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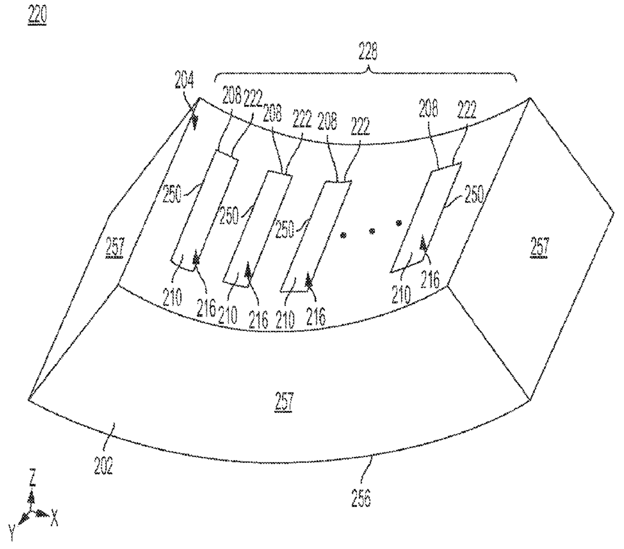

FIG. 1

(57) **Abstract:** Making a curved metallic grating for matching angular divergence of incident radiation includes: providing a mandrel with a curved receiving surface; disposing a planar substrate on the curved receiving surface; applying a clamping force to the planar substrate at the planar field surface; bending the planar substrate to shape-wise conform to the radius of curvature of the curved receiving surface of the mandrel in response to applying the clamping force, such that the planar substrate changes to a curved substrate; and superconformally filling the recessed feature with a metallic superconformal filling comprising a metal to form the curved metallic grating.

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CURVED METALLIC GRATING AND PROCESS FOR MAKING SAME

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0001] This invention was made with United States Government support from the National Institute of Standards and Technology (NIST), an agency of the United States Department of Commerce. The Government has certain rights in the invention.

CROSS REFERENCE TO RELATED APPLICATIONS

[0002] This application is a continuation in part of U.S. Patent Application No. 17/972,816 (filed October 25, 2022), which is a division of U.S. Patent Application No. 16/897,531 (filed June 10, 2020), which is a continuation in part of U.S. Patent Application No. 16/043,358 (filed July 24, 2018), which is a continuation in part of U.S. Patent Application No. 15/489,089 (filed April 17, 2017), which is a continuation in part of U.S. Patent Application No. 15/146,888 (filed May 4, 2016), the disclosure of each of which is incorporated herein by reference in its entirety. U.S. Patent Application No. 15/146,888 claims priority to U.S. Provisional Patent Application No. 62/165,360 (filed May 22, 2015) and is a continuation in part of U.S. Patent Application No. 14/012,830 (filed August 28, 2013), which claims priority to U.S. Provisional Patent Application No. 61/701,818 (filed February 28, 2017), the disclosure of each of which is incorporated herein by reference in its entirety. U.S. Patent Application No. 15/489,089 also is a continuation in part of U.S. Patent Application No. 14/812,134 (filed July 29, 2015), which claims priority to U.S. Provisional Patent Application No. 62/194,320 (filed July 20, 2015), the disclosure of each of which is incorporated herein by reference in its entirety.

BRIEF DESCRIPTION

[0003] Disclosed is a process for making a curved metallic grating for matching angular divergence of incident radiation that includes: providing a mandrel comprising a curved receiving surface; disposing a planar substrate on the curved receiving surface of the mandrel, the planar substrate comprising: a backing face; a planar field surface spaced apart from the backing face by a thickness of the planar substrate; an edge that peripherally bounds the backing face and the planar field surface; and a plurality of recessed features disposed in the planar substrate such that the recessed features are spaced apart from one another by the planar field surface of the planar substrate, and each of the recessed features comprising: a bottom member; and a sidewall that separates the bottom member from the planar field surface, such that the backing face faces and opposes the curved receiving surface; applying a clamping force to the planar substrate at the planar field surface proximate to the edge; bending the planar substrate to shape-wise conform to the radius of curvature of the curved receiving surface of the mandrel in response to applying the clamping force, such that the planar substrate changes to a curved substrate, and the curved substrate comprises: a curved field surface formed from deformation of the planar field surface and arranged to be exposed to a superconformal filling composition; a curved substrate radius of curvature; and the backing face disposed on and opposing the curved receiving surface of the mandrel; and superconformally filling the recessed feature with a metallic superconformal filling comprising a metal to form the curved metallic grating.

[0004] Disclosed is a curved metallic grating for matching angular divergence of incident radiation comprising: a curved substrate; a plurality of recessed features disposed in the curved substrate such that the recessed features are spaced apart from one another by a curved field surface of the curved substrate; a metallic superconformal filling formed and disposed in the recessed features and that receives the incident radiation and matches angular divergence of the incident radiation; and a curved grating comprising a spatial arrangement of the recessed features that are filled with the metallic superconformal filling such that the metallic superconformal filling is void-free, and the recessed features are bottom-up filled with the metallic superconformal filling, such that the radius of curvature of the curved grating is from 1 cm to 1000 cm, wherein an aspect ratio of the recessed features is from 0.5 to 200, and a height of the recessed features is from 50 nm to 5 mm, and a height of the metallic superconformal filling is less than or equal to the height of the recessed features.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] The following description cannot be considered limiting in any way. Various objectives, features, and advantages of the disclosed subject matter can be more fully appreciated with reference to the following detailed description of the disclosed subject matter when considered in connection with the following drawings, in which like reference numerals identify like elements.

[0006] FIG. 1 shows, according to some embodiments, a perspective view of a curved metallic grating.

[0007] FIG. 2 shows, according to some embodiments, a plan view of the curved metallic grating shown in FIG. 1.

[0008] FIG. 3 shows, according to some embodiments, a cross-section along line A-A for the curved metallic grating shown in FIG. 2.

[0009] FIG. 4 shows, according to some embodiments, a cross-section along line B-B for the curved metallic grating shown in FIG. 2.

[0010] FIG. 5 shows, according to some embodiments, a perspective view of a curved metallic grating that includes a metallic superconformal filling.

[0011] FIG. 6 shows, according to some embodiments, a plan view of the curved metallic grating shown in FIG. 5.

[0012] FIG. 7 shows, according to some embodiments, a cross-section along line A-A of the curved metallic grating shown in FIG. 5.

[0013] FIG. 8 shows, according to some embodiments, a cross-section view of a curved substrate that includes a curved field surface and a recessed feature.

[0014] FIG. 9 shows, according to some embodiments, an overlayer disposed on the curved substrate shown in FIG. 8.

[0015] FIG. 10 shows, according to some embodiments, a mandrel in plan view (A), a cross-section along line A-A (B), and a cross-section along line B-B (C).

[0016] FIG. 11 shows, according to some embodiments, a side view of a mandrel.

[0017] FIG. 12 shows, according to some embodiments, (A) a planar substrate disposed on a mandrel with indication of a clamping force to be subjected to the planar field surface proximate to the edge of the planar substrate, and (B) a curved substrate disposed on the curved receiving surface of the mandrel after application of the clamping force.

[0018] FIG. 13 shows, according to some embodiments, a plan view of the curved substrate disposed on the mandrel shown in panel B of FIG. 12.

[0019] FIG. 14 shows, according to some embodiments, a side view of the curved substrate disposed on the mandrel shown in panel B of FIG. 12.

[0020] FIG. 15 shows, according to some embodiments, a curved substrate disposed on the curved receiving surface of the mandrel after disposed in a superconformal filling composition 214 with electrodes in a container for making metallic superconformal filling 210 from superconformal filling composition 214, wherein (A) shows prior to formation of metallic superconformal filling 210, and (B) shows post formation of metallic superconformal filling 210.

[0021] FIG. 16 shows, according to some embodiments, (A) a side view of a curved metallic grating 220 disposed on the mandrel and (B) a side view of the curved metallic grating 220 after removal from the mandrel.

[0022] FIG. 17 shows, according to some embodiments, (A) a plan view of a clamping ring 265 for retaining and exerting a clamping force to a planar substrate in combination with a mandrel, (B) a side view of the clamping ring, (C) a plan view of the clamping ring, a curved substrate, and mandrel, (D), a side view of the curved substrate prior to formation of the metallic superconformal filling 210 in recessed features 250, and (E) a curved metallic grating 220 after formation of the metallic superconformal filling 210 in the recessed features 250.

[0023] FIG. 18 shows, according to some embodiments, a shape of the curved receiving surface of the mandrel that has non-zero curvature in two orthogonal directions that can be, e.g., a portion of a sphere, wherein curvatures in the two orthogonal directions can be equal, unequal, constant, or non-constant across the curved receiving surface, and solid lines below are contours of constant height z on the curved receiving surface of a mandrel that is facing downward in panels (A), (B), and (C).

[0024] FIG. 19 shows, according to some embodiments, (A) a photograph of a curved substrate disposed on a mandrel, (B) a curved metallic grating after filling trenches in the curved substrate with gold, and (C) a planar ruler disposed across curved metallic grating on the mandrel to emphasize nonplanarity of curved metallic grating, wherein the 30 cm radius of curvature mandrel was used for the Au superconformal filling.

[0025] FIG. 20 shows, according to some embodiments, (A) the curved metallic grating as in panel B of FIG. 19 and free-standing after removal from the mandrel, and (B) **a** plan view height map of the same Au-filled grating after removal from the mandrel, wherein the 100 mm diameter (100) oriented Si wafer substrate is patterned with trenches along a (011) in-plane crystal direction. Curvature during deposition was imposed along x, which is oriented along the orthogonal $(01\bar{1})$ in-plane crystal direction. The grating is patterned over a nominally 8 cm × 8 cm area centered on the wafer that is clipped in the corners slightly inside the edge of the wafer. The trenches are nominally 2.62 μm wide and 100 μm deep at a pitch of 5.25 μm. Bridges every 100 μm across pairs of adjacent trenches, also nominally 2.6 μm wide and their locations staggered by 50 μm between pairs of adjacent trenches, improve the integrity of the structure.

[0026] FIG. 21 shows, according to some embodiments, plan views and a cross-section for curved metallic gratings with bottom-up superconformal gold-filled vias arranged in a square grid.

[0027] FIG. 22 shows, according to some embodiments, perspective views of a curved metallic grating with bottom-up superconformal gold-filled vias arranged in a checkerboard pattern.

[0028] FIG. 23 shows, according to some embodiments, plan views and a cross-section for curved metallic gratings with bottom-up superconformal gold-filled recessed features arranged in a fractal pattern, wherein different size recessed features have different depths.

[0029] FIG. 24 shows, according to some embodiments, a superconformal filling composition in contact with the overlayer shown in FIG. 9.

[0030] FIG. 25 shows, according to some embodiments, growth of a metallic superconformal filling in the recessed feature of the substrate shown in FIG. 9 from the superconformal filling composition to make an article.

[0031] FIG. 26 shows, according to some embodiments, a graph of potential and cathodic current versus time in panels A and B that occur during making a metallic superconformal filling.

[0032] FIG. 27 shows, according to some embodiments, an article that includes a metallic superconformal filling disposed on a field surface and a recessed feature of the article.

[0033] FIG. 28 shows, according to some embodiments, a process for making a metallic grating.

[0034] FIG. 29 shows, according to some embodiments, a process for making an article.

[0035] FIG. 30 shows, according to some embodiments, a graph of deposition potential versus height of a high aspect ratio trench for forming a metallic superconformal filling.

[0036] FIG. 31 shows, according to some embodiments, a graph of deposition potential versus height of a high aspect ratio trench for forming a metallic superconformal filling.

[0037] FIG. 32 shows, according to some embodiments, a graph of deposition potential versus rotation rate for forming a metallic superconformal filling.

[0038] FIG. 33 shows, according to some embodiments, a graph of current density versus deposition potential for forming a metallic superconformal filling in a high aspect ratio trench in panel A and an enlarged view of a portion thereof in panel B; wherein panel A includes data for cyclic voltammetry in 160 mmol/L $Na_3Au(SO_3)_2$ + 0.64 mol/L Na_2SO_3 electrolyte of pH 9.5 containing 20 μmol/L Bi^{3+}. RDE rotation rates are as indicated. Current densities are obtained from measured current using the nominal RDE surface area of 0.79 cm^2. The two current density values in the potential range -0.9 V to -0.6 V for each cycle represent Au deposition rates expected on a bottom (higher current density) and sidewall (lower current density) of filling recessed features during bottom-up superconformal gold filling.

[0039] FIG. 34 shows, according to some embodiments, (A) a cross-section view of a wafer with a grating composed of parallel trenches subject to applied moment M and force F indicated at the ends with associated internal stress s(z) within the thickness of the wafer. The patterned volume of the grating necessarily rests upon a thickness of solid material. (B) Schematic of the grating bent to a uniform radius of curvature by uniform applied moment. The elastic strain associated with bending varies linearly over the height z within the underlying material, crossing through zero at a centroidal plane located at height c_p midway through the thickness of the underlying material in the patterned area and at height c_w midway through the full thickness of the wafer in the un-patterned area; the stress is proportional to the strain. Both curvature and thickness of the substrate relative to the radius of curvature have been increased substantially to facilitate visualization of the (strain) stress distributions. (C) Planview schematic of a 100 mm diameter Si wafer patterned with a nominally 8 cm × 8 cm grating (shown in gray) mounted on a holder with a concave surface that is cylindrical about y. In this geometry four pairs of low-profile clamps along the perimeter of the wafer, placed symmetrically about the midline of the wafer at x = 0 and spaced at 2 cm intervals in x, are used to bend and maintain the grating during Au deposition (drawn to scale). The wafer is bent along x with the trenches in the grating aligned along y. Flats that define the (110) crystal direction are seen at the +x/-x ends of the wafer.

[0040] FIG. 35 shows, according to some embodiments, predicted radius of curvature of a grating upon release after Au fill, expressed as a multiple of the radius imposed during Au fill plotted against the trench depth as a fraction of the full wafer thickness. The corresponding height of the centroid within the Si wafer as a fraction of wafer thickness is also shown and contrasted with the midline of the unetched Si that underlies the volume of the Si-Au grating. Consistent with (110) oriented Si and bulk Au, the ratio of the moduli of Au and Si is assumed to be 13/17 in the evaluation. The width of the Au filled trenches in the grating is presumed to equal one-half their pitch.

[0041] FIG. 36 shows, according to some embodiments, (A) increase of the principal radius of curvature R_x (cm) from the value of 30 cm imposed as a function of position (x, y) in the unrotated frame across the 8 cm × 8 cm area of the nominally square grating. Values were obtained from fitting of the height map within the 0.25 cm^2 square area centered at each location. (B) In-plane rotation of the direction yielding the minimum value of the radius of curvature, i.e., the principal curvature R_x, from the x-direction (along which the 30 cm radius of curvature was imposed during deposition); a positive value indicates a clockwise rotation. c) The values of R_x at the x coordinates yielding smaller radii of curvature plotted as a function of y.

[0042] FIG. 37 shows, according to some embodiments, photographs of un-patterned 100 mm diameter Si wafer viewed obliquely (A) resting unmounted on a planar holder and (B) mounted on the 30 cm radius of curvature holder by clamping around the full circumference of the wafer. The reflected grids capture the curved state of the mounted wafer.

[0043] FIG. 38 shows, according to some embodiments, results from imaging two curved (bent) metallic gratings and a planar metallic grating.

DETAILED DESCRIPTION

[0044] A detailed description of one or more embodiments is presented herein by way of exemplification and not limitation.

[0045] Curved metallic gratings with high aspect ratio features can improve the performance of divergent X-ray sources by reducing the shadowing of the beams, wherein curved metallic gratings communicate X-rays more uniformly than planar gratings, resulting in a more intense, uniform X-ray beam. Additionally, the curved metallic gratings can improve the signal-to-noise ratio of imaging and other X-ray beam applications.

[0046] X-ray phase contrast imaging systems use X-rays for imaging of soft tissue rather than just bones (and in an absence of gadolinium injection as is required in CAT scans), including assessment of emphysema and breast cancer. Here, a gold-filled diffraction grating is placed close to an X-ray source and another is placed beyond the patient by an X-ray detector. The gold filled gratings can include silicon wafers where one side has been etched to have parallel trenches that are micron scale and of high aspect ratio and then gold filled. High aspect ratio (very deep and narrow) trenches are necessary for the high energy X-rays required for imaging of thick regions such as the human chest. With respect to the instant description, the curved metallic grating has a radius that can be selected to match a distance to an X-ray source to achieve high-quality performance across the entire area of the grating.

