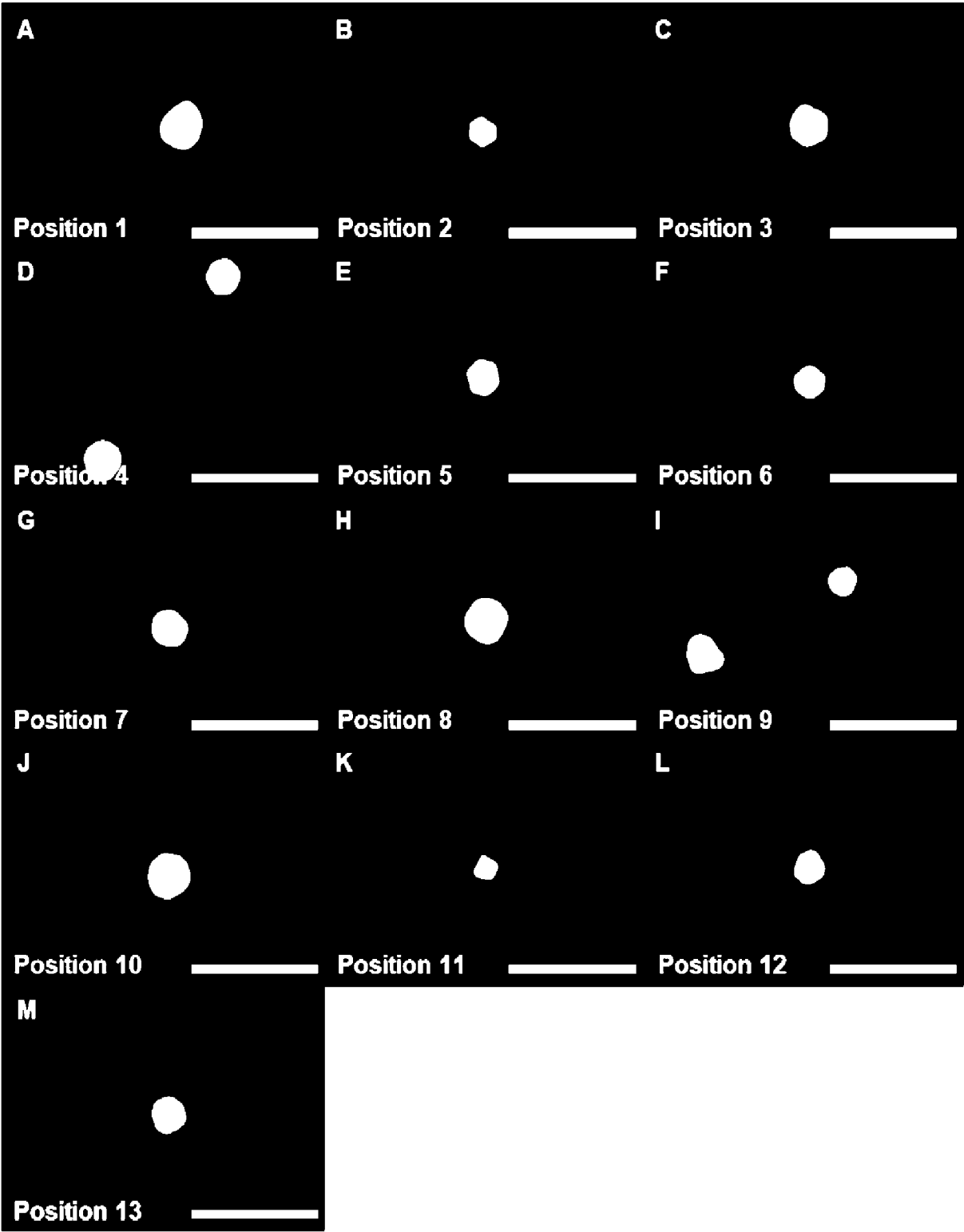


FIG. 26

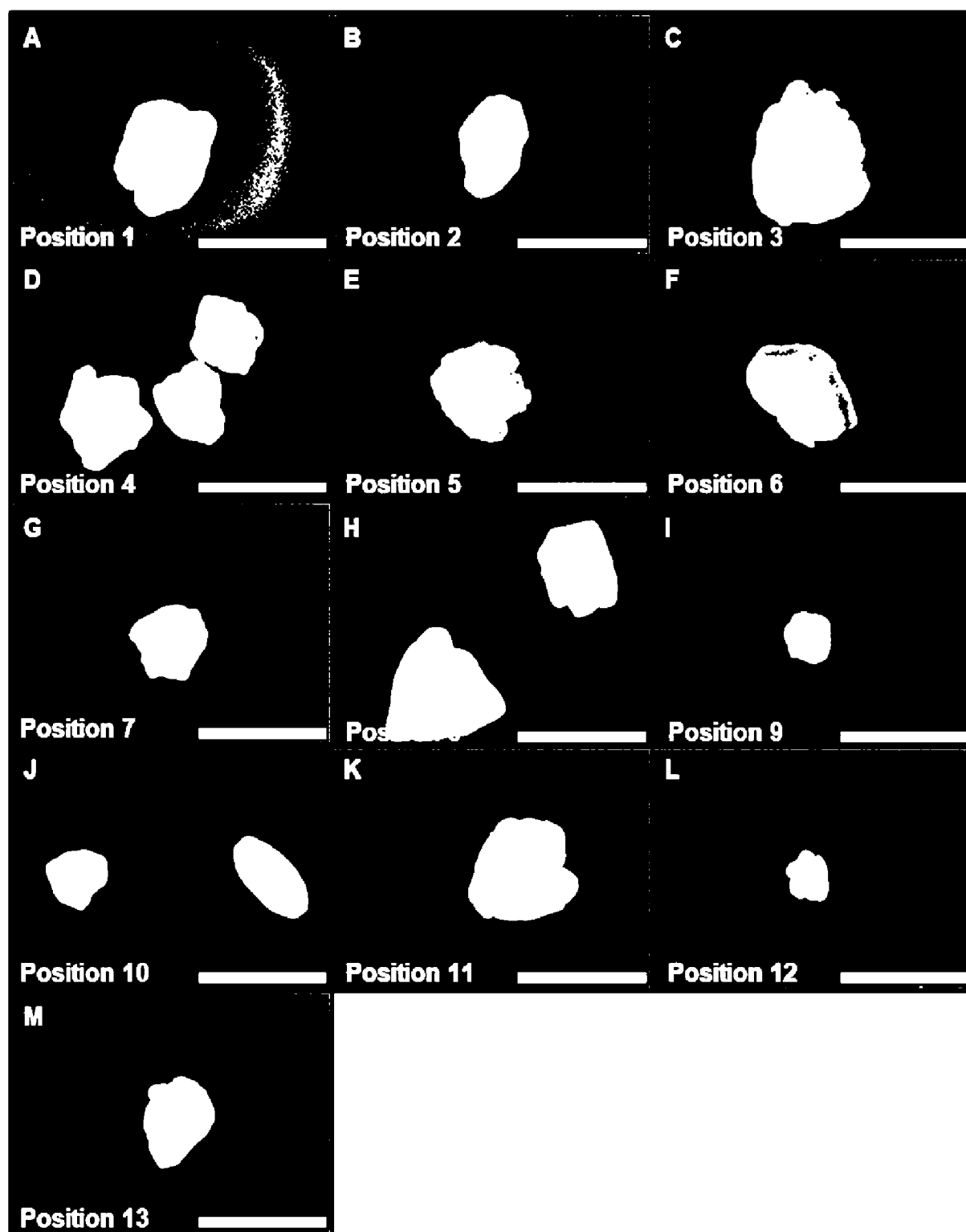


FIG. 27

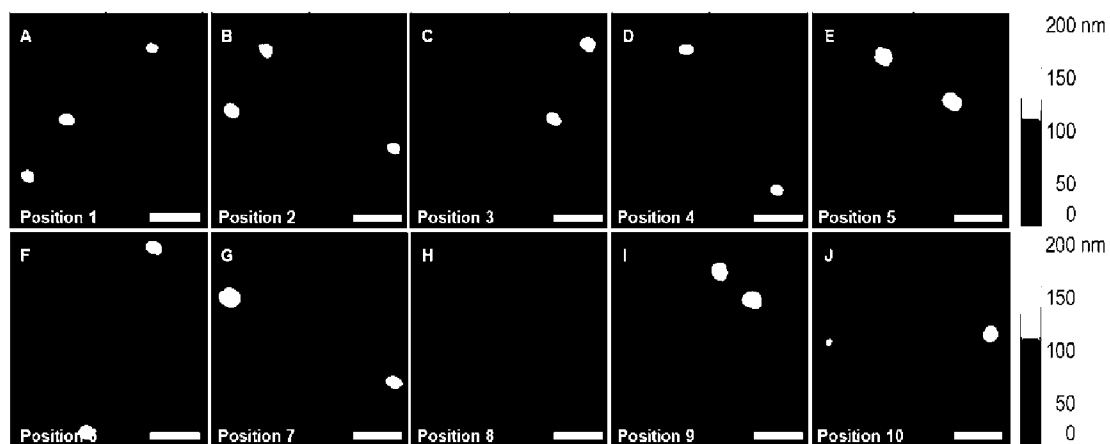


FIG. 28

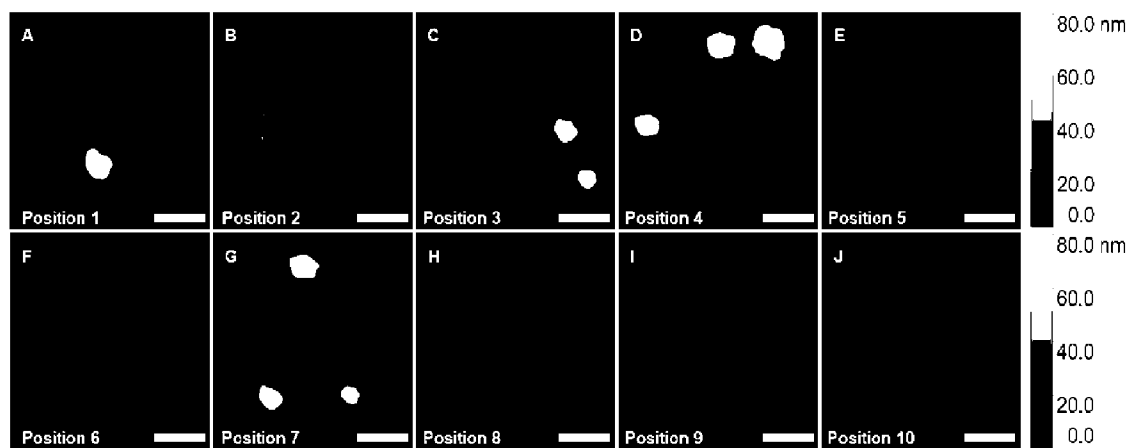


FIG. 29

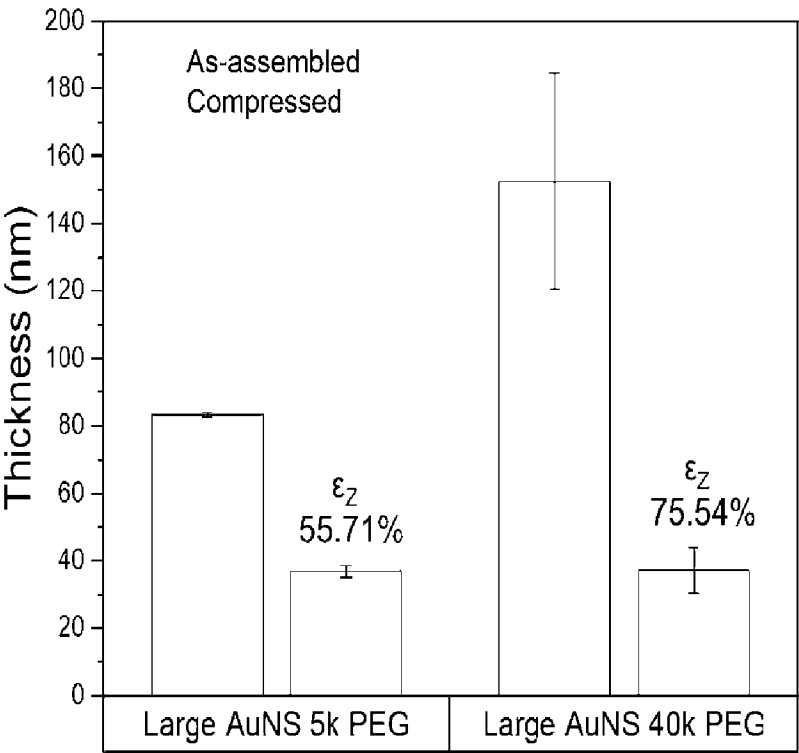


FIG. 30

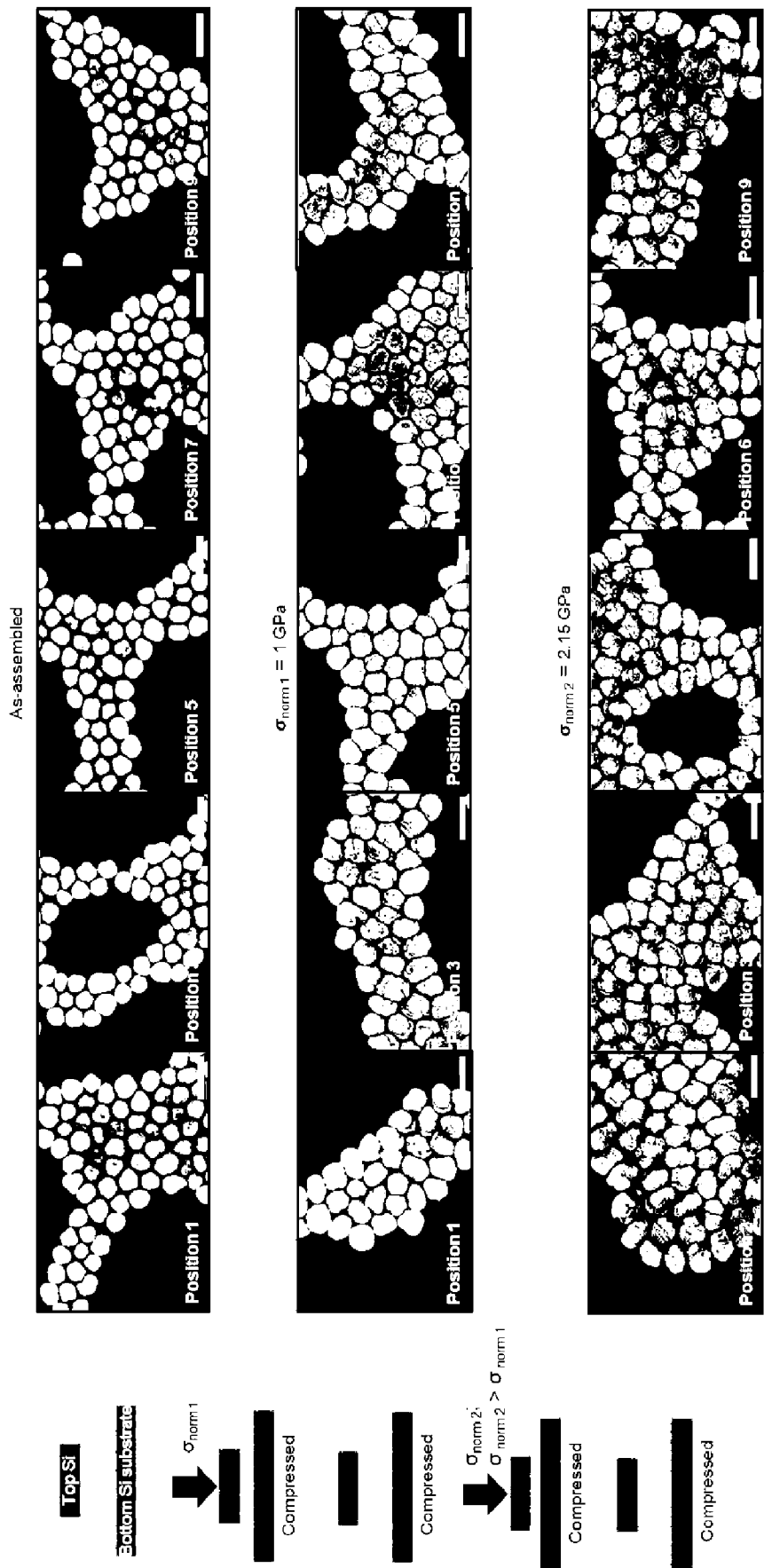


FIG. 31

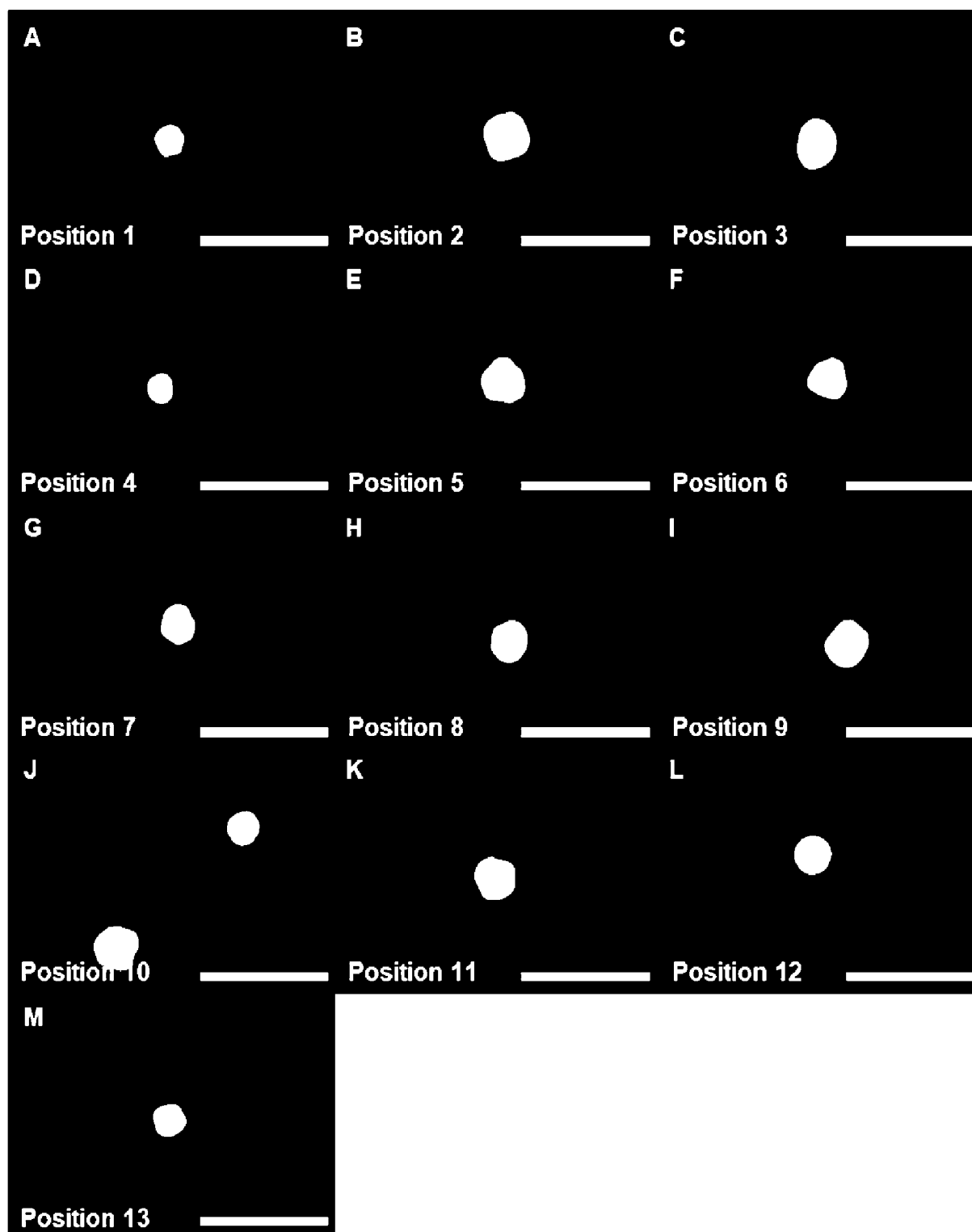


FIG. 32

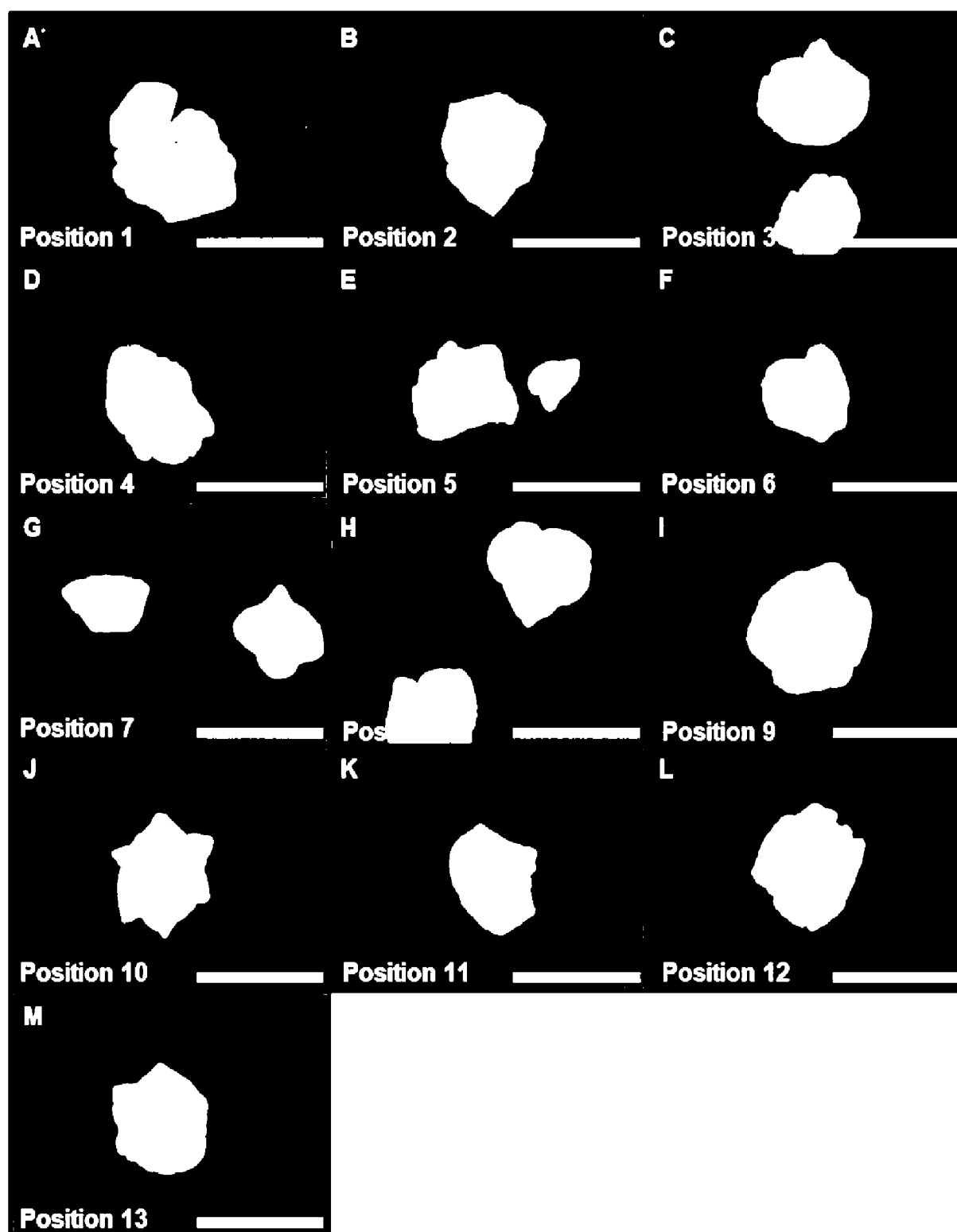


FIG. 33

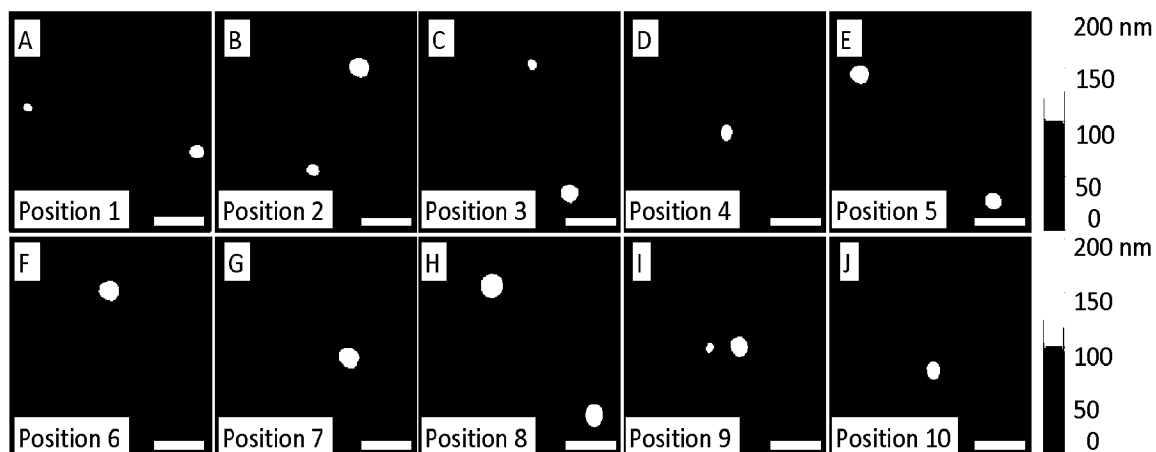


FIG. 34

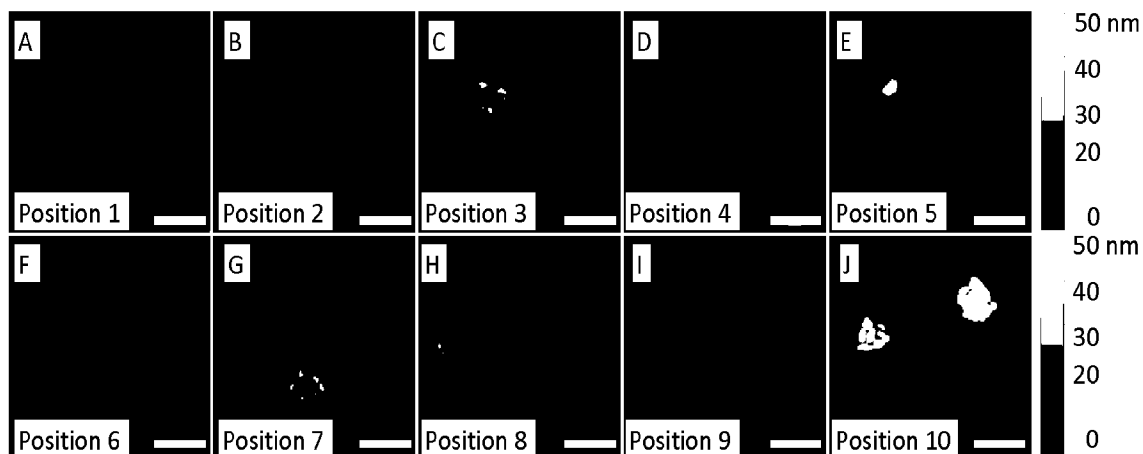


FIG. 35

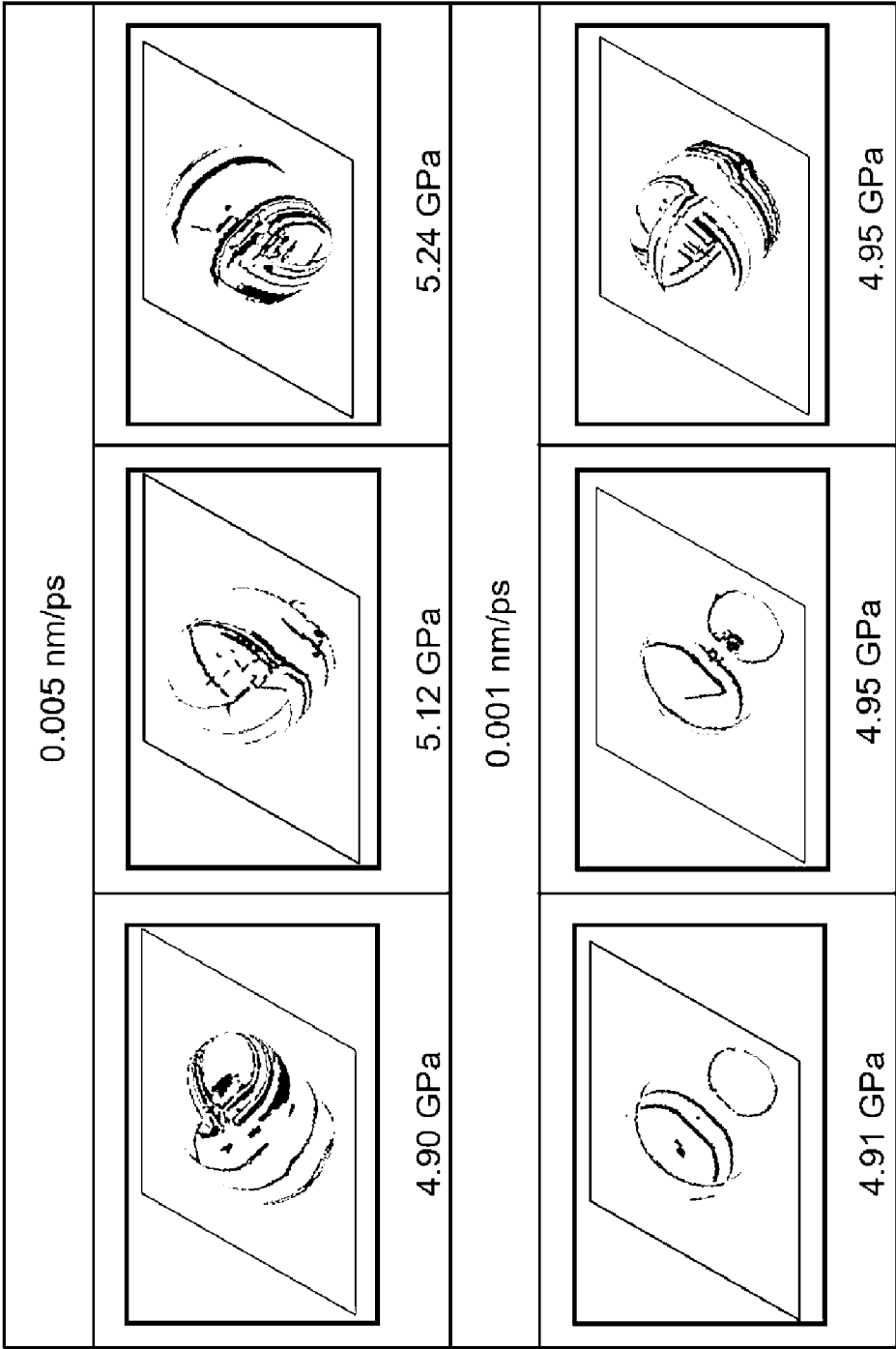


FIG. 36

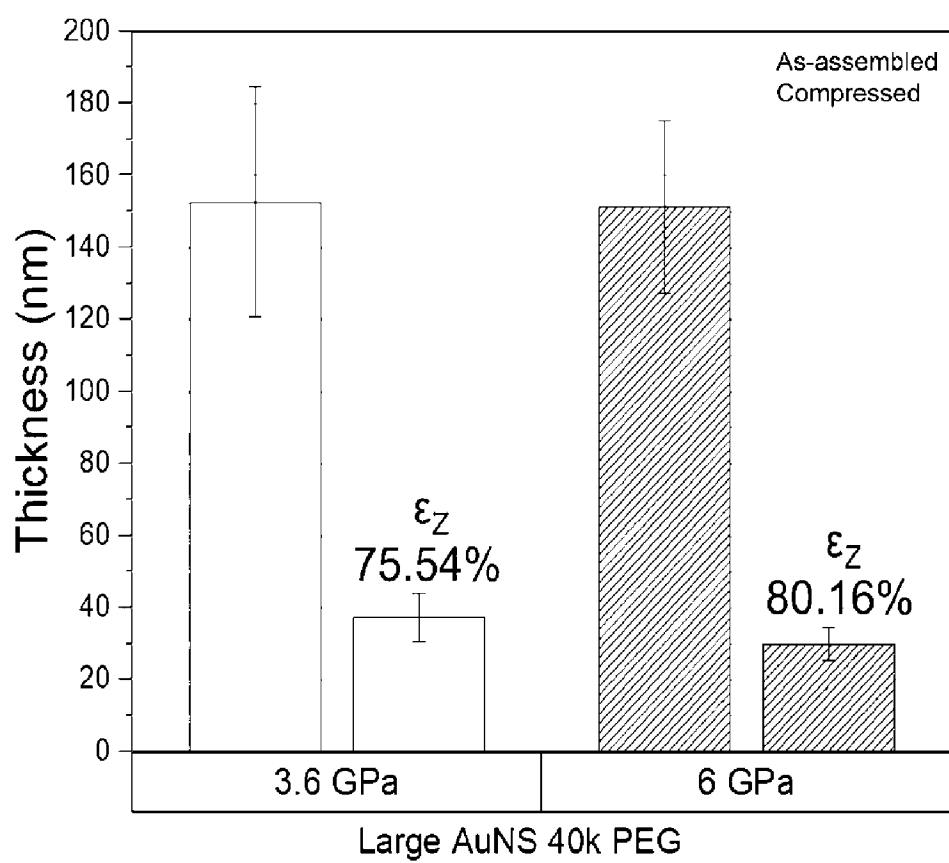