[0047] In an embodiment, with reference to FIG. 1 to FIG. 23, a curved metallic grating 220 matches angular divergence of incident radiation 252 and includes: curved substrate 202; a plurality of recessed features 250 disposed in curved substrate 202 such that recessed features 250 are spaced apart from one another by curved field surface 204 of curved substrate 202;

metallic superconformal filling 210 formed and disposed in recessed features 250 and that receives incident radiation 252 and matches angular divergence of incident radiation 252; and curved grating 228 including a spatial arrangement of recessed features 250 that are filled with metallic superconformal filling 210 such that metallic superconformal filling 210 is void-free, and recessed features 250 are bottom-up filled with metallic superconformal filling 210, such that the radius of curvature of curved grating 228 is from 1 cm to 1000 cm, wherein an aspect ratio of recessed features 250 is from 0.5 to 200, and a height of recessed features 250 is from 50 nm to 5 mm, and a height of metallic superconformal filling 210 is less than or equal to the height of recessed features 250. In an embodiment, the curved substrate radius of curvature of curved substrate 202 is from 1 cm to 1000 cm. In an embodiment curved substrate 202 is electrically conductive. In an embodiment, curved substrate 202 includes silicon and a dopant that provide electrical conductivity to curved substrate 202. In an embodiment, a width of metallic superconformal filling 210 is from 10 nm to 100 µm. In an embodiment, a length of metallic superconformal filling 210 is from 0.5 µm to 1 m. In an embodiment, the height of metallic superconformal filling 210 is from 50 nm to 5 mm. In an embodiment, metallic superconformal filling 210 consists essentially of gold and bismuth. In an embodiment, recessed features 250 include high aspect ratio trench 222, via 258, or a combination including at least one of the foregoing recessed features. In an embodiment, recessed features 250 are vias 258, and vias 258 are arranged as square pattern 259, checkerboard pattern 260, or fractal pattern 261. In an embodiment, curved metallic grating 220 includes a cylindrical shape formed in response to shape-wise deformation to a radius of curvature of curved receiving surface 254 of mandrel 253, wherein curved receiving surface 254 includes the cylindrical shape. In an embodiment, curved metallic grating 220 includes a concave shape formed in response to shape-wise deformation to a radius of curvature of curved receiving surface 254 of mandrel 253, wherein curved receiving surface 254 includes the concave shape. In an embodiment, curved metallic grating 220 includes a convex shape formed in response to shape-wise deformation to a radius of curvature of curved receiving surface 254 of mandrel 253, wherein curved receiving surface 254 includes the convex shape. In an embodiment, curved metallic grating 220 includes mandrel 253 including curved receiving surface 254, on which curved substrate 202 is disposed. In an embodiment, the metal of metallic superconformal filling 210 includes gold, copper, platinum, rhodium, rhenium, nickel, cobalt, mercury, or a combination includes at least one of the foregoing metals.

[0048] In an embodiment, with reference to FIG. 1, FIG. 2, and FIG. 3, curved metallic grating 220 includes: curved substrate 202; a plurality of high aspect ratio trench 222 disposed in curved substrate 202 such that high aspect ratio trench 222 are spaced apart from one another by curved field surface 204 of curved substrate 202; metallic superconformal filling 210 formed and disposed in high aspect ratio trench 222; and curved grating 228 including a spatial arrangement of high aspect ratio trenches 222 that are filled with metallic superconformal filling 210 such that metallic superconformal filling 210 is void-free, and high aspect ratio trenches 222 are bottom-up filled with metallic superconformal filling 210. An aspect ratio of high aspect ratio trench 222 independently can be from 0.5 to 1000, specifically from 5 to 500, and more specifically from 5 to 200. A height of high aspect ratio trench 222 independently can be from 50 nanometers to 5 mm, specifically from 0.5 µm to 5 mm, and more specifically from 1 µm to 1 mm. A height of metallic superconformal filling 210 is less than or equal to the height of high aspect ratio trench 222. A width of high aspect ratio trench 222 independently can be from 5 nm to 100 µm, specifically from 0.1 µm to 50 µm, and more specifically from 0.1 µm to 10 µm. A length of metallic superconformal filling 210 can be from 1 µm to 1 m, specifically from 5 µm to 300 mm, and more specifically from 10 µm to 150 mm. The height of metallic superconformal filling 210 can be from 50 nanometers to 5 mm, specifically from 1 µm to 1 mm, and more specifically from 1 µm to 0.1 mm. In an embodiment, curved substrate 202 is electrically conductive. In an embodiment, curved substrate 202 includes silicon and a dopant (e.g., an n-dopant such as phosphorous or a p-dopant such as boron) that provides electrical conductivity to curved substrate 202. In an embodiment, metallic superconformal filling 210 includes gold. It is contemplated that trace amounts of another element can be included with the gold. Exemplary trace elements include bismuth. In an embodiment, metallic superconformal filling

210 consists essentially of gold and bismuth. According to an embodiment, metallic superconformal filling 210 includes an alloy of gold, referred to as a gold alloy. Exemplary gold alloys include binary gold alloys such as cobalt-gold or ternary gold alloys such as cobalt-copper-gold.

[0049] It should be appreciated that that high aspect ratio trench 222 is an embodiment of recessed feature 250 described herein.

[0050] In an embodiment, with reference to FIG. 5, FIG. 6, FIG. 7, and FIG. 25, curved metallic grating 220 includes curved substrate 202; curved field surface 204 disposed on curved substrate 202; recessed feature 250 disposed on curved substrate 202; curved field surface 204 that surrounds recessed feature 250. In some embodiments, overlayer 212 is disposed on curved metallic grating 220 so that curved field surface 204, recessed feature 250, or a combination thereof are partially or fully metallized during contact with superconformal filling composition 214. Recessed feature 250 includes bottom member 206 and sidewall 208 that separates bottom member 206 from curved field surface 204. metallic superconformal filling 210 has exposed surface 216 disposed distal to bottom member 206.

[0051] Mandrel 253 (also referred to as a holder) imposes a radius of curvature (e.g., 30 cm but no limited thereto) on planar substrate 203 that is disposed thereon and subsequently subjected to a clamping force. In an embodiment, a 100 mm silicon wafer patterned with diffraction gratings is disposed on mandrel 253, subjected to the clamping force to bend planar substrate 203 into curved substrate 202, and then curved substrate 202 subjected to bottom-up superconformal gold filling to achieve bottom-up gold filling of trenches and making curved metallic grating 220. It should be appreciated that the shape and radius of curvature of curved receiving surface 254 is arbitrary and can be selected based on application of curved metallic grating 220.

[0052] With reference to FIG. 13, a grating can be mounted on a cylindrical holder such that the grating height z varies with x and can be attached to the holder by clamps (e.g., four pairs of clamps) such that the grating generally conforms to the surface of the holder. The clamp provides can be electrically conductive to provide electrical connection to the grating but do not obscure the recessed features of the grating. With reference to FIG. 14, a grating can be mounted on a curved holder, e.g., attached by two pairs of clamps along its perimeter.

[0053] With reference to FIG. 15 (top pane), a curved grating mounted on a curved holder can be suspended into electrolyte (i.e., immersed) from a rotor shaft to a rotator that can rotate the immersed assembly during gold electrodeposition. The rotor with wire connected to clamps provides electrical connection to the grating that serves as a cathode electrode for gold electrodeposition. With reference to FIG. 15 (bottom panel), a curved grating mounted on a curved holder can be suspended in electrolyte from a shaft to a rotator that can rotate the assembly during gold deposition at rotation rates from 1 rotation per minute to 1000 rotations per minute. Rotor connected to clamp(s) provides electrical connection to grating and rotates holder and mounted grating in which bottom-up gold filling by gold electrodeposition has been started but not completed. FIG. 16 shows a curved grating with recessed features that are bottom-up gold filled (i.e., a bottom-up gold filled grating) while the curved grating was mounted on the curved holder. FIG. 16 (bottom panel) shows the bottom-up gold filled grating whose recessed features were bottom-up gold filled while the grating was mounted on a curved holder and has retained a cylindrical shape with radius between 1x to 10x that of the curved holder after removal from the curved holder.

[0054] With reference to FIG. 17, clamping ring can be a curved metal ring for mounting a curved grating around its perimeter to a holder using four pairs of clamps, e.g., bolts. Neither the circular ring nor the bolts obscure the recessed features of the grating. The circular ring through the clamp(s) can provide electrical connection to the grating during gold electrodeposition. The curved metal ring for mounting a grating around its perimeter to a holder can have through holes that receive bolts. The outer radius of the ring can equal the inner radius of the holder, or it can be larger or smaller. Neither the circular ring nor the bolts that go through the pass-through holes obscure the recessed features of the grating. The circular ring or clamps can provide electrical connection to the grating during gold electrodeposition. A grating mounted on a curved holder also is shown attached by a curved metal ring around the entire perimeter of the grating, the metal ring held in place by four pairs of bolts.

[0055] Various components are planar, e.g., planar field surface 205 of planar substrate 203. Various components (e.g., curved substrate 202, curved field surface 204, curved metallic grating 220, mandrel 253) have non-zero radius of curvature, wherein the radius of curvature can be from 1 cm to 1000 cm, more specifically from 5 cm to 100 cm. In an embodiment, the radius of curvature is 5 cm for curved metallic grating 220 proximate to an X-ray source, and curved metallic grating 220 proximate to a detector is about 100 cm, wherein both radii of curvature can be selected based on the size and divergence of the imaging system or selected based on an object to be imaged. It is contemplated that more compact systems involve smaller radii. Accordingly, curved received surface of mandrel 253 can be cylindrical, hemispherical, concave, convex, and the like.

[0056] The patents and patent applications recited and incorporated by reference in the CROSS REFERENCE TO RELATED APPLICATIONS describe elements, processes, conditions, and materials that can be used herein as various described elements, processes, conditions, and materials. In particular, planar substrate 203 is described in the cross-referenced related applications.

[0057] The stresses required to bend planar substrate 203 to a selected radius of curvature increase with its thickness. A grating with fully gold filled trenches in a silicon wafer is effectively as thick as the original, unetched silicon wafer. When the wafer is bent, stresses are high, and the brittle silicon of the grating can shatter. If the wafer is bent before gold filling, then the thickness of the wafer in the grating area is only the thickness of the silicon left underneath the etched trenches, as far as elastic stresses are concerned. This can be less than half the thickness of the original wafer. As the bottom-up filling process accomplished in curved substrate 202 adds no new stresses, bottom-up gold deposition in the curved substrate 202 creates curved metallic grating

220 with substantially reduced stresses and risk of fracture. This enables bending to smaller radii without failure of curved metallic grating 220 than otherwise achievable with conventional planar filled substrates.

[0058] In an embodiment, a process for making curved metallic grating 220 for matching angular divergence of incident radiation 252 incudes: providing a mandrel 253 comprising a curved receiving surface 254; disposing a planar substrate 203 on the curved receiving surface 254 of the mandrel 253, the planar substrate 203 comprising: a backing face 256; a planar field surface 205 spaced apart from the backing face 256 by a thickness of the planar substrate 203; an edge 257 that peripherally bounds the backing face 256 and the planar field surface 205; and a plurality of recessed features 250 disposed in the planar substrate 203 such that the recessed features 250 are spaced apart from one another by the planar field surface 205 of the planar substrate 203, and each of the recessed features 250 comprising: a bottom member 206; and a sidewall 208 that separates the bottom member 206 from the planar field surface 205, such that the backing face 256 faces and opposes the curved receiving surface 254; applying a clamping force to the planar substrate 203 at the planar field surface 205 proximate to the edge 257; bending the planar substrate 203 to shape-wise conform to the radius of curvature of the curved receiving surface 254 of the mandrel 253 in response to applying the clamping force, such that the planar substrate 203 changes to a curved substrate 202, and the curved substrate 202 comprises: a curved field surface 204 formed from deformation of the planar field surface 205 and arranged to be exposed to a superconformal filling composition 214; a curved substrate radius of curvature; and the backing face 256 disposed on and opposing the curved receiving surface 254 of the mandrel 253; and superconformally filling the recessed feature 250 with a metallic superconformal filling 210 comprising a metal to form the curved metallic grating 220.

[0059] In an embodiment, making curved metallic grating 220 includes: releasing the clamping force from the curved field surface 204 of the curved metallic grating 220; and removing the curved metallic grating 220 from the mandrel 253. In an embodiment, curved metallic grating 220 maintains the curved substrate radius of curvature after removing the curved metallic grating 220 from the mandrel 253.

[0060] In an embodiment of making curved metallic grating 220, curved receiving surface 254 of the mandrel 253 comprises a mandrel radius of curvature 255 from 1 cm to 1000 cm. In an embodiment of making curved metallic grating 220, the curved substrate radius of curvature of the curved substrate 202 is from 1 cm to 1000 cm. In an embodiment of making curved metallic grating 220, recessed features 250 comprise a high aspect ratio trench 222, a via 258, or a combination comprising at least one of the foregoing recessed features. In an embodiment of making curved metallic grating 220, recessed features 250 are vias 258, and the vias 258 are arranged as a square pattern 259, a checkerboard pattern 260, or a fractal pattern 261. In an embodiment of making curved metallic grating 220, each of the recessed features 250 includes high aspect ratio trench 222 that includes an aspect ratio of a depth to a width from 0.5 to 200 before filling the recessed feature 250 with the metallic superconformal filling 210, the aspect ratio decreasing during filling the recessed feature 250 with the metallic superconformal filling 210. In an embodiment of making curved metallic grating 220, a height of the high aspect ratio trench 222 is from 50 nm to 5 mm, and a height of the metallic superconformal filling 210 is less than or equal to the height of the high aspect ratio trench 222. In an embodiment, making curved metallic grating 220 includes forming a cylindrical shape in the curved field surface 204 such that the curved metallic grating 220 has the cylindrical shape in response to bending the planar substrate 203 to shape-wise conform to the radius of curvature of the curved receiving surface 254 of the mandrel 253, wherein the curved receiving surface 254 comprises the cylindrical shape. In an embodiment, making curved metallic grating 220 includes forming a concave shape in the curved field surface 204 such that the curved metallic grating 220 has the concave shape in response to bending the planar substrate 203 to shape-wise conform to the radius of curvature of the curved receiving surface 254 of the mandrel 253, wherein the curved receiving surface 254 comprises the concave shape. In an embodiment, making curved metallic grating 220 includes forming a convex shape in the curved field surface 204 such that the curved metallic grating 220 has the convex shape in response to bending the planar substrate 203 to shape-wise conform to the radius of curvature of the curved receiving surface 254 of the mandrel 253, wherein the curved receiving surface 254 comprises the convex shape. In an embodiment of making curved metallic grating 220, overlayer 212 is disposed on the bottom member 206. In an embodiment of making curved metallic grating 220, the metal of metallic superconformal filling 210 comprises gold, copper, Pt, Rh, Re, nickel, cobalt, mercury, or a combination comprises at least one of the foregoing metals.

[0061] In an embodiment, making curved metallic grating 220 includes: contacting the overlayer 212 on the bottom member 206 with a superconformal filling composition 214, the superconformal filling composition 214 having a near-neutral pH and comprising: a plurality of $Au(SO_3)_2^{3-}$ anions as a source of gold that is superconformally deposited as the metallic superconformal filling 210 in the recessed features 250; a plurality of SO_3^{2-} anions; and a plurality of Bi^{3+} cations as a brightener and an accelerator for superconformally depositing gold in the recessed features 250; convectively transporting the $Au(SO_3)_2^{3-}$ anions and the Bi^{3+} cations to the bottom member 206 by actively moving the curved substrate 202 relative to superconformal filling composition 214; subjecting the bottom member 206 of the recessed features 250 to an electrical current to superconformally deposit gold from the $Au(SO_3)_2^{3-}$ anions on the bottom member 206 relative to the sidewall 208 and the curved field surface 204, the electrical current providing a cathodic voltage, and a first deposition ratio of a first deposition rate of gold on the bottom member 206 relative to a second deposition rate of gold on the sidewall 208; and increasing the electrical current subjected to the curved field surface 204 and the recessed features 250 to maintain the cathodic voltage during superconformally depositing gold in the recessed features 250 to form the metallic superconformal filling 210 comprising gold in the recessed features 250 such that the metallic superconformal filling 210 is void-free and seam-free.

[0062] In an embodiment of making curved metallic grating 220, the process is performed in an absence of through-mask plating.

[0063] In an embodiment, making curved metallic grating 220includes: forming a conductive seed layer on the recessed features 250, the seed layer comprising: 10 nm to 100 nm of platinum grown over exposed sidewalls and bottom members of the recessed features 250 and followed by forming an overlying Au layer formed on the platinum; contacting the recessed features 250 with a superconformal filling composition 214 comprising from 40 mmol/L to 1000 mmol/L $Na_3Au(SO_3)_2$ and from 0.1 mol/L to 1.0 mol/L Na_2SO_3, wherein a pH of the superconformal filling composition 214 is from 8.0 to 10.0; providing Bi^{3+} to the superconformal filling composition 214; contacting the recessed features 250 with the Bi^{3+}; rotating the curved substrate 202 in the superconformal filling composition 214 at a rotation rate from 25 RPM to 2000 RPM; subjecting the recessed features 250 to a deposition potential relative to a Hg/Hg_2SO_4/saturated K_2SO_4 reference electrode from -0.6 V to -0.85 V; and superconformally filling the recessed features 250 such that superconformal filling is bottom-up with upward growth forming the metallic superconformal filling 210 that comprises gold at the deposition potential relative to a Hg/Hg_2SO_4/saturated K_2SO_4 reference electrode from -0.6 V to -0.85 V; and automatically passivating a growth front of the recessed features 250 from 10 minutes to 1 week after beginning of forming the metallic superconformal filling 210 in the recessed features 250 to make the curved metallic grating 220.

[0064] In an embodiment, making curved metallic grating 220 includes subjecting the field surface and the recessed feature to an electrical current to superconformally deposit gold from the $Au(SO_3)_2^{3-}$ anions on the bottom member relative to the sidewall and the field surface, the electrical current providing a cathodic voltage (V_{SSE}) from -0.6 V to -1.0 V relative to a saturated sulfate electrode (SSE), and a first deposition ratio of a first deposition rate of gold on the bottom member relative to a second deposition rate of gold on the sidewall being from 1.5 to 10^6; and increasing the electrical current subjected to the field surface and the recessed feature to maintain the V_{SSE} from -0.6 V to -1.0 V relative to the SSE during superconformally depositing gold on the substrate to superconformally fill the recessed feature of the article with gold as a metallic superconformal filling comprising gold, the metallic superconformal filling being void-free and seam-free, such that in a presence of the superconformal filling composition: passivation of the field surface and the recessed feature occurs at the V_{SSE} greater than -0.6 V relative to the SSE, sub-conformal deposition of gold occurs at the V_{SSE} less than -1.0 V relative to the SSE, and superconformal deposition of gold occurs at the V_{SSE} from -0.6 V to -1.0 V relative to the SSE.

[0065] In an embodiment, making curved metallic grating 220 includes catalyzing superconformal deposition of gold with underpotential deposited Bi from the Bi^{3+} cations.

[0066] In an embodiment of making curved metallic grating 220, actively moving the substrate relative to the superconformal filling composition comprising rotating the substrate at a rotation rate from 25 revolutions per minute (RPM) to 2000 RPM.

[0067] In an embodiment, making curved metallic grating 220 includes changing the rotation rate from a first rotation rate to a second rotation rate during superconformally depositing gold.

[0068] In an embodiment, making curved metallic grating 220 includes maintaining the VSSE from -0.6 V to -1.0 V relative to the SSE until the recessed feature is partially filled with the aspect ratio of the recessed feature that remains unfilled being less than or equal to 0.5; and thereafter changing a deposition condition to fill the recessed feature sub-conformally, conformally, or a combination comprising at least one of the foregoing non-superconformal filling regimes.

[0069] In an embodiment of making curved metallic grating 220, V_{SSE} is maintained from -0.6 V to -1.0 V relative to the SSE until the recessed feature is completely filled with the metallic superconformal filling.

[0070] In an embodiment of making curved metallic grating 220, the superconformal filling composition consists essentially of the $Au(SO_3)_2^{3-}$ anions, the SO_3^{2-} anions, the Bi^{3+} cations, and an additive in an aqueous liquid in an absence of a suppressor.

[0071] In an embodiment of making curved metallic grating 220, the near-neutral pH of the superconformal filling composition is from 6.5 to 10.5.

[0072] In an embodiment of making curved metallic grating 220, the field surface is passivated during bottom-up filling.

[0073] In an embodiment of making curved metallic grating 220, depositing the gold on the field surface and the recessed feature automatically stops before completely filling the recessed feature with gold while the V_{SSE} is from -0.6 V to -1.0 V relative to the SSE.

[0074] In an embodiment, with reference to FIG. 8, FIG. 9, FIG. 24, FIG. 25, FIG. 26, FIG. 27, and FIG. 29, a process for superconformally filling recessed feature 250 of curved metallic grating 220 with gold includes: contacting curved field surface 204 and recessed feature 250 with superconformal filling composition 214 optionally in an absence of cyanide, lead, thallium, or a combination thereof; convectively transporting $Au(SO_3)_2^{3-}$ anions and Bi^{3+} cations from superconformal filling composition 214 to bottom member 206 by actively moving curved substrate 202 relative to superconformal filling composition 214; subjecting curved field surface 204 and recessed feature 250 to an electrical current to superconformally deposit gold from the $Au(SO_3)_2^{3-}$ anions on bottom member 206 relative to sidewall 208 and curved field surface 204, the electrical current providing a cathodic voltage (V_{SSE}) from -0.6 V and -1.0 V relative to a saturated sulfate electrode (SSE), and a first deposition ratio of a first deposition rate of gold on bottom member 206 relative to a second deposition rate of gold on sidewall 208 being from 1.5 to 10^6; and increasing the electrical current subjected to curved field surface 204 and recessed feature 250 to maintain the V_{SSE} from -0.6 V to -1.0 V relative to the SSE during superconformally depositing gold on curved substrate 202 to superconformally fill recessed feature 250 of curved metallic grating 220 with gold as metallic superconformal filling 210 including gold. metallic superconformal filling 210 is void-free and seam-free. It is contemplated that, in a presence of superconformal filling composition 214: passivation of curved field surface 204 and recessed feature 250 occurs at the V_{SSE} greater than -0.6 V relative to the SSE, sub-conformal deposition of gold occurs at the V_{SSE} less than -1 V relative to the SSE, and superconformal deposition of gold occurs at the V_{SSE} from -0.6 V to -1.0 V relative to the SSE. It should be appreciated that, according to the process thus far, that superconformal deposition of gold occurs since the V_{SSE} is maintained from -0.6 V to -1.0 V relative to the SSE. The electrical current can be provided in a continuous ramp that is linear (e.g., solid curve in panel A of FIG. 26) or nonlinear, provided in a plurality of steps (e.g., dashed curve in panel A of FIG. 26), or a combination thereof. Without wishing to be bound by theory, it is believed that although electrical current increases from I_{Low} to I_{High}, voltage is maintained from first voltage V1 to second voltage V2 because time-dependent adsorption or electrochemical transformation of adsorbed bismuth-containing compounds (e.g., oxo-complexes, sulfite complexes, hydroxide complexes) accelerate Au deposition.

[0075] The process also can include selectively disposing overlayer 212 on curved metallic grating 220 such that curved field surface 204 or recessed feature 250 are independently not metallized, partially metallized, or fully metallized for contact with superconformal filling composition 214. In some embodiments, the process includes disposing overlayer 212 on curved metallic grating 220 such that field 204 and bottom member 206 are metallized for contact with superconformal filling composition 214 in an absence of metallization of sidewall 208. It is contemplated that for curved substrate 202 that is electrically conductive, formation of metallic superconformal filling 210 in recessed feature 250 can occur in an absence of overlayer 212. A seed layer, e.g., a gold seed layer, can be selectively formed on bottom of recessed feature 250 before deposition of gold as metallic superconformal filling 210. Disposing overlayer 212 on curved metallic grating 220 can include evaporation, electrochemical or electroless deposition, sputter deposition, chemical vapor deposition, or atomic layer deposition. In an embodiment, disposing overlayer 212 includes evaporation of a layer of titanium followed by a layer of gold.

[0076] In the process, contacting curved field surface 204 and recessed feature 250 with superconformal filling composition 214 can include transferring a wafer patterned with recessed features into the superconformal filling composition.

[0077] In the process, convectively transporting $Au(SO_3)_2^{3-}$ anions and Bi^{3+} cations from superconformal filling composition 214 to bottom member 206 includes actively moving curved substrate 202 relative to superconformal filling composition 214. Actively moving curved substrate 202 relative to superconformal filling composition 214 can include displacing superconformal filling composition 214 across bottom member 206, exposed surface 216, sidewall 208, or curved field surface 204. Displacing can include rotating curved substrate 202, bubbling a gas (e.g., argon, nitrogen, carbon dioxide, and the like) through superconformal filling composition 214, stirring superconformal filling composition 214, heating superconformal filling composition 214 or curved substrate 202, recirculating superconformal filling composition 214, sonication of superconformal filling composition 214, vibration of curved substrate 202, and the like. In an embodiment, actively moving includes rotating the patterned wafer using equipment for rotating disk electrodes to which the patterned wafer is attached and suspended within the superconformal filling composition. In an embodiment, actively moving curved substrate 202 relative to the superconformal filling composition includes rotating curved substrate 202 at a rotation rate from 0 revolutions per minute (RPM) to 3000 RPM, specifically at rotation rates from 100 RPM to 1600 RPM. The rotation rate can be variable or fixed.

[0078] The process can include changing a rate of superconformal deposition of gold or changing from superconformally depositing gold to conformally or sub-conformally depositing gold. Here, it is contemplated that the process includes changing the rotation rate from a first rotation rate to a second rotation rate during superconformally depositing gold. The first rate can be, e.g., from 400 RPM to 3000 RPM, specifically 1600 RPM, and the second rate can be from 400 RPM to 100 RPM, specifically 100 RPM.

[0079] In the process, subjecting curved field surface 204 and recessed feature 250 to an electrical current can include attaching the specimen to a corrosion resistant metal holder such as a Pt holder that is rotating with a contact to a galvanostat or potentiostat that applies current or potential.

[0080] In the process, increasing the electrical current subjected to curved field surface 204 and recessed feature 250 to maintain the V_{SSE} from -0.6 V to -1.0 V relative to the SSE can include stepping or ramping the potential or current to maintain the potential in the range -0.6 V and -1.0 V relative to the SSE. Here, superconformal filling self terminates because electrical current increases and then decreases back toward zero, wherein the electrical current is negative.

[0081] As shown in FIG. 25, growth proceeds from bottom member 206 in a direction of filling toward curved field surface 204. Here, with reference to FIG. 26, the electrical current can be subjected to overlayer 212 from low electrical current I_{Low} to high electrical current I_{High} to maintain the potential at curved field surface 204 and bottom member 206 from first voltage V1 to second voltage V2, wherein V1 is greater than or equal to V2, and V1 and V2 are from -0.6 V to -1.0 V relative to the SSE. In an embodiment, increasing the electrical current includes increasing the current through a series of steps of discrete and equal size at intervals that maintain potential in the specified interval.

[0082] According to an embodiment, the V_{SSE} is maintained from -0.6 V to -1.0 V relative to the SSE until recessed feature 250 is completely filled with metallic superconformal filling 210. In an embodiment, the VSSE is maintained from -0.6 V to -1.0 V relative to the SSE until recessed feature 250 is partially filled with the aspect ratio being less than or equal to 0.5; and thereafter the process includes changing a deposition condition to fill recessed feature 250 sub-conformally, conformally, or a combination of at least one of the foregoing non-superconformal filling regimes (i.e., sub-conformally filling or conformally filling).

[0083] According to an embodiment, with reference to FIG. 28, a process for making curved metallic grating 220 includes: providing curved substrate 202 with the plurality of high aspect ratio trench 222 disposed in curved substrate 202 such that high aspect ratio trench 222 are spaced apart from one another by curved field surface 204 of curved substrate 202, and each of high aspect ratio trench 222 including: bottom member 206; sidewall 208 that separates bottom member 206 from curved field surface 204, and an aspect ratio of a height to a width from 0.5 to 200 before filling the high aspect ratio trench with metallic superconformal filling 210, the aspect ratio decreasing during filling the high aspect ratio trench with metallic superconformal filling 210; and optionally an overlayer disposed on the bottom member; contacting bottom member 206 with superconformal filling composition 214, superconformal filling composition 214 having a near-neutral pH and including: a plurality of $Au(SO_3)_2^{3-}$ anions as a source of gold that is superconformally deposited as metallic superconformal filling 210 in high aspect ratio trench 222; a plurality of SO_3^{2-} anions; and a plurality of Bi^{3+} cations as a brightener and an accelerator for superconformally depositing gold in high aspect ratio trench 222; convectively transporting the $Au(SO_3)_2^{3-}$ anions and the Bi^{3+} cations to bottom member 206 by actively moving curved substrate 202 relative to superconformal filling composition 214; subjecting bottom member 206 of high aspect ratio trench 222 to an electrical current to superconformally deposit gold from the $Au(SO_3)_2^{3-}$ anions on relative to sidewall 208 and curved field surface 204, the electrical current providing an overvoltage for gold deposition, and a first deposition ratio of a first deposition rate of gold on bottom member 206 relative to a second deposition rate of gold on sidewall 208; and increasing the electrical current subjected to curved field surface 204 and high aspect ratio trench 222 to maintain the cathodic voltage during superconformally depositing gold in high aspect ratio trench 222 to form metallic superconformal filling 210 including gold in high aspect ratio trench 222 such that metallic superconformal filling 210 is void-free and seam-free.

[0084] Curved substrate 202 can include a material such as silicon, silicon dioxide, germanium, or a compound semiconductor such as gallium arsenide, silicon nitride, gallium nitride, other nitrides, oxides, diamond or other carbons or polymers, boron, beryllium, aluminum, templated porous aluminum oxide. These materials can be used for applications in electrodepositing gold on substrates for diffraction gratings, microelectronics, microelectromechanical devices such as an accelerometer, or jewelry. In an embodiment, curved substrate 202 is a semiconductor, e.g., silicon. Curved substrate 202 can be multi-layered such a first layer is disposed on a second layer. The first layer can be, e.g., a semiconductor, and the second layer, e.g., can be a high-K dielectric such as a nitride of the material of the first layer, e.g., silicon nitride. It is contemplated that field 204 and recessed feature 250 including sidewall 208 and bottom member 206 are metallized to be electrically conductive for electrodeposition of gold thereon through superconformally depositing gold. Alternatively, it is contemplated that curved substrate 202 is electrically conductive and is metallized on none, some, or all of field 204, sidewall 208 and bottom member 206 for electrodeposition of gold thereon through superconformally depositing gold.

[0085] Overlayer 212 provides full metallization of field 204 and recessed feature 250. Overlayer 212 can include a material such as gold, platinum, iridium, nickel, titanium, tantalum, ruthenium, palladium, rhodium, silver, and alloys thereof. Such materials can be used for adhesion to the substrate or wetting of the superconformal filling composition and superconformal filling. In an embodiment, overlayer 212 is a transition metal, e.g., Ti, Ta, or a combination thereof. A thickness of overlayer 212 can be from 1 nm to 1 μm, specifically from 10 nm to 100 nm or specifically from 100 nm to 1 μm. It is contemplated that in some embodiments overlayer 212 is an electrically conductive composite such as an electrically conductive polymer or an electrically conductive glass. Exemplary electrically conductive composites include indium tin oxide and the like.

[0086] Curved substrate 202 has recessed feature 250 that includes bottom member 206 and sidewall 208. Recessed feature 250 can be a trench, via, or another feature in which metallic superconformal filling 210 is formed. For electrical applications, metallic superconformal filling 210 can function as an electrical interconnect. A shape of recessed feature as viewed from curved field surface 204 toward bottom member 206 can be a via, trench, or a combination thereof. Before superconformally filling recessed feature 250, recessed feature 250 can have an aspect ratio of depth D (also referred to herein ad height) to width W from 0.5 to 1000, specifically from 1 to 60, wherein the aspect ratio increases during superconformally filling recessed feature 250 or the aspect ratio provided above for high aspect ratio trench 222. A length of width W can be from 5 nm to 50 μm, specifically from 1 μm to 10 μm, or the width provided above for high aspect ratio trench 222. A length of depth D can be from 50 nm to 5 mm, specifically from 0.5 μm to 5 μm, or the aspect height provided above for high aspect ratio trench 222.

[0087] Metallic superconformal filling 210 is void-free and seam-free. It is contemplated that, in a presence of superconformal filling composition 214, passivation of curved field surface 204 and recessed feature 250 occurs at V_{SSE} greater than -0.6 V relative to the SSE. Further in a presence of superconformal filling composition 214, sub-conformal deposition of gold occurs at the V_{SSE} less than -1 V relative to the SSE, and superconformal deposition of gold occurs at the V_{SSE} from -0.6 V to -1.0 V relative to the SSE. Accordingly, superconformal deposition of gold occurs when V_{SSE} is maintained from -0.6 V to -1.0 V relative to the SSE. As used herein, a potential being greater than a recited voltage means that the potential is more positive and less negative than the recited voltage. As used herein, a potential being less than a recited voltage means that the potential is less positive and more negative than the recited voltage.

[0088] With reference to FIG. 27, an amount of metallic superconformal filling 210 superconformally deposited on bottom member 206 relative to sidewall 208 is a filling ratio given by thickness B of metallic superconformal filling 210 disposed on bottom member 206 relative to thickness S of metallic superconformal filling 210 disposed on sidewall 208, i.e., B/S, that can be from 2 to 10000, specifically from 2 to 100. An amount of metallic superconformal filling 210 superconformally deposited on bottom member 206 relative to curved field surface 204 is a bottom coverage given by thickness B relative to thickness F of metallic superconformal filling 210 disposed on curved field surface 204, i.e., B/F, that can be from 2 to 10000, specifically from 2 to 1000.

[0089] Metallic superconformal filling 210 includes gold or an alloy of gold. Exemplary alloys include gold-silver, gold-cobalt, and gold-nickel. Elements in the alloy can be provided in superconformal filling composition 214. A purity of metallic superconformal filling 210 can be from 97 at% Au to 100 at% Au, specifically based on the elements in the metallic superconformal filling. An alloying element can be present in super conformal filling 210 in an amount from 0 at% to 3 at%, based on the elements in the metallic superconformal filling. Exemplary alloying elements are Ag, Co, and Ni. Trace elements can be present and can include Na, K, Pb, Tl, and the like.

[0090] Advantageously, and unexpectedly, metallic superconformal filling 210 can be crystalline, dense, void-free, and seam-free of the macroscale, microscale, and nanoscale. In an embodiment, metallic superconformal filling 210 is completely crystalline and is not amorphous. Crystalline domains of metallic superconformal filling 210 include face centered cubic gold. Voids and seams include voids and seams along the centerline of the feature as well as pores within grains, and along grain boundaries, and the like, which are absent in metallic superconformal filling 210 using an electron microscope at magnifications up to 100,000. As used here in, “macroscale” refers to dimensions that are of size 100 μm to 1 mm. As used here in, “microscale” refers to 0.1 μm to 100 μm. As used here in, “nanoscale” refers to 1 nm to 0.1 μm. In this regard, metallic superconformal filling 210 is shiny and planar at exposed surface 216 on a submicron level with a brightness of metallic superconformal filling 210 occurring in an absence of dendrites on exposed surface 216.