FIG. 37

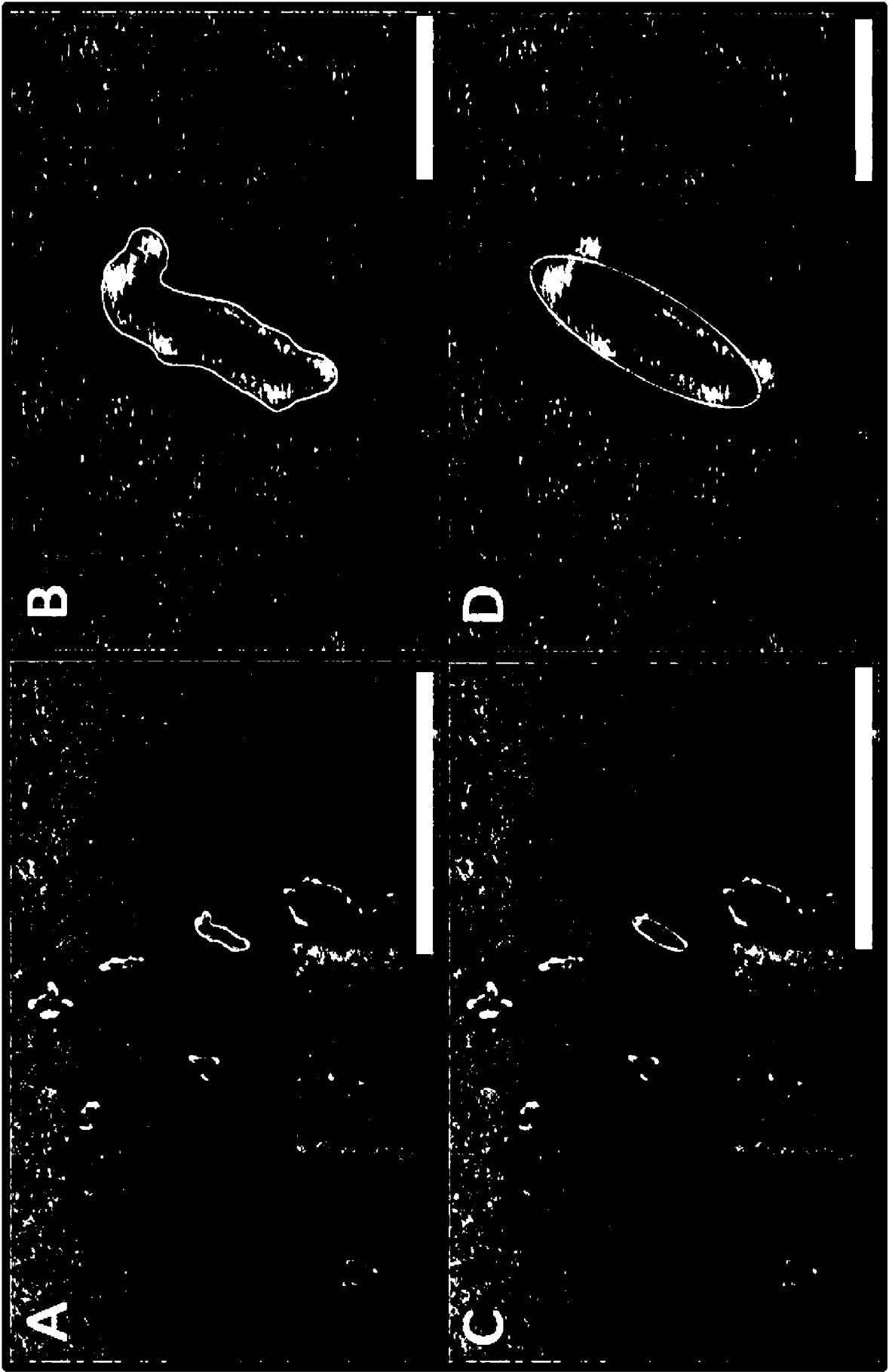


FIG. 38

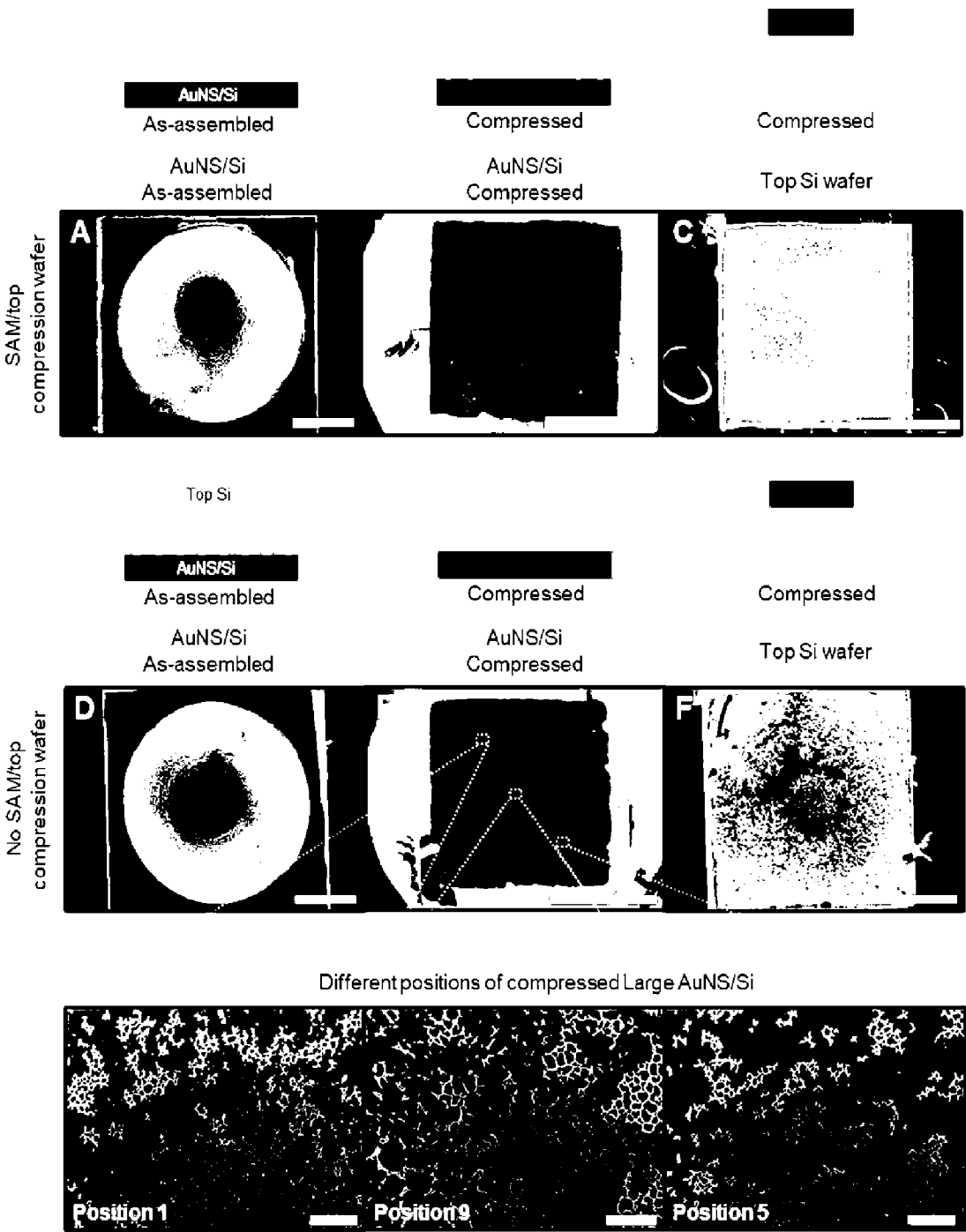


FIG. 39

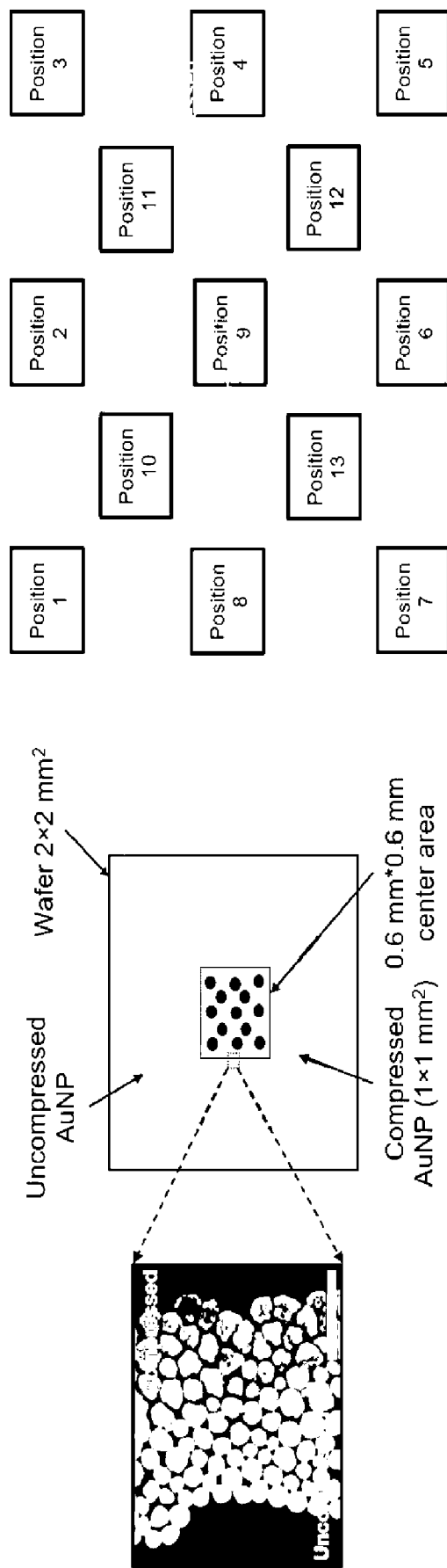


FIG. 40

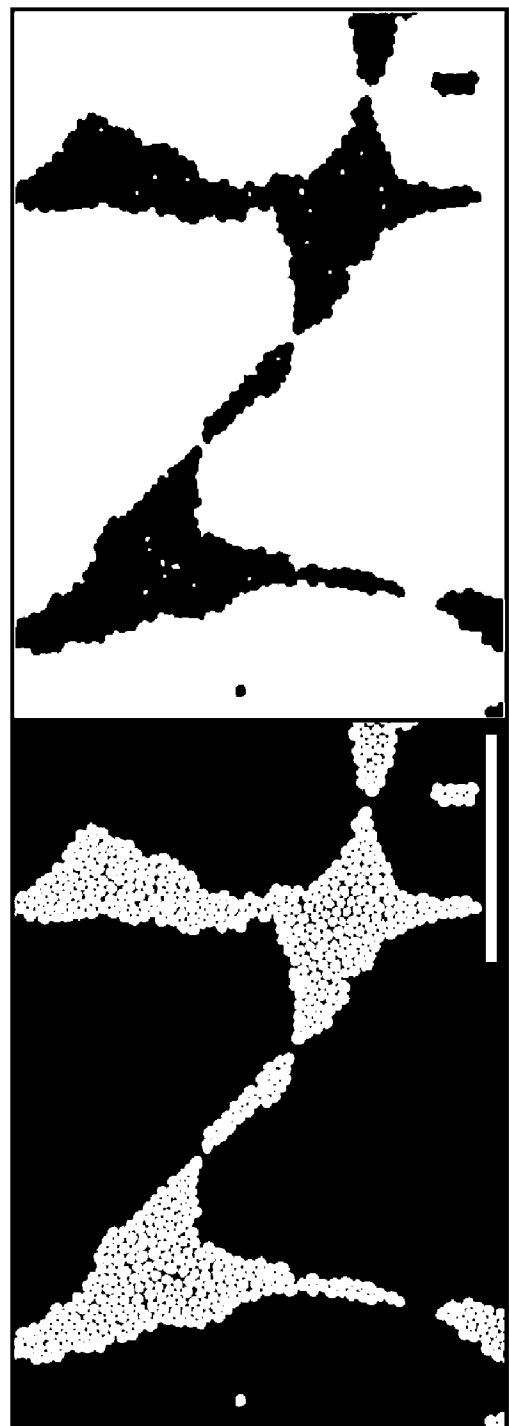


FIG. 41

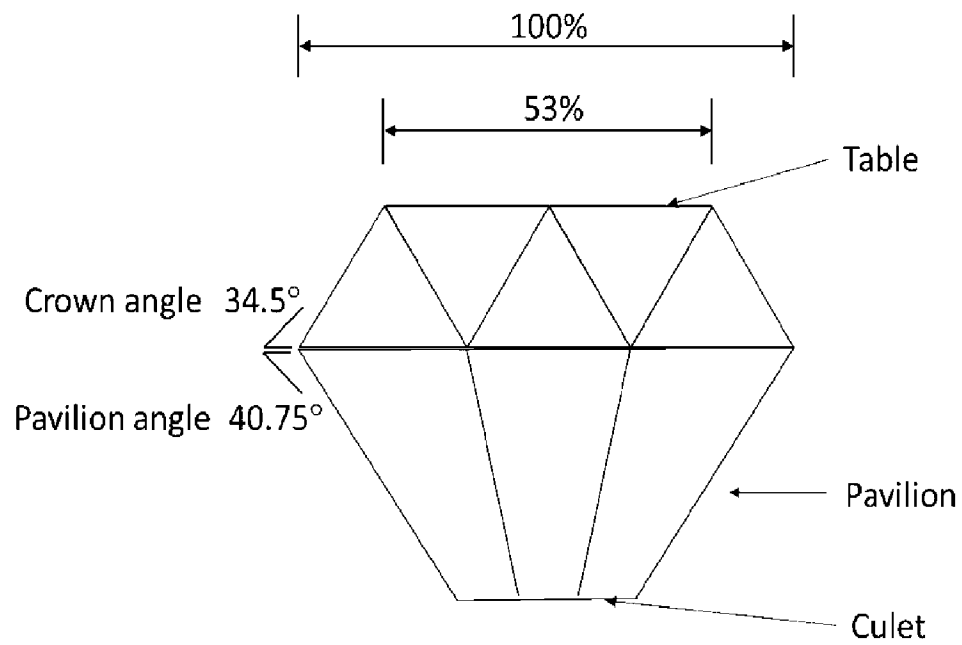


FIG. 42



FIG. 43

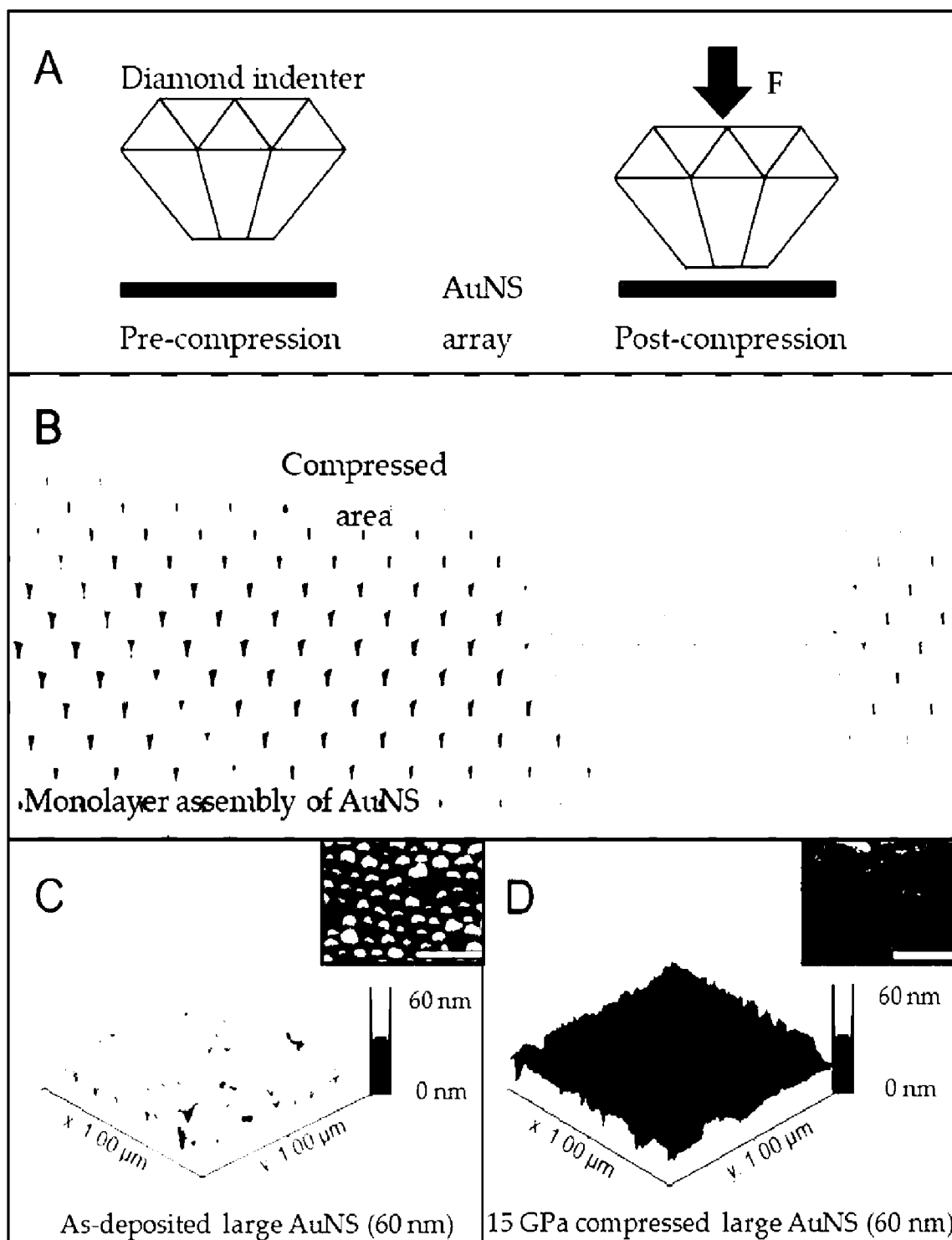


FIG. 44

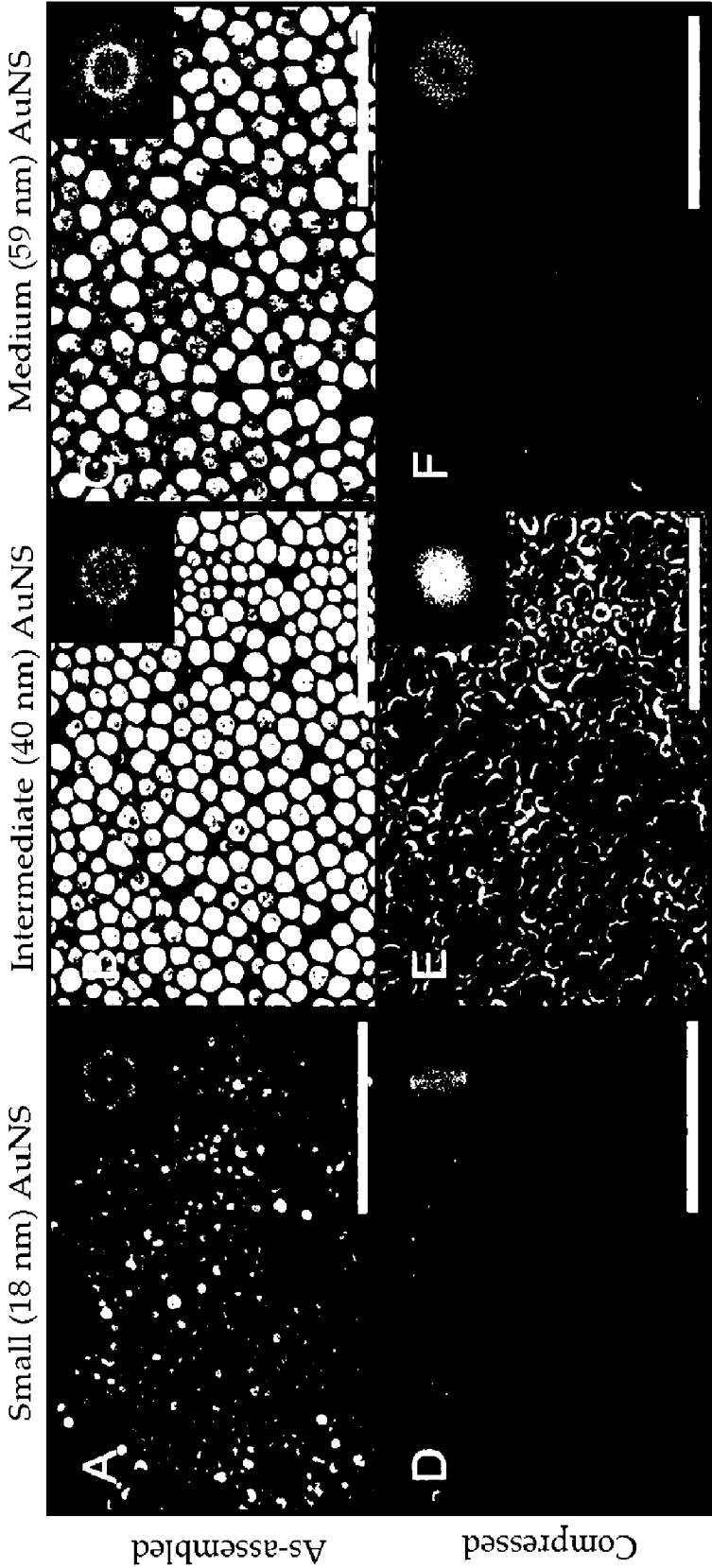
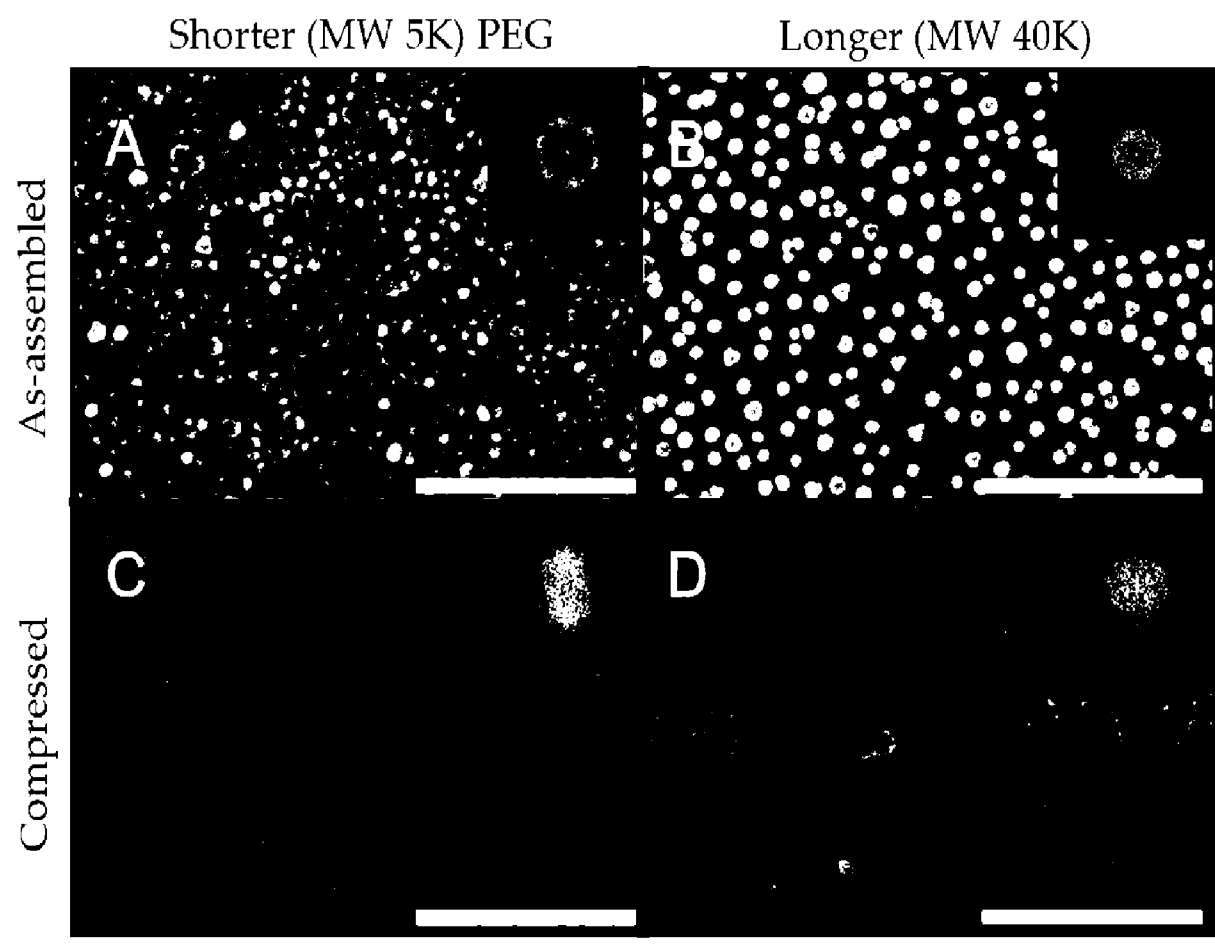


FIG. 45



INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/041990

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	B22F1/054	B22F1/07
		B22F1/142
		B22F3/03
ADD.	B30B1/00	