[0091] Various types of fillings can be deposited in a recess of a substrate such as a sub-conformal filling, conformal filling, or, as herein, metallic superconformal fillings 210. It should be appreciated that sub-conformal fillings have thicker deposits closer to the feature entrance (i.e., top) with deposit thickness decreasing farther down (i.e., within) the feature. Further, conformal fillings can have uniform deposit thickness over the surface of the deposit. Moreover, metallic superconformal filling 210 can have a thinner deposit proximate to the feature entrance (i.e., top) and deposit thickness increasing monotonically farther down (i.e., within) the feature. Metallic superconformal filling 210 is bottom-up and forms with essentially superconformal deposition starting on the bottom surface and matches the surface profile of the surface to which it deposits.

[0092] Superconformal filling composition 214 forms metallic superconformal filling 210 on bottom member 206 and has a near-neutral pH. As used herein, "near-neutral pH" refers to a pH that is from 5 to 11.5, with the lower value provided by instability of the superconformal filling composition. In an embodiment, the near-neutral pH of the superconformal filling composition is from 6.5 to 9.5. Moreover, superconformal filling composition 214 includes a plurality of $Au(SO_3)_2^{3-}$ anions as a source of gold for superconformally depositing gold in recessed feature 250; a plurality of SO_3^{2-} anions; and a plurality of Bi^{3+} cations as a brightener and an accelerator for superconformally depositing gold in recessed feature 250. The $Au(SO_3)_2^{3-}$ anions can be provided by a compound that includes the $Au(SO_3)_2^{3-}$ anions such as $Na_3Au(SO_3)_2$. The $Au(SO_3)_2^{3-}$ anions can be present in superconformal filling composition 214 in an amount from 5 millimolar (mM) to 350 mM, specifically from 80 mM to 160 mM. The SO_3^{2-} anions can be provided by a compound that includes the SO_3^{2-} anions such as K_2SO_3, Na_2SO_3, $(NH_4)_2SO_3$ and alkyl ammonium derivatives thereof or a combination thereof. The SO_3^{2-} anions can be present in superconformal filling composition 214 in an amount from 0.1 molar (M) to 1 M, specifically from 0.6 M to 0.7 M. It is contemplated that a source of the $Au(SO_3)_2^{3-}$ anions and the SO_3^{2-} anions are independent. Moreover, the concentration of SO_3^{2-} anions is independent from the concentration of $Au(SO_3)_2^{3-}$ anions in that the SO_3^{2-} anions are not part of the $Au(SO_3)_2^{3-}$ anions present in superconformal filling composition 214. The Bi^{3+} cations can be provided by a compound that includes the Bi^{3+} cations such as bismuth sulfate or bismuth oxide or may be added through electrochemical dissolution from a Bi metal source. The Bi^{3+} cations can be present in superconformal filling composition 214 in an amount from 1 micromolar (that can be written as mmM or μM or μmol/L) to 100 μM, specifically from 2 μM to 40 μM. Without wishing to be bound by theory, it is believed that in the process for superconformally filling, the superconformal deposition of gold is catalyzed by Bi or its complexes adsorbed on the surface from the Bi^{3+} cations.

[0093] Superconformal filling composition 214 can include an additive. Exemplary additives include hardeners, such as and Sb, surfactants or deposition suppressing additives. In an embodiment, superconformal filling composition 214 includes Bi in the absence of additive.

[0094] According to an embodiment, superconformal filling composition 214 consists essentially of $Au(SO_3)_2^{3-}$ anions, SO_3^{2-} anions, Bi^{3+} cations in an aqueous liquid.

[0095] In the process, the electrical current provides a cathodic voltage (V_{SSE}) from -0.6 V to -1.0 V relative to a saturated sulfate electrode (SSE), specifically from -0.6 V to -0.95 V. In an embodiment, the V_{SSE} is -0.74 V. In an embodiment, the cathodic electrical current changes from 0.1 mA/cm^2 to 10 mA/cm^2 to maintain V_{SSE} from -0.6 V to -1.0 V.

[0096] With reference to FIG. 30, formation of metallic superconformal filling 210 in high aspect ratio trench 222 selectively occurs over a controllable range of deposition potentials. The range of deposition potential depends upon a height of high aspect ratio trench 222 for a set of conditions such as concentration of various electrolytes in superconformal filling composition 214 and pH in view of the aspect ratio and rotation rate of curved substrate 202. Further, the deposition potential for formation of metallic superconformal filling 210 increases as the height of high aspect ratio trench 222 increases for a set of conditions. Exemplary, though non-limiting, deposition potentials V_{SSE} from -1 V to -0.6 form metallic superconformal filling 210 versus height of high aspect ratio trench 222 is shown in FIG. 31. Similarly, FIG. 32 shows deposition potential versus rotation rate over various conditions. For FIG. 32, exemplary conditions for making metallic superconformal filling 210 include performing deposition of gold in 80 mmol/L $Na_3Au(SO_3)_2$ + 0.64 mol/L Na_2SO_3 electrolyte of pH 9.5 containing 4 µmol/L Bi^{3+} in 3 µm deep trenches of aspect ratio 1.3; deposition of gold in 80 mmol/L $Na_3Au(SO_3)_2$ + 0.64 mol/L Na_2SO_3 electrolyte of pH 9.5 containing 24 µmol/L Bi^{3+} in 45 µm deep trenches of aspect ratio 11;deposition in 80 mmol/L $Na_3Au(SO_3)_2$ + 0.64 mol/L Na_2SO_3 electrolyte of pH 9.5 containing 24 µmol/L Bi^{3+} in 210 µm deep trenches of aspect ratio 30. Within these conditions, FIG. 33a, shows an exemplary cyclic voltammogram for gold deposition for rotation of a substrate at 100 RPM, 400 RPM, and 1600 RPM, wherein deposition is in 160 mmol/L

$Na_3Au(SO_3)_2$ + 0.64 mol/L Na_2SO_3 electrolyte of pH 9.5 containing 20 μmol/L Bi^{3+}. RDE rotation rates are indicated in revolution per minute (RPM) (200π rad/min). Current densities are obtained from measured current using the nominal RDE surface area of 0.79 cm^2. Data was acquired at a scan rate of 2 mV/s using software compensation for 90% of the measured (3.6 to 3.8) Ω cell resistance with ≈ 0.4 Ω of uncompensated cell resistance. It should be appreciated that gold deposition occurs at potentials where the forward portion and the reverse portion of the hysteresis curve (for a given rotation rate) cross at a most-positive potential through a most-negative potential where the forward and reverse portions of the hysteresis curve asymptotically converge and overlap. Under the exemplary conditions for FIG. 33, it should be appreciated that subjecting the substrate to the electrical current provides deposition of gold from $Au(SO_3)_2^{3-}$ anions from slightly negative of -0.63 V to -1.0 V as shown in FIG. 33b. Increasing the deposition time, changing the pH, changing the temperature, changing the feature dimensions, or changing electrolyte concentrations can provide deposition of gold for more positive potentials, e.g., up to -0.60 V.

[0097] With V_{SSE} from -0.6 V to -1.0 V, a first deposition ratio of a first deposition rate of gold on bottom member 206 relative to a second deposition rate of gold on sidewall 208 can be from 2 to 1000. In an embodiment, a deposition ratio of a thickness of gold deposited on curved field surface 204 to a thickness of gold deposited on bottom member 206 is from 1:20 to 1:100.

[0098] According to an embodiment, superconformally filling recessed feature 250 is bottom-up filling. In an embodiment, curved field surface 204 is passivated during bottom-up filling. In a particular embodiment, the bottom-up filling is uniform over the entirety of bottom member 206.

[0099] Curved metallic grating 220, including curved metallic grating 220, and processes for superconformally filling recessed feature 250, including high aspect ratio trench 222, with gold have numerous beneficial uses, including defect-free (i.e., seam-free and void-free) gold metallization as metallic superconformal filling 210. Further, the processes can be used to make defect-free gold metallic superconformal filling 210 structures in microelectromechanical system (MEMS). In an embodiment, a process for making a MEMS device with curved metallic grating 220 includes: processes described herein and removing selected material by a subtractive process to form a mechanical separation that provides a suspended mass that can be used a mass reference device.

[00100] In an embodiment, a process for making an electronic device with curved metallic grating 220 includes, includes: the superconformal deposition processes described herein followed by chemical mechanical planarization to remove the electrically conductive overlayer leaving gold metallic superconformal filling as electrically isolated wires and vias disposed in the substrate.

[00101] Moreover, processes and metallic superconformal filling 210 herein have numerous advantageous and beneficial properties. In an aspect, the process yields defect-free metal features for electrical conduction. The superconformal formation of the process yields reduced metal deposition on the field surface that decreases process cost, including reduced gold consumption in the superconformal filling composition as well as time and cost required to remove gold from the field surface. As with curved metallic grating 220, processes herein beneficially provide defect-free metallic superconformal filling 210 in high aspect ratio trench 222 so that curved metallic grating 220 can be used as a diffraction grating for x-ray scattering. Processes produce metallic superconformal filling 210 that can have a selected height, wherein the plurality of metallic superconformal fillings 210 can have a uniform height. Additionally, passivation after forming metallic superconformal filling 210 to a selected height produces reproducible feature filling.

[00102] The processes and metallic superconformal filling 210 herein unexpectedly enable exclusively bottom-up metallic superconformal filling of recessed features as well as more general metallic superconformal filling of recessed features, selectable using processing parameters including concentrations, convectively transporting, potential, or adjusting temperature. Moreover, the processes and metallic superconformal filling 210 herein overcomes technical limitations, shortcomings, and problems of conventional

processes. In this respect, gold filling by conventional conformal electrodeposition processes leaves voids and seams in features of intermediate aspect ratio and leaves voids in reentrant features. Conventional conformal deposition processes deposit metal on the field surrounding recessed features, lengthens post-deposition processing time that involves removing extra deposited material, wastes gold deposited on the field of the substrate, and more rapidly depletes electrolyte than the processes described herein.

[00103] The articles and processes herein are illustrated further by the following Example, which is non-limiting.

EXAMPLE

[00104] Bottom-up Au Filling of Trenches in Bent Wafers

[00105] A process based on Bi^{3+}-stimulated extreme bottom-up Au filling in slightly alkaline $Na_3Au(SO_3)_2 + Na_2SO_3$ electrolytes has been demonstrated for void-free filling of trenches with aspect ratios (height/width) exceeding 60 in gratings that are key to advanced X-ray imaging technologies patterned across 100 mm Si wafers. However, effective use of the full area of the gratings with the divergent X-rays from conventional X-ray sources requires the gratings be bent to a finite radius of curvature to improve alignment of the high aspect ratio Au-filled trenches with the X-rays across the area of the grating. Because bending of filled gratings can cause fracture of the brittle Si, with maximum internal stress scaling with the thickness of the grating, this work demonstrates bottom-up Au filling in gratings that are maintained in a bent configuration during the deposition process. Because the recessed trenches of the grating are empty, only the thinner Si under the etched features of the grating is stressed during bending so that the maximum stress is lower for a given curvature. The Au-filled grating can be retained in the bent state for actual application. Alternatively, substantial curvature can be retained if the bent wafer is released after filling. In either case, stresses in in the Au/Si layers of the grating as well as the underlying Si are substantially below those that would occur in gratings that are Au filled first and then bent to the same curvature. Mapping of curvature and strains across gratings is used to understand

relaxation in the Au filled gratings after release from the substrates used for deposition. Deposition behavior during Au filling of the bent gratings and measurements evaluating function of the released gratings in X-ray imaging applications demonstrate that the use of bent substrates during Au deposition improves utility of the fabricated gratings without negative impact on the processing.

[00106] Development and extension of a bottom-up Au filling process to high aspect ratio trenches and vias in gratings on 100 mm wafers, and the process enables dense, void-free Au fill in high aspect ratio trenches in the manufacture of Au/Si gratings for X-ray interferometry and imaging applications for which the high absorption contrast between the Au-filled features and surrounding Si is especially well-suited[9-15]. Void-free, bottom-up filling was demonstrated in gratings composed of arrays of trenches as deep as 305 μm as well as arrays of trenches having aspect ratio (depth/width) exceeding 60. Uniform void-free filling of even the most aggressive features, demonstrated in gratings patterned across 100 mm Si wafers, and correspondingly good performance of the Au-filled gratings, including X-ray phase contrast imaging of biological samples, demonstrates the potential for biomedical applications of these gratings, explored to date only using gratings filled by other processes.

[00107] For broad application, uniform performance across the area of a grating requires it be bent to a radius of curvature equal to its distance from the X-ray sources given the divergent beams from commercial X-ray sources. Use of a flat grating yields decreased performance (i.e., “visibility) farther off-axis due to the increasingly large angular misalignment of the X-rays and tall Au-filled trenches.

[00108] This Example describes the bottom-up Au electrodeposition process to fill trenches in bent gratings such as that shown in FIG. 34. The Au-filled gratings can be used for imaging in the mounted state using a holder that permits the curvature imposed during Au filling to be maintained throughout transfer of the filled grating to an imaging system. However, the grating may also be used free-standing upon release after filling as a wafer that has been Au filled in the bent state and released also maintains a curved state. Either

alternative contrasts positively with the alternatives of Au filled gratings that are either maintained in planar geometry, with the utilized area restricted by degraded performance, or bent after Au filling to increase functional area. Bending and then filling as demonstrated here reduces internal stresses in the bent state, producing more robust devices and/or enabling greater bending and thereby more compact imaging geometries.

[00109] Simple elastic strain analyses are used to estimate the stress distributions associated with the bend and fill approach rather than the reversed process of fill and *then* bend, in curved states including both the imposed curvature of deposition while the grating is mounted on the curved holder and when the substrate is released and allowed to relax under free-standing conditions. The latter, relaxed state manifests balance of the homogeneous Si underlying the grating, which seeks to return to its planar stress-free state, and the overlying Au-filled patterned volume of the grating itself, which seeks to retain the bent state of the stress-free Au deposition.

[00110] ELASTICITY FOR BENT SUBSTRATES

[00111] There has been analysis of the curvature induced by thin film deposition on one surface of uniformly thick substrates. The earliest analysis considered post-deposition elastic deformation associated with unidirectional curvature after a thin film on a thick substrate is released from constraints imposing a planar deposition geometry. Later works considered more complex geometries, including thick films, biaxial curvature and mismatch of film and substrate elastic moduli as well as time-dependent constraint conditions imposed during the film deposition process. During bending of a uniformly thick substrate in the geometry pictured schematically FIG. 34, basic mechanics relates the stress distribution $\sigma(z)$ as a function of height within the substrate of thickness T to the force F_L and moment M_L applied per unit width of the substrate

$$F_L = \int_0^T \sigma(z)dz \qquad [1]$$

$$M_L = \int_0^T z\sigma(z)dz \qquad [2]$$

[00112] For elastically straining substrates that are thin compared to the radius of curvature *R* of the bending, geometrical considerations allow the fractional elongation of material, i.e., the strain $\varepsilon(z)$, within the substrate to be related to the radius *R* and vertical distance z from the centroidal plane located at height $z = c$ whose length remains unchanged by the bending deformation. With assumption of a linear elastic modulus *E* relating stress σ and strain ε the relationship is given by

$$\sigma(z) = E\varepsilon(z) = E\frac{c-z}{R} \qquad [3]$$

[00113] If the wafer is uniformly thick and subject only to pure bending ($F_L = 0$) it is straightforward to show that these equations are satisfied by $c = T/2$ and $R = T^3/12M$ such that

$$\sigma(z) = E\varepsilon(z) = 12ME\frac{T/2-z}{T^3} \qquad [4]$$

[00114] The plane of zero strain thus lies midway through the thickness of the bent wafer, and the bending moment required to achieve a given radius of curvature increases as the cube of the wafer thickness. With the location of the centroid indicating the position of the plane within the wafer whose length is unchanged as the wafer is bent, the material above the centroid ($z > c$) experiences negative in-plane strain (reduced length) and associated stress that is compressive while the material below the centroid ($z < c$) experiences positive in-plane strain (increased length) and thus associated stress that is tensile. The maximum and minimum stresses occur on the opposing surfaces of the substrate and equal $\sigma_{max/min} = \pm ET/2R$, scaling as the substrate thickness divided by the imposed radius of curvature. For brittle substrates such as Si wafers the positive (tensile) stress is most significant.

[00115] The patterned areas of gratings relevant to X-ray imaging applications have deep and high aspect ratio trenches at a pitch of order 1 $\mu\mathrm{m}$ overlying Si beneath the pattern that is of order 100 $\mu\mathrm{m}$ thick. In these structures the tall and thin Si walls between the trenches do not contribute substantially to the stiffness of the substrate; these card-like sheets of Si can shift and tilt independently of each other in accord with bending of the underlying Si, as

suggested in the schematic, and thus without significant impact on the stress distribution in the underlying material. The mechanical properties of a Si wafer in the patterned region are thus similar to those of a wafer whose thickness is that of the unetched Si beneath the patterned volume. As such, the centroid of a wafer subject to a bending moment in this region is approximately mid-height in the unetched Si. Significantly, with the relationship of the moment and the substrate thickness related as in Eq. 4, where M is uniform across the wafer, e.g., with bending moment applied at the edges of the substrate, the radius of curvature R in this region will be smaller than that in the thicker un-patterned material adjacent to it. A substrate mounted on a holder imposing a uniform curvature across the wafer is necessarily subject to additional forces or moments applied by the holder in the vicinity of the border between patterned and un-patterned Si.

[00116] This study is focused on the electrochemical processing of intentionally bent gratings composed of Au deposited into etched Si wafers including assessment of residual curvatures after separation from the holders used during the Au deposition and associated analysis of grating performance. Analysis of the underlying deformation does not go beyond the basic mechanics summarized in the fundamental force and moment equations derived above. With the imposition of uniform wafer curvature throughout the deposition process, the relationship $R = T^3/12M$ indicates that localized forces are applied where the wafer rests on the curved holder to adjust the moment as necessary across the transition from unetched Si wafer to patterned and etched Si grating. The stress distribution in the vicinity of that transition is complicated. However, detailed understanding of the distribution is not necessary to realize that local curvature will thereby also vary between patterned and un-patterned regions as a wafer is in the process of being bent to fit a curved wafer holder. Under uniform moment the bending of the wafer during installation will be disproportionately localized to the effectively thinner, patterned regions. Decrease of the local radius of curvature to values below the targeted value of the holder can cause fracture of the brittle Si wafers. Thus, although bending before Au fill may be expected to reduce internal stresses of Au-filled gratings as compared to gratings that are bent only after Au filling, there can be

complications during installation of patterned and etched wafers on the curved surface of the holder prior to Au filling.

[00117] As such, several empirical and for the most part intuitive observations are made regarding the gratings that were successfully bent and mounted for Au filling. Firstly, thinner wafers are compatible with bending to a smaller minimum radius R_{min} before spontaneous wafer fracture. Using the expression for the maximum stress in the wafer $\sigma_{max} = ET/2R$ and a critical value of stress σ_{crit} in the Si wafer above which fracture initiates at surface defects, one readily obtains $R_{min} = ET/2\sigma_{crit}$. A study of the role of surface defects associated with wafer cutting in determining the mechanical strength of wafers found characteristic fracture strengths of approximately 250 MPa for σ_{crit} of cut Si wafers. That said, studies using wafers with polished surfaces obtain fracture stresses of 2.8 GPa, with a standard deviation of 1.2 GPa, that are also consistent with ≈3.5 GPa and ≈2.2 GPa values obtained for 1 μm and 20 μm diameter Si whiskers, respectively. Using a value of 2.5 GPa consistent with such well controlled surfaces along with an elastic modulus Y of approximately 130 GPa for single crystal Si loaded along the (100) crystal direction (the modulus obtained using a standard tensor analysis from values of 166 GPa, 0.64 GPa and 0.80 GPa for the unique nonzero elements C_{1111}, C_{1122} and C_{2323} of the stiffness tensor in the crystal frame) yields $R_{min} = 26T$ for loading along the (100) direction; i.e., the radius of curvature must be at least 26 times the wafer thickness or failure by fracture will necessarily occur. For tensile loading along the (110) direction the modulus Y is approximately 170 GPa so that $R_{min} = 34T$, i.e., the radius of curvature must be at least 34 times the wafer thickness. For a grating patterned in (100) oriented Si wafers with trenches aligned along the (011) direction, bending and stress along the orthogonal in-plane $(01\bar{1})$ direction is thus anticipated to be more restrictive than bending of gratings in the same wafer but with trenches patterned along (010) and bending and stress along the orthogonal (001) direction. That said, the above analysis indicates a 0.5 mm thick Si wafer can, in the limit, be bent even along the more restrictive $(01\bar{1})$ direction to a radius of curvature as small as ≈1.7 cm (and 1 cm for a 0.3 mm thick wafer) if the tensile surface is polished. Gratings on wafers bent as in FIG. 34 will fail at larger radii if the rear surfaces,

which is under tension, is not polished. Furthermore, the minimum radius obtained from the fracture behavior of uniform wafers is likely rather optimistic with etched gratings, even if the patterned surface is under compression, due to spatial variation of stress introduced by the nonuniform geometry.

[00118] In this context, it is significant that the position of the centroid indicates the location within the wafer below which stresses are tensile for the bending geometry pictured in FIG. 34. Given the location of the centroid at mid-height of the underlying material thickness, the Si immediately under the patterned region is under compression; as such, crack propagation from the bottoms of the patterned features, natural crack initiation sites given their narrow and thin geometry, should not occur. However, if the trench depth exceeds half the wafer thickness, the centroid in the adjacent un-patterned area of the wafer, located at mid-thickness of the full wafer for pure bending, lies above the bottoms of the trenches in the patterned region. This lateral proximity of tensile stresses might be anticipated to make the endmost trenches more susceptible to fracture. As such, trench depths did not exceed half the wafer thickness in this study. Silicon bridges incorporated between the Si sheets, of the same width as the sheets themselves but spaced at 100 μm intervals and staggered by 50 μm in adjacent trenches, stabilize the unfilled grating structure, including during Au filling. Widely spaced as they are, the impact of these bridges has been ignored in the preceding discussions.

[00119] It is conceivable that the superconformal Au filling process required to avoid formation of a keyhole-void in the high aspect ratios of the trenches in these gratings will be impacted by modification of the surface topology introduced by bending. However, deposition conditions for bottom-up filling processes in high aspect ratio features are already strongly defined by the feature depth, rather than the nature of fluid flow above the patterned grating, with potentials shifted substantially positive and active deposition rates decreased accordingly for void-free filling of taller features. Further, while substantial fluid flow is necessary to achieve bottom-up filling as well as self-passivation upon its completion at more negative potentials, at the less negative potentials used for the deepest and highest aspect ratio trenches, bottom-up

filling and self-passivation are observed even with minimal imposed transport. As for modification of the geometry to be filled itself, a substrate 0.4 mm thick bent to a 20 cm radius of curvature contracts less than 1 % at its surface according to Eq. 4; the openings of trenches in a grating having trench width equal to one half their pitch will narrow 2 % (absent deformation in the stress-free Si spacers), which is insignificant in comparison to the periodic oscillations of trench width seen in gratings fabricated by the Bosch process. As such, significant impact of the bent geometry on filling of the tallest features is not anticipated, with little change anticipated in void-free filling through the Bi^{3+}-stimulated Au deposition process in bent gratings from that in planar gratings.

[00120] EXPERIMENTAL

[00121] GOLD ELECTRODEPOSITION

[00122] Au electrodeposition experiments were conducted at room temperature in a three-electrode electrochemical cell containing 400 mL of electrolyte. This study utilized the well explored composition of 0.16 mol·L^{-1} $Na_3Au(SO_3)_2$ + 0.64 mol·L^{-1} Na_2SO_3 of pH 9.0 containing 50 µmol·L^{-1} Bi^{3+}. Potentials were measured relative to a Hg/Hg_2SO_4/saturated K_2SO_4 reference electrode (SSE) separated from the main cell by a Vycor fritted bridge. The electrolytes were derived from 0.32 mol·L^{-1} $Na_3Au(SO_3)_2$ source solution (Technic Gold 25-F replenisher concentrate) and 0.64 mol·L^{-1} Na_2SO_3 salt in 18 MΩ·cm water. The Bi^{3+} additive was introduced by anodic dissolution of 99.999 mass % fused Bi metal electrode on the assumption of a 100 % efficient $Bi \Longrightarrow Bi^{3+} + 3e^-$ dissolution reaction at -0.58 V SSE, making the stated Bi^{3+} concentration an upper bound.

[00123] In light of the previously noted impact of pH on Bi^{3+} adsorption kinetics4 the pH was monitored and adjusted to maintain a value of 9.0 prior to activation of bottom-up filling (pH deviations were typically < 0.05). The pH was adjusted down using H_2SO_4 (sufficiently prediluted in distilled water to avoid gold precipitation) and up using $NaOH$ (dissolved in distilled water for greater control). No adjustments were made after the start of bottom-up filling, nor was

any attempt made to compensate for ohmic losses from the applied potential associated with current flow between the working and reference electrodes.

[00124] Elastic strains in the grating on the wafer mounted prior to Au deposition are restricted to the unetched Si underlying the pattern. After the grating has been released from the holder following Au filling Eqs. 1 and 2 can be rewritten for zero force and zero moment and accounting for the bilayer structure of the Au filled grating lying upon the unetched portion of the Si wafer. The resulting equations are

$$0 = \int_0^{T_{Si}} \sigma(z)dz + \int_{T_{Si}}^{T_W} \sigma(z)dz \qquad [5]$$

$$0 = \int_0^{T_{Si}} z\sigma(z)dz + \int_{T_{Si}}^{T_W} z\sigma(z)dz \qquad [6]$$

[00125] The integrals cover the thickness of the unetched Si lying beneath the grating $z: [0, T_{Si}]$ and the composite Au/Si of the grating itself $z: [T_{Si}, T_W]$ that together comprise the full wafer thickness T_w. In the lower portion of unetched Si, the stress is defined in terms of the strain using Eq. 3

$$\sigma(z) = E_{Si}\varepsilon(z) = E_{Si}\frac{c_f - z}{R_f} \qquad [7]$$

with the modulus E_{Si} that of Si and the final radius of curvature R_f and location of the centroid c_f to be determined. Although electrodeposits can develop stresses, possibly through excess defects or the convergence of nuclei, the absence of visible warpage in bottom-up Au filled gratings suggests such stresses are relatively modest in this system. This being the case, it is assumed that the Au deposit is strain- and stress-free upon deposition in the bent wafer. In the upper portion of the grating itself, with its vertical layers of Au and Si, the stress in the released wafer is thus also defined using Eq. 3, but accounting for the unstrained state $\varepsilon_o(z)$ existing in the initial geometry of the bent wafer mounted prior to, and during, the Au fill

$$\sigma(z) = E_{Avg}[\varepsilon(z) - \varepsilon_o(z)] = E_{Avg}\left[\frac{c_f - z}{R_f} - \frac{c_o - z}{R_o}\right] \qquad [8]$$

[00126] In this region the effective (average) elastic modulus is given by $\frac{E_{Avg}}{d_{Si}+d_{Au}} = \left[\frac{d_{Si}}{E_{Si}} - \frac{d_{Au}}{E_{Au}}\right]^{-1}$ for the composite of Au and Si layers, d_{Au} and d_{Si} thick, respectively; deformation in the material loaded in series is dominated by the behavior of the softer constituent. With the initial radius of curvature R_o that of the holder used for the deposition and the initial centroid c_o located midway through the thickness of the unetched Si, i.e., $c_o = T_{Si}/2$, Eqs. 5 through 8 allow R_f and c_f of the released state to be evaluated. Rewriting the equations in non-dimensional form, with lengths and positions scaled by wafer thickness and moduli by that of the Si wafer, the radius of curvature of the Au filled wafer after release from the holder used for the Au deposition, scaled by the radius of the holder, is shown as a function of the normalized trench depth D_{Trench}, i.e., $T_W - T_{Si}$, in FIG. 35. Wafers with Au-filled trenches that are a substantial fraction of the wafer thickness are predicted to retain a radius of curvature close to that imposed during the Au deposition; intuitively, the behavior of the system is dominated by the larger volume of the overlying Au/Si composite. Also intuitively, wafers with shallower trenches are predicted to unbend toward the planar geometry of the unstressed state in the comparatively thick underlying Si. The location of the centroid across the range is shown on the same plot. Comparison to the dashed line, representing one-half the thickness of the underlying Si, shows that the centroid lies below the midline of the unetched material, asymptotically approaching its center as the Si under the grating thins (i.e., the trench depth increases).

[00127] The wafer height was measured. The variation of height across the wafers associated with their curved states, substantially exceeding that of equipment designed for nanoscale substrates and vertical displacements, was measured. Images of a grating mounted on a curved holder both prior to Au-fill (FIG. 19a) and after the Au deposition (FIG. 19b and FIG. 19c) as well as the curved state retained by the grating after dismounting (FIG. 20a). The height map of the Au-filled wafer dismounted from the holder is shown in FIG. 20b. The macroscopic curvature of the dismounted wafer evident in the image can be analyzed quantitatively across the grating using the data in the height map.

[00128] Consistent with nonzero curvature having been imposed only along the x direction during deposition, the height map after release in FIG. 20b is nearly independent of y. The height data h_i were fit within an array of 0.5 cm × 0.5 cm regions across the grating area, with each area fit to a function quadratic in x and y as indicated in Eq. 9.

$$Error = \sum_{i,j=0}^{2} (z_{Fit}(x,y) - h_i)^2 = \sum_{i,j=0}^{2} \left(C_{ij} x^i y^j - h_i\right)^2 \qquad [9]$$

[00129] Minimization of the error associated with the fit yielded the nine coefficients C_{ij} of the function in each 0.25 cm2 region. The local radius of curvature in the x-direction was obtained from the first and second partial derivatives with respect to x of the fitted polynomials

$$\frac{1}{R_x} = \frac{z_{Fit,xx}}{\left(1+(z_{Fit,x})^2\right)^{3/2}} \qquad [10]$$

[00130] An analogous expression yielded the radius of curvature R_y in the orthogonal direction. Because the constant-height contours on the topographical map are not strictly aligned along the y axis the principal axes defining the radii of curvature do not lie uniformly parallel to the axes of the measurement. To account for such rotation of the principal axes, the wafer height data was fit in (x,y) reference frames rotated in +/-1° increments over a range of angles about the z-axis. Appropriate for the definition of the principal axis, R_x in a region was taken to be the minimum value of R_x obtained from Eq. 10 where an unambiguous minimum as a function of the rotation angle was observed. Such was the case for 235 of the 256 regions. The associated R_y values, being generally much larger in magnitude, were not considered. The rotation angles yielding minimum R_x are oriented within the range + 2° to - 2° in 113 of these regions, consistent with the 0° value expected given the cylindrical holder on which the grating was mounted during the Au filling. Minimization of the fitting Error generally occurred at an angle that was within a few degrees of the angle that minimized R_x, further supporting the analysis approach. In regions where a larger angular difference was associated with minimizing the two different parameters, the rotations associated with the fits

were themselves generally large. More complex variation of the grating height $h_i(x,y)$ in these regions may underlie the difference.

[00131] The radius curvature R_x obtained for the 235 regions within which the height data was successfully fit are shown on a map over the area of the grating in FIG. 36a. The values of R_y obtained in the analyses are of magnitude 104 cm to 107 cm, aside from a few locations near the perimeter. Thus, having been Au filled while mounted on a cylindrically shaped holder, the grating has remained nominally cylindrical upon release. The local value of the principal radius curvature R_x ranges from a low of 33.8 cm to values in excess of 150 cm. Significant oscillations of R_x in the x direction are captured in FIG. 36a. They correlate with the 2 cm spacing of the clamps used to bend the wafer to the curved holder as per the schematic in FIG. 36c. The clamped region of the wafer evidently did not conform uniformly to the 30 cm radius of the surface of the holder during the Au deposition. Asymmetry in the x-direction, with higher R_x values near x = -4 cm than near x = +4 cm, reflects further deviation from the nominally imposed curvature due to the differing geometry of the unclamped wafer beyond; specifically, greater relaxation at x = -4 cm reflects the closer 3 cm long flat on that side while less relaxation at x = +4 cm reflects the more distant 2 cm long flat (FIG. 34c). The generally smaller values of R_x found at six x values are plotted as a function of position y in FIG. 36c. It is seen that R_x increases modestly with larger |y| within the patterned region at positions x farther from the flats. This is likely due to relaxation of the un-patterned region at |y| > 4 cm upon release from the holder.

[00132] The rotation associated with the fit of $h_i(x,y)$ yielding the principal radius of curvature R_x in each 0.25 cm2 region is mapped across the area of the grating in FIG. 36b. As the R_x values reflect height variation approximately orthogonal to the iso-height contours in FIG. 20a, consistent with the approximate mirror symmetry of that height data in both x and y, i.e., $h_i(x,y) = h_i(-x,y)$ and $h_i(x,y) = h_i(x,-y)$, the rotation of R_x generally alternates sign (i.e., clockwise versus counterclockwise) in adjacent quadrants. Increase of the magnitude of the rotation, no more than a degree or two at the

center of wafer, toward the perimeter of the wafer reflects larger deviation from a purely cylindrical shape.

[00133] The earlier analysis provides a qualitative understanding of the observed variation of curvature over most of the patterned area of gratings upon release of the wafer after Au fill in the curved state. The results thereby provide guidance as to how both lower and more uniform values of R_x can be obtained with free-standing grating as well as gratings still mounted on the curved holder. It is a given that mounting of the etched Si wafer on a holder with the smallest possible radius of curvature is paramount. Furthermore, because the bending limit defined by fracture is tied to the wafer thickness, the thinnest Si wafer compatible with the desired depth of the trenches in the grating should be used. In addition, the results in FIG. 36 indicate that clamping should be applied along as much as the wafer perimeter as possible. A 450 mm thick un-patterned Si wafer attached to the holder having 30 cm radius of curvature using such clamping is shown in FIG. 37. Wafers of this thickness all fractured when attempts were made to attach them to the same holder using just the four pairs of clamps as per FIG. 34; local stress concentration is unavoidable with the discrete contacts.

[00134] Because the unetched Si outside the pattern also drives the released grating back toward the planar state, as per the data in FIG. 36c, the patterned area should be increased to the greatest extent possible subject to maintaining unetched Si along the wafer's perimeter for structural integrity during wafer handling and mounting. Wafers with shorter flats are also desirable given the relaxation of curvature noted particularly approaching x = -4 cm in FIG. 36a. Finally, because Si exhibits an anisotropic elastic modulus, relaxation upon release can be reduced by patterning the trenches such that the wafers are bent with the strains and stresses aligned along the direction exhibiting the lowest modulus, barring complications arising from the orientation of the flats.

[00135] X-ray diffraction was used to directly assess strains in the Si underlying the Au filled grating in the released state.