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)		
B22F B30B		
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)		
EPO - Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LI BINSONG ET AL: "Superfast assembly and synthesis of gold nanostructures using nanosecond low-temperature compression via magnetic pulsed power", NATURE COMMUNICATIONS, [Online] vol. 8, no. 1, 16 March 2017 (2017-03-16), XP093223052, UK ISSN: 2041-1723, DOI: 10.1038/ncomms14778 Retrieved from the Internet: URL:https://www.nature.com/articles/ncomms14778> [retrieved on 2024-11-12]	1 - 11, 13, 15 - 25
Y	Results; page 2 Magnetic dynamic compression and sample recovery; page 3 TEM of gold nanostructures from dynamic - / - -	26, 46
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of 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
13 November 2024		02/01/2025
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Forestier, Gilles

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/041990

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	compression; page 3 figures 1, 3a-f -----	
X	MAHARAJ DAVE ET AL: "Scale effects of nanomechanical properties and deformation behavior of Au nanoparticle and thin film using depth sensing nanoindentation", BEILSTEIN JOURNAL OF NANOTECHNOLOGY, [Online] vol. 5, 14 May 2014 (2014-05-14), pages 822-836, XP093223048, DE ISSN: 2190-4286, DOI: 10.3762/bjnano.5.94 Retrieved from the Internet: URL:https://www.beilstein-journals.org/bjnano/content/pdf/2190-4286-5-94.pdf> [retrieved on 2024-11-12] Compression; page 828 figure 6(a) Nanomechanical characterization; page 827 -----	26-37, 43-45
X	PALACIO MANUEL L B ET AL: "Depth-sensing indentation of nanomaterials and nanostructures", MATERIALS CHARACTERIZATION, ELSEVIER, NEW YORK, NY, US, vol. 78, 8 February 2013 (2013-02-08), pages 1-20, XP028529295, ISSN: 1044-5803, DOI: 10.1016/J.MATCHAR.2013.01.009 figures 1a, 2a -----	26-33, 36-43