[00136] IMAGING

[00137] Gratings that were filled while bent were incorporating into an XPCI system for mapping of the associated visibility across their area. The imaging geometry includes inserting two gold-filled gratings between the X-ray source and the imaging detector (in addition to a phase-shift grating as well as any object to be imaged between them); the G0 grating is placed nearest the x-ray source while the G2 grating is placed nearest the imaging detector. In this study, the X-ray source to G0 distance was set to 30 cm to match the nominal radius of curvature R_x of the grating and then, consistent with the 3rd order Talbot distance for 28 keV X-rays and the 5.25 mm pitch of the gratings, the distance from the G0 grating to the G2 grating was set to 93.4 cm, with the phase shift grating located midway between. For qualification of the gratings rather than imaging, no other object was placed in the imaging system. Consistent with expectation, the visibility that characterizes performance of the imaging system decreases less with distance from the centerline of the measurement system when the intrinsically curved grating is used as G0 in place of the flat grating. Improved alignment of the Au-filled trenches in the bent grating and the X-rays from the divergent X-ray source (see FIG. 34b) underlies the change. Further improvement is obtained when, in addition to the intrinsically bent G0 grating, a planar grating bent to a radius of 123.4 cm is used for G2. The decrease of visibility farthest from the center is almost halved from that observed with two flat gratings. Improvement in-line with the detector, where a local minimum observed with the two planar gratings is eliminated using the intrinsically bent G0 grating in place of the flat G0 grating, results from nonzero transmission for this thickness of Au deposit in the flat grating. Use of the intrinsically bent grating for G0 nearly eliminates this dip.

[00138] Bottom-up Au filling of high aspect ratio trenches can be achieved in substrates bent to radii of curvature consistent with improved function in X-ray imaging applications. It is seen that modified flow or electric fields that can negatively impact deposit uniformity in some electrodeposition processes do not prevent function of the bottom-up Au filling mechanism or self-passivation of features once features have been successfully filled. Electric fields are small under typical operating conditions and play an insignificant role in models of feature filling. Further, at the relatively positive potentials

associated with filling of high aspect ratio features, modest variations of flow over them does not substantially impact the variation of transport within them that underlies self-passivation.

[00139] It is possible to retain these gratings in their initial bent state after Au fill for use in imaging applications using a suitably designed holder. For that matter it is possible to bend the gratings back to their original state even after they have been permitted to relax upon removal from the substrate upon which they were mounted for the Au fill. However, this study has explored the extent to which curvature imposed during Au filling is retained upon release. Through topographical as well as X-ray strain measurements the impact of pattern geometry as well as substrate orientation and thickness on both the magnitude of relaxation and the uniformity of the curvature of Au filled grating in their released state has been highlighted. Maximization of trench depth as a fraction of wafer thickness as well as minimization of un-patterned area are key to (fractional) maintenance of the originally imposed radius of curvature and minimization of its variation.

[00140] Comparison of XPCI visibility maps obtained in an imaging system where the grating nearest the X-ray source had been filled while flat versus filled in a curved state were used to observe the impact on system performance.

[00141] While one or more embodiments have been shown and described, modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustrations and not limitation. Embodiments herein can be used independently or can be combined.

[00142] Reference throughout this specification to “one embodiment,” “particular embodiment,” “certain embodiment,” “an embodiment,” or the like means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment. Thus, appearances of these phrases (e.g., “in one embodiment” or “in an

embodiment") throughout this specification are not necessarily all referring to the same embodiment, but may. Furthermore, particular features, structures, or characteristics may be combined in any suitable manner, as would be apparent to one of ordinary skill in the art from this disclosure, in one or more embodiments.

[00143] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other. The ranges are continuous and thus contain every value and subset thereof in the range. Unless otherwise stated or contextually inapplicable, all percentages, when expressing a quantity, are weight percentages. The suffix "(s)" as used herein is intended to include both the singular and the plural of the term that it modifies, thereby including at least one of that term (e.g., the colorant(s) includes at least one colorants). "Optional" or "optionally" means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event occurs and instances where it does not. As used herein, "combination" is inclusive of blends, mixtures, alloys, reaction products, and the like.

[00144] As used herein, "a combination thereof" refers to a combination comprising at least one of the named constituents, components, compounds, or elements, optionally together with one or more of the same class of constituents, components, compounds, or elements.

[00145] All references are incorporated herein by reference.

[00146] The use of the terms "a" and "an" and "the" and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. "Or" means "and/or." Further, the conjunction "or" is used to link objects of a list or alternatives and is not disjunctive; rather the elements can be used separately or can be combined together under appropriate circumstances. It should further be noted that the terms "first," "second," "primary," "secondary," and the like herein do not denote any order, quantity, or importance, but rather are used to

distinguish one element from another. The modifier “about” used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., it includes the degree of error associated with measurement of the particular quantity).

What is claimed is:

1. A process for making a curved metallic grating for matching angular divergence of incident radiation, the process comprising:

providing a mandrel comprising a curved receiving surface;

disposing a planar substrate on the curved receiving surface of the mandrel, the planar substrate comprising:

a backing face;

a planar field surface spaced apart from the backing face by a thickness of the planar substrate; an edge that peripherally bounds the backing face and the planar field surface; and

a plurality of recessed features disposed in the planar substrate such that the recessed features are spaced apart from one another by the planar field surface of the planar substrate, and each of the recessed features comprising:

a bottom member; and

a sidewall that separates the bottom member from the planar field surface,

such that the backing face faces and opposes the curved receiving surface;

applying a clamping force to the planar substrate at the planar field surface proximate to the edge;

bending the planar substrate to shape-wise conform to the radius of curvature of the curved receiving surface of the mandrel in response to applying the clamping force, such that the planar substrate changes to a curved substrate, and the curved substrate comprises:

a curved field surface formed from deformation of the planar field surface and arranged to be exposed to a superconformal filling composition;

a curved substrate radius of curvature; and

the backing face disposed on and opposing the curved receiving surface of the mandrel; and

superconformally filling the recessed feature with a metallic superconformal filling comprising a metal to form the curved metallic grating.

2. The process of claim 1, further comprising:

releasing the clamping force from the curved field surface of the curved metallic grating; and

removing the curved metallic grating from the mandrel.

3. The process of claim 2, wherein the curved metallic grating maintains the curved substrate radius of curvature after removing the curved metallic grating from the mandrel.

4. The process of claim 1, wherein the curved receiving surface of the mandrel comprises a mandrel radius of curvature from 1 cm to 1000 cm.

5. The process of claim 1, wherein the curved substrate radius of curvature of the curved substrate is from 1 cm to 1000 cm.

6. The process of claim 1, wherein the recessed features comprise a high aspect ratio trench, a via, or a combination comprising at least one of the foregoing recessed features.

7. The process of claim 6, wherein the recessed features are vias, and the vias are arranged as a square pattern, a checkerboard pattern, or a fractal pattern.

8. The process of claim 6, wherein each of the recessed features comprises a high aspect ratio trench that comprises an aspect ratio of a depth to a width from 0.5 to 200 before filling the recessed feature with the metallic superconformal filling, the aspect ratio decreasing during filling the recessed feature with the metallic superconformal filling.

9. The process of claim 6, wherein a height of the high aspect ratio trench is from 50 nm to 5 mm, and a height of the metallic superconformal filling is less than or equal to the height of the high aspect ratio trench.

10. The process of claim 1, further comprising forming a cylindrical shape in the curved field surface such that the curved metallic grating has the cylindrical shape in response to bending the planar substrate to shape-wise conform to the radius of curvature of the curved receiving surface of the mandrel, wherein the curved receiving surface comprises the cylindrical shape.

11. The process of claim 1, further comprising forming a concave shape in the curved field surface such that the curved metallic grating has the concave shape in response to bending the planar substrate to shape-wise conform to

the radius of curvature of the curved receiving surface of the mandrel, wherein the curved receiving surface comprises the concave shape.

12. The process of claim 1, further comprising forming a convex shape in the curved field surface such that the curved metallic grating has the convex shape in response to bending the planar substrate to shape-wise conform to the radius of curvature of the curved receiving surface of the mandrel, wherein the curved receiving surface comprises the convex shape.

13. The process of claim 1, wherein an overlayer is disposed on the bottom member.

14. The process of claim 1, wherein the metal of the metallic superconformal filling comprises gold, copper, Pt, Rh, Re, nickel, cobalt, mercury, or a combination comprises at least one of the foregoing metals.

15. The process of claim 1, further comprising:

contacting the overlayer on the bottom member with a superconformal filling composition, the superconformal filling composition having a near-neutral pH and comprising:

a plurality of $Au(SO_3)_2^{3-}$ anions as a source of gold that is superconformally deposited as the metallic superconformal filling in the recessed features;

a plurality of SO_3^{2-} anions; and

a plurality of Bi^{3+} cations as a brightener and an accelerator for superconformally depositing gold in the recessed features;

convectively transporting the $Au(SO_3)_2^{3-}$ anions and the Bi^{3+} cations to the bottom member by actively moving the curved substrate relative to superconformal filling composition;

subjecting the bottom member of the recessed features to an electrical current to superconformally deposit gold from the $Au(SO_3)_2^{3-}$ anions on the bottom member relative to the sidewall and the curved field surface, the electrical current providing a cathodic voltage, and a first deposition ratio of a first deposition rate of gold on the bottom member relative to a second deposition rate of gold on the sidewall; and

increasing the electrical current subjected to the curved field surface and the recessed features to maintain the cathodic voltage during superconformally depositing gold in the recessed features to form the metallic superconformal filling comprising gold in the recessed features such that the metallic superconformal filling is void-free and seam-free.

16. The process of claim 1, wherein the process is performed in an absence of through-mask plating.

17. The process of claim 1, further comprising:

forming a conductive seed layer on the recessed features, the seed layer comprising: 10 nm to 100 nm of platinum grown over exposed sidewalls and bottom members of the recessed features and followed by forming an overlying Au layer formed on the platinum;

contacting the recessed features with a superconformal filling composition comprising from 40 mmol/L to 1000 mmol/L $Na_3Au(SO_3)_2$ and from 0.1 mol/L to 1.0 mol/L Na_2SO_3, wherein a pH of the superconformal filling composition is from 8.0 to 10.0;

providing Bi^{3+} to the superconformal filling composition;

contacting the recessed features with the Bi^{3+};

rotating the curved substrate in the superconformal filling composition at a rotation rate from 25 RPM to 2000 RPM;

subjecting the recessed features to a deposition potential relative to a Hg/Hg_2SO_4/saturated K_2SO_4 reference electrode from -0.6 V to -0.85 V; and

superconformally filling the recessed features such that superconformal filling is bottom-up with upward growth forming the metallic superconformal filling that comprises gold at the deposition potential relative to a Hg/Hg_2SO_4/saturated K_2SO_4 reference electrode from -0.6 V to -0.85 V; and

automatically passivating a growth front of the recessed features from 10 minutes to 1 week after beginning of forming the metallic superconformal filling in the recessed features to make the curved metallic grating.

18. A curved metallic grating for matching angular divergence of incident radiation comprising:

a curved substrate;

a plurality of recessed features disposed in the curved substrate such that the recessed features are spaced apart from one another by a curved field surface of the curved substrate;

a metallic superconformal filling formed and disposed in the recessed features and that receives the incident radiation and matches angular divergence of the incident radiation; and

a curved grating comprising a spatial arrangement of the recessed features that are filled with the metallic superconformal filling such that the metallic superconformal filling is void-free, and the recessed features are bottom-up filled with the metallic superconformal filling, such that the radius of curvature of the curved grating is from 1 cm to 1000 cm, wherein an aspect ratio of the recessed features is from 0.5 to 200, and a height of the recessed features is from 50 nm to 5 mm, and a height of the metallic superconformal filling is less than or equal to the height of the recessed features.

19. The curved metallic grating of claim 18, wherein the curved substrate radius of curvature of the curved substrate is from 1 cm to 1000 cm.

20. The curved metallic grating of claim 18, wherein the curved substrate is electrically conductive.

21. The curved metallic grating of claim 18, wherein the curved substrate comprises silicon and a dopant that provide electrical conductivity to the curved substrate.

22. The curved metallic grating of claim 18, wherein a width of the metallic superconformal filling is from 10 nm to 100 μm.

23. The curved metallic grating of claim 18, wherein a length of the metallic superconformal filling is from 0.5 μm to 1 m.

24. The curved metallic grating of claim 18, wherein the height of the metallic superconformal filling is from 50 nm to 5 mm.

25. The curved metallic grating of claim 18, wherein the metallic superconformal filling consists essentially of gold and bismuth.

26. The curved metallic grating of claim 18, wherein the recessed features comprise a high aspect ratio trench, a via, or a combination comprising at least one of the foregoing recessed features.

27. The curved metallic grating of claim 18, wherein the recessed features are vias, and the vias are arranged as a square pattern, a checkerboard pattern, or a fractal pattern.

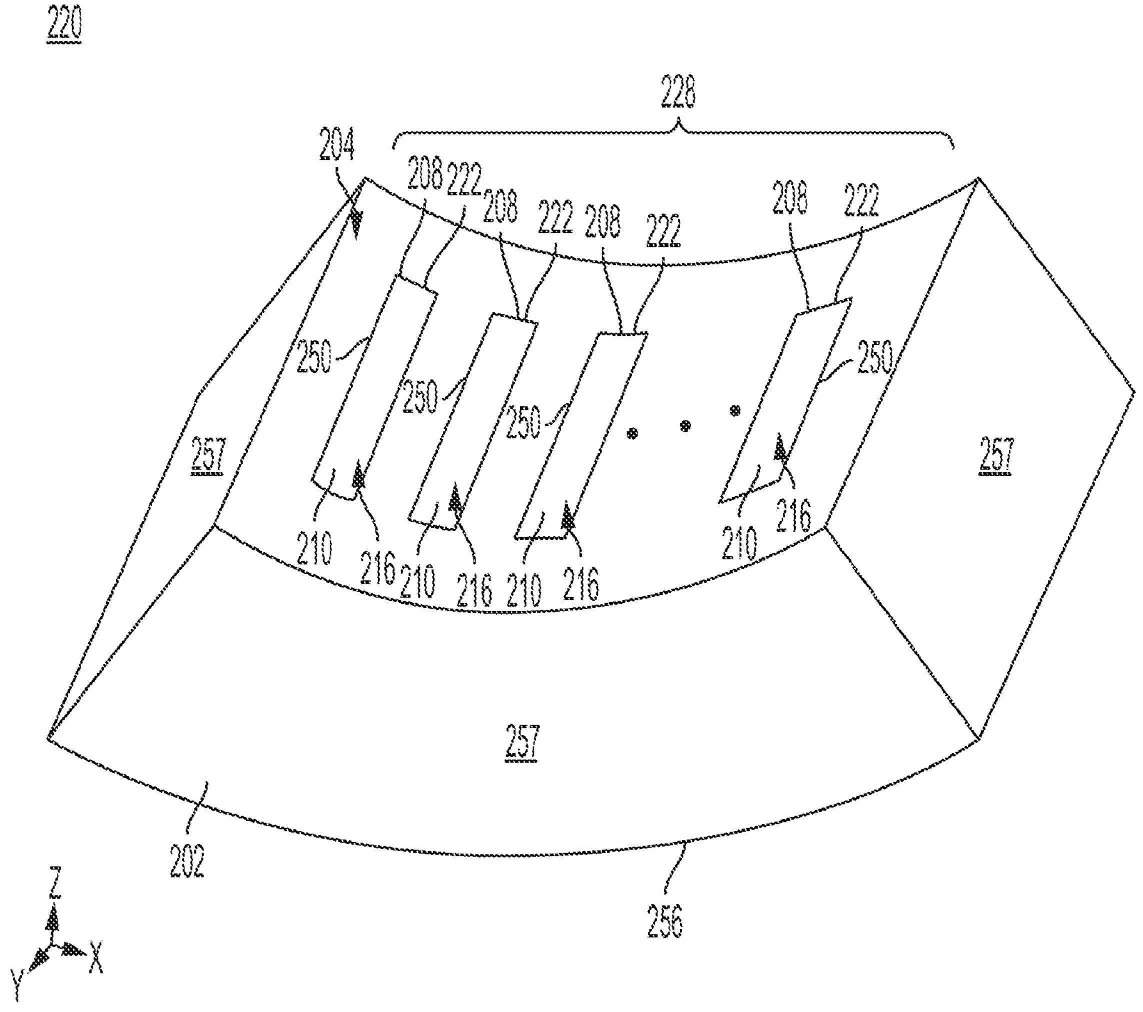
28. The curved metallic grating of claim 18, wherein the curved metallic grating comprises a cylindrical shape formed in response to shape-wise deformation to a radius of curvature of a curved receiving surface of a mandrel, wherein the curved receiving surface comprises the cylindrical shape.

29. The curved metallic grating of claim 18, wherein the curved metallic grating comprises a concave shape formed in response to shape-wise deformation to a radius of curvature of a curved receiving surface of a mandrel, wherein the curved receiving surface comprises the concave shape.

30. The curved metallic grating of claim 18, wherein the curved metallic grating comprises a convex shape formed in response to shape-wise deformation to a radius of curvature of a curved receiving surface of a mandrel, wherein the curved receiving surface comprises the convex shape.

31. The curved metallic grating of claim 18, further comprising a mandrel comprising a curved receiving surface, on which the curved substrate is disposed.

32. The curved metallic grating of claim 18, wherein the metal of the metallic superconformal filling comprises gold, copper, platinum, rhodium, rhenium, nickel, cobalt, mercury, or a combination comprises at least one of the foregoing metals.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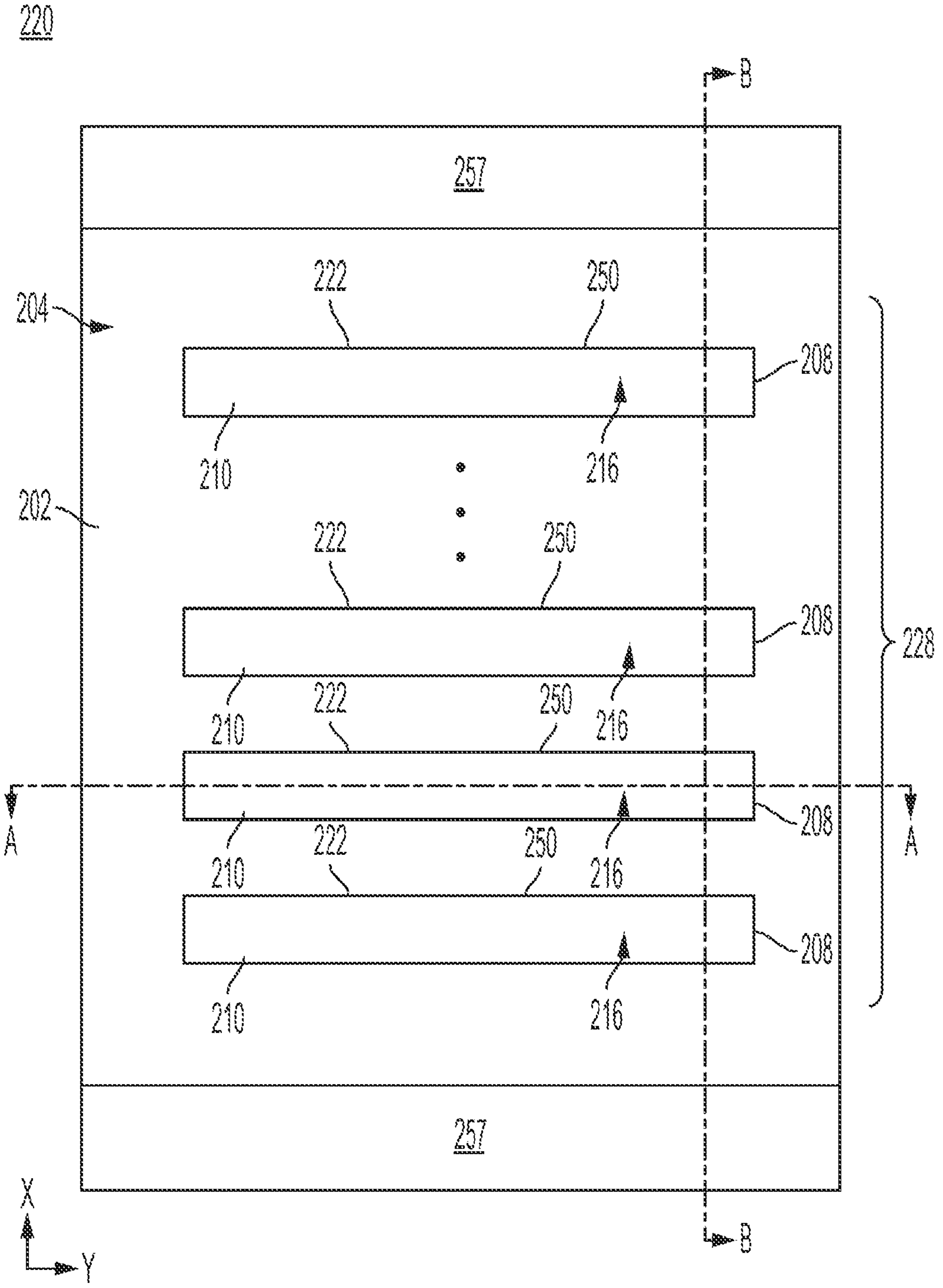
216
210
216
210
216
202
256
Z
Y
X

FIG. 1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B
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222
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208
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A
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A
210
222
250
216
208
210
216
257
X
Y
B

FIG. 2

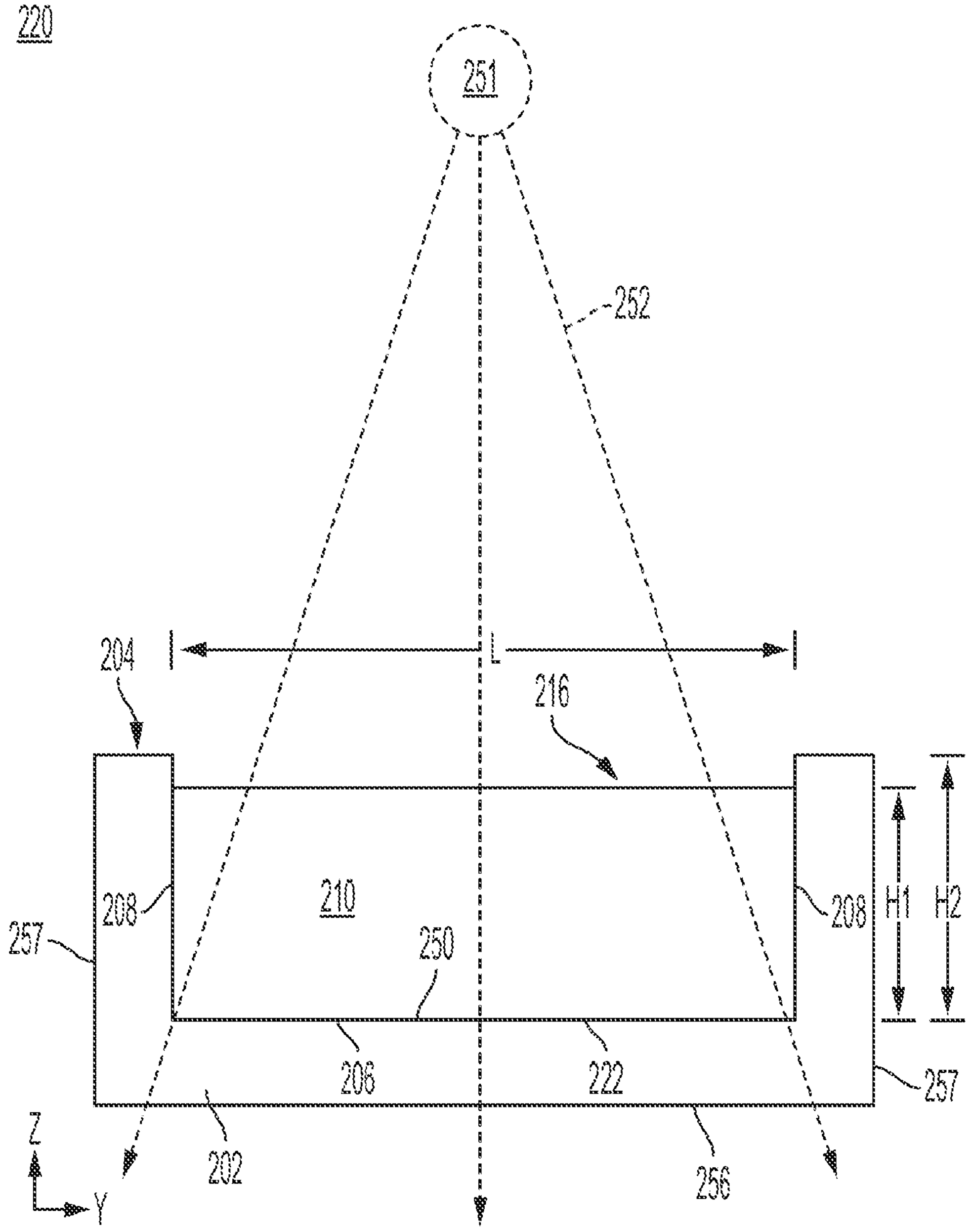
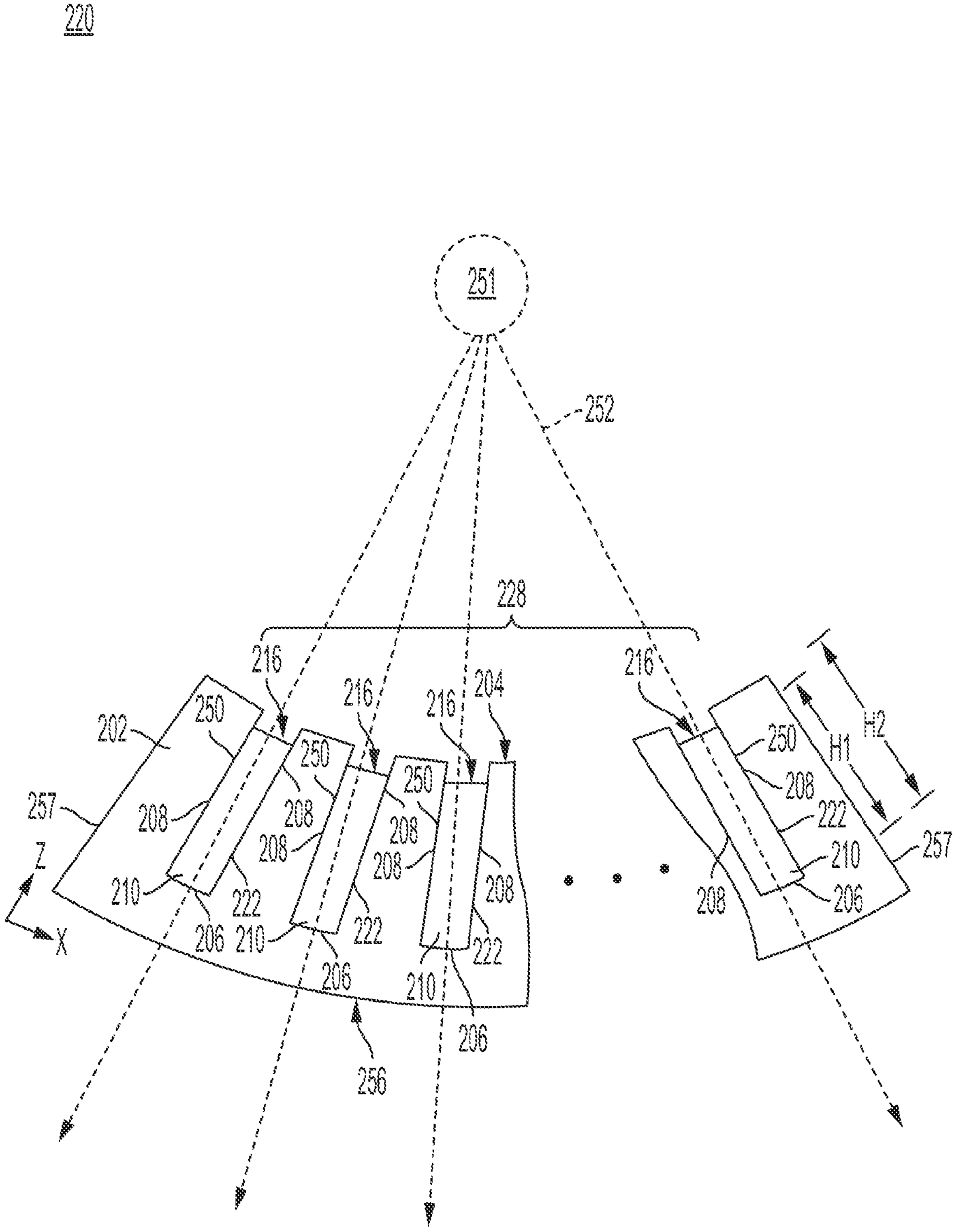

220
251
252
L
204
216
208
210
208
H1
H2
257
250
206
222
257
Z
Y
202
256

FIG. 3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251
252
228
216
216
216
204
216
202
250
250
250
250
257
208
208
208
208
208
208
208
208
210
210
210
210
206
206
206
206
222
222
222
222
256
257
H1
H2
Z
X