X	ROMEIS S ET AL: "A novel apparatus for compression of submicron structures and particles in a high resolution SEM", REVIEW OF SCIENTIFIC INSTRUMENTS, AMERICAN INSTITUTE OF PHYSICS, 2 HUNTINGTON QUADRANGLE, MELVILLE, NY 11747, vol. 83, no. 9, 1 September 2012 (2012-09-01), pages 95105-95105, XP012162662, ISSN: 0034-6748, DOI: 10.1063/1.4749256 [retrieved on 2012-09-11] Experimental setup; page 2 figure 1 ----- -/-	26-33, 36-44

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/041990

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	TOMMY AO, JAMES R. ASAY, SOPHIE CHANTRENNE, RANDY J. HICKMAN, MICHAEL D. WILLIS, ANDREWS W. SHAY, SUZI A. GRINE-JONES: "The VELOCE pulsed power generator for isentropic compression experiments", , 1 December 2007 (2007-12-01), XP093223127, Retrieved from the Internet: URL:https://www.osti.gov/servlets/purl/1324445/ [retrieved on 2024-11-12] 7.2 Launching of flyer plates for shock compression experiments; page 67 figure 7.2	26,46
X	----- WANG H ET AL: "Nanomechanical properties of a Ni nanodot-patterned surface", NANOTECHNOLOGY, INSTITUTE OF PHYSICS PUBLISHING, BRISTOL, GB, vol. 19, no. 29, 23 July 2008 (2008-07-23), page 295708, XP020136773, ISSN: 0957-4484 2.1. Sample preparation and characterization; pages 2, 3 2.2. Nanoindentation test details; page 3 2.3. Indentation deformation characterization; page 4 figures 4b, 7	1,2, 7-13, 15-18, 25-33, 36,37, 43,44,46
X	----- MOOK W M ET AL: "Compression of freestanding gold nanostructures: from stochastic yield to predictable flow", NANOTECHNOLOGY, vol. 21, no. 5, 21 December 2009 (2009-12-21), page 055701, XP093223423, Bristol, GB ISSN: 0957-4484, DOI: 10.1088/0957-4484/21/5/055701 2. Experimental details; page 2 3. Results; page 3 figures 1, 5 -----	1-3,7, 9-11, 13-18, 25-33, 36,37,44