FIG. 4

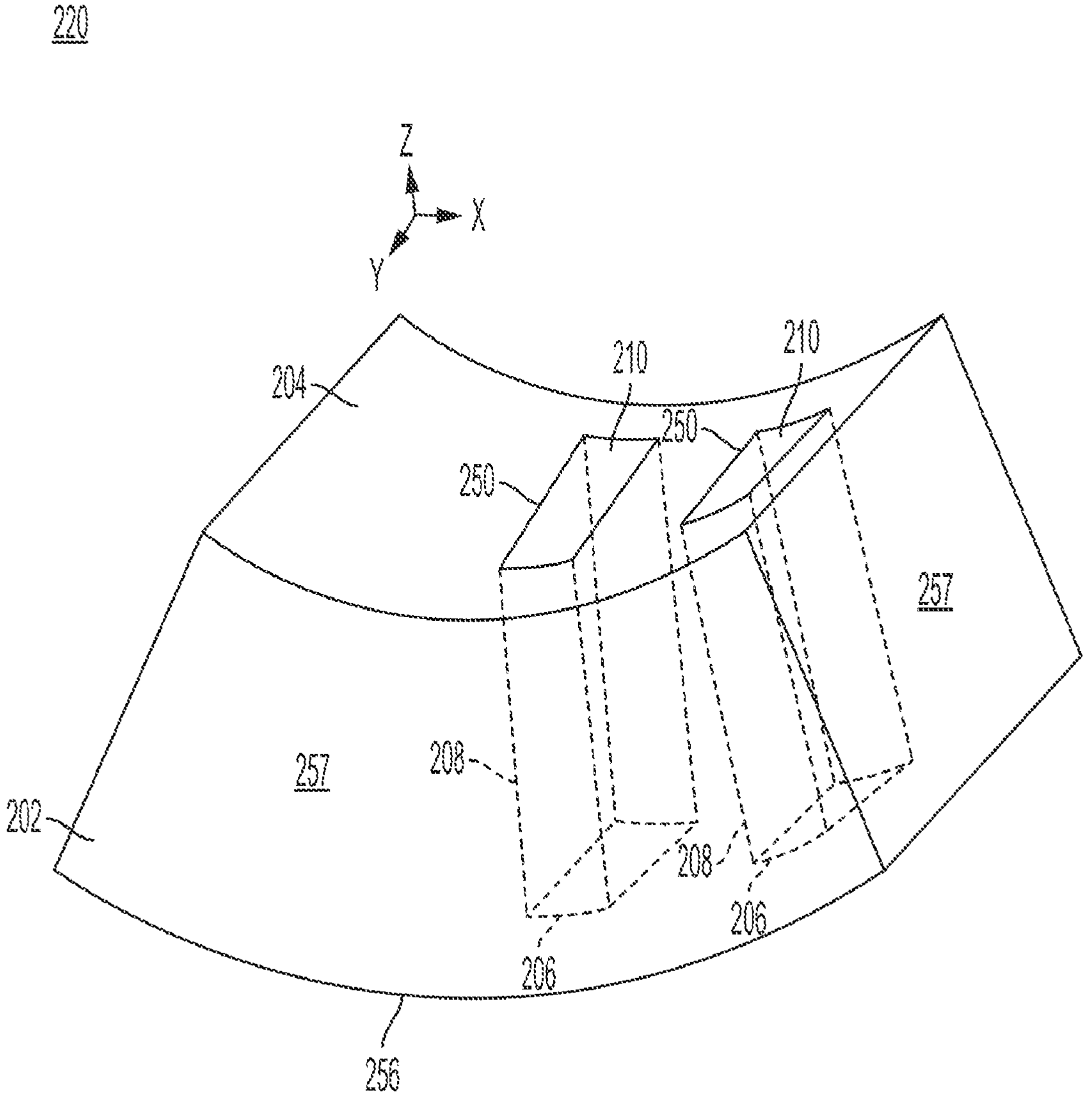


FIG. 5

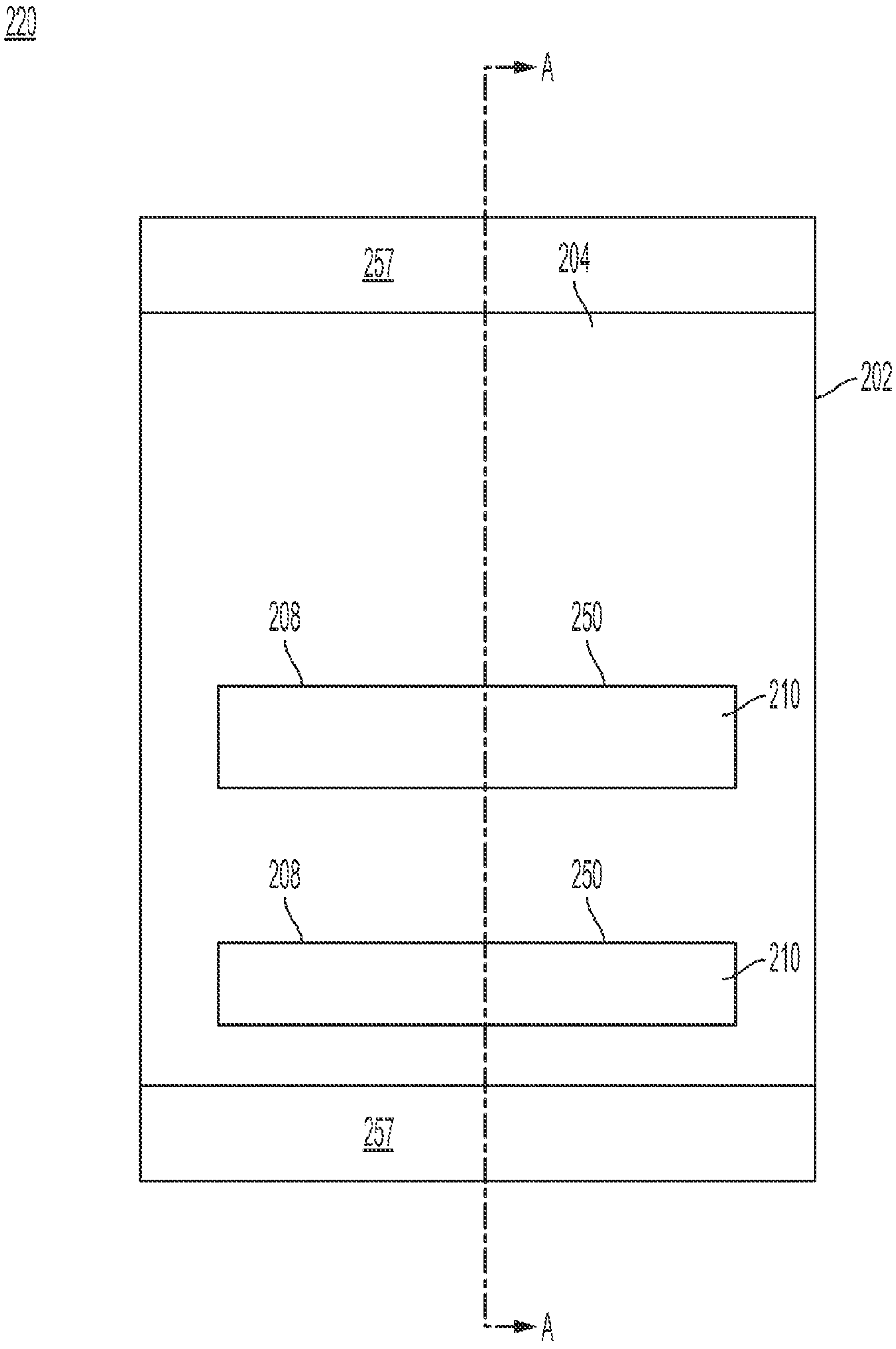


FIG. 6

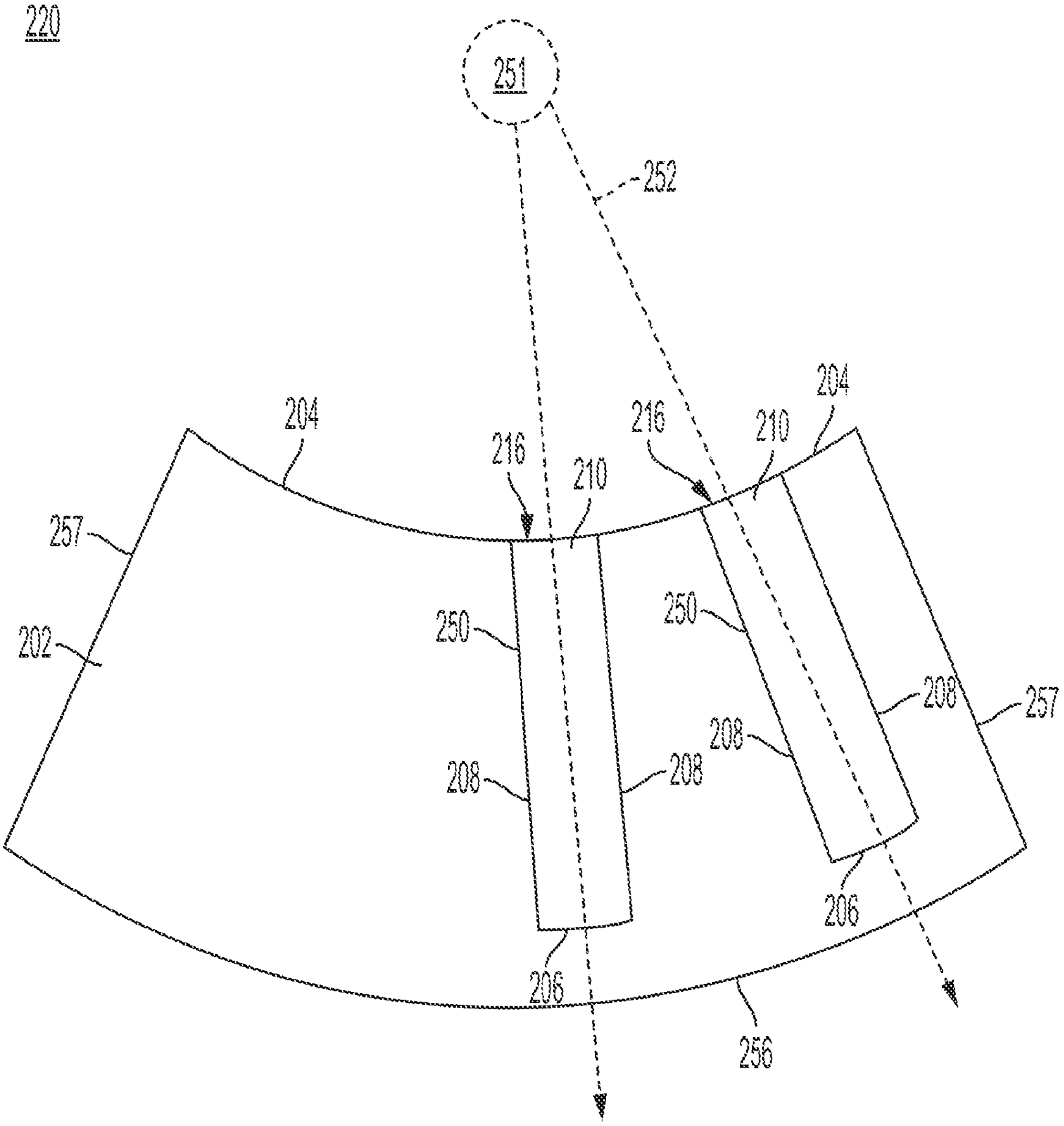

220
251
252
204
216
210
216
210
204
257
202
250
250
208
208
208
208
257
206
206
256

FIG. 7

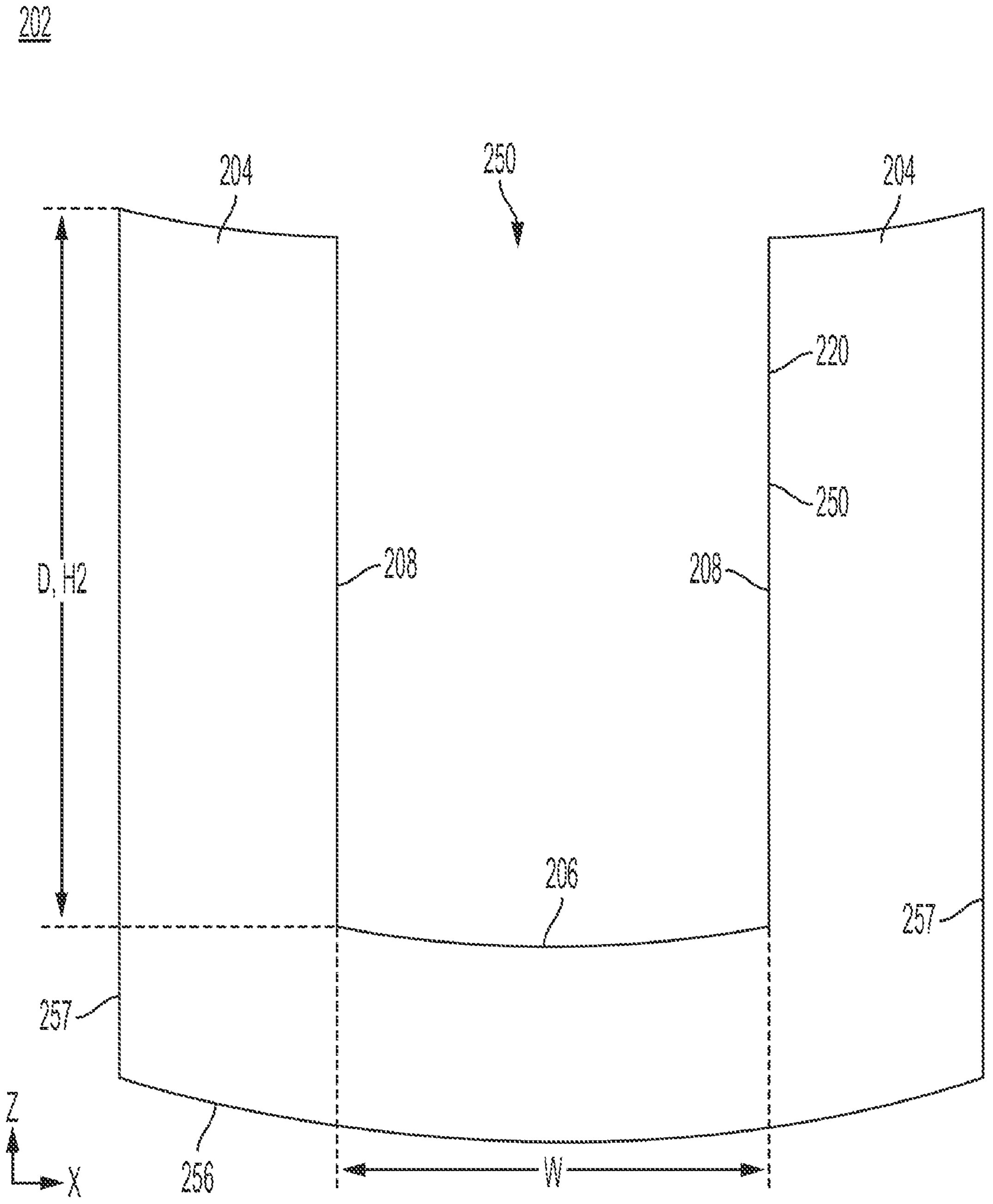


FIG. 8

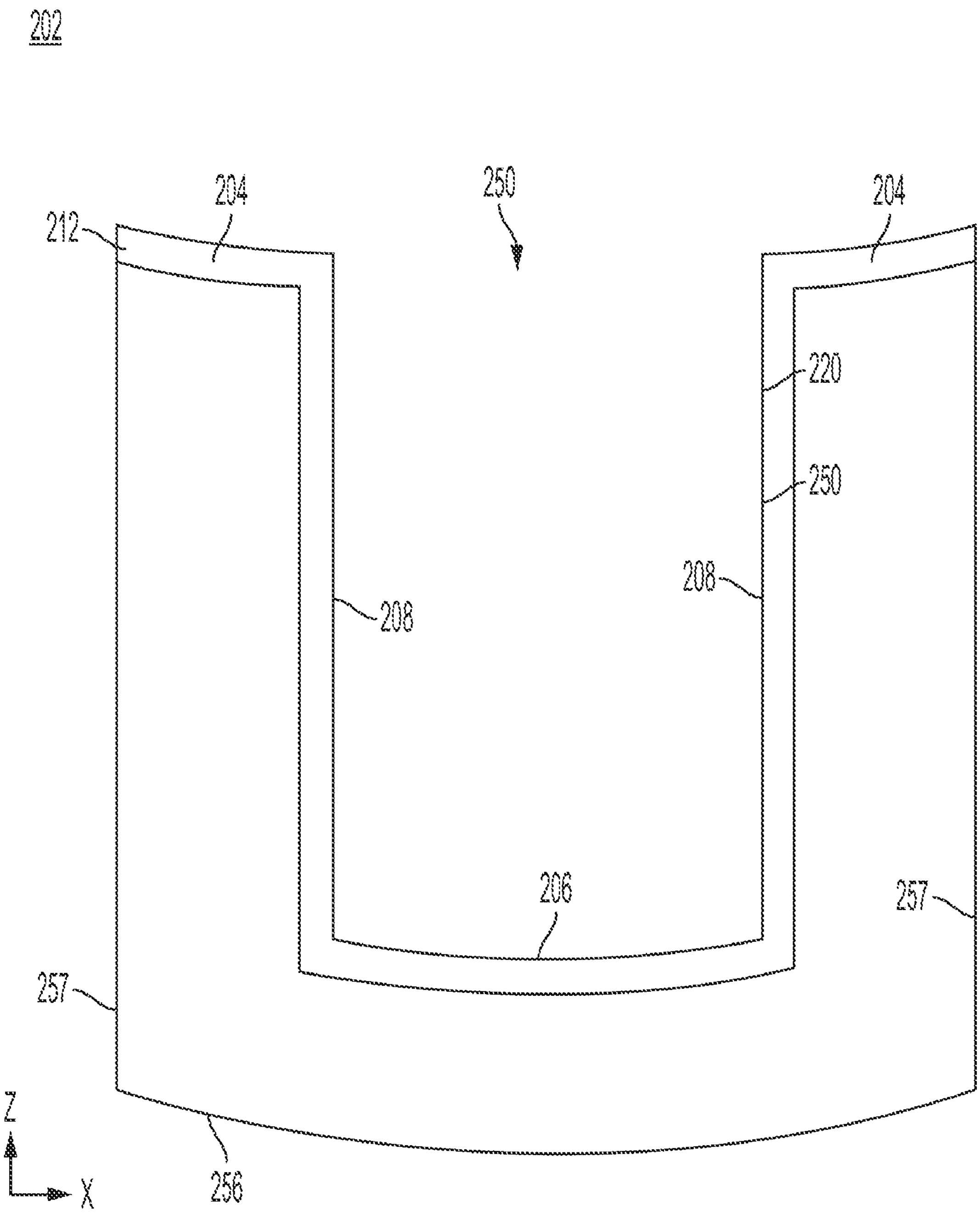


FIG. 9

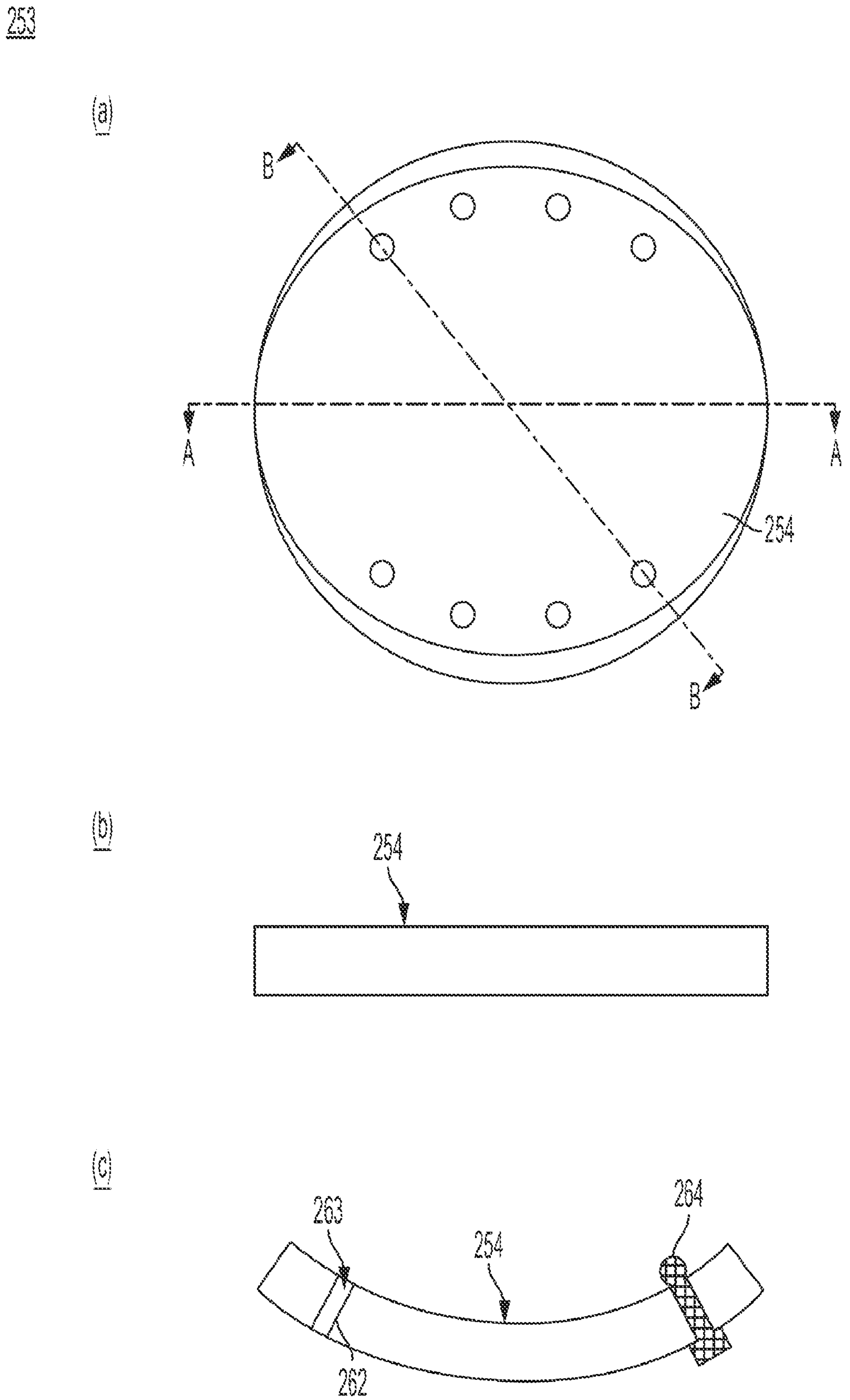


FIG. 10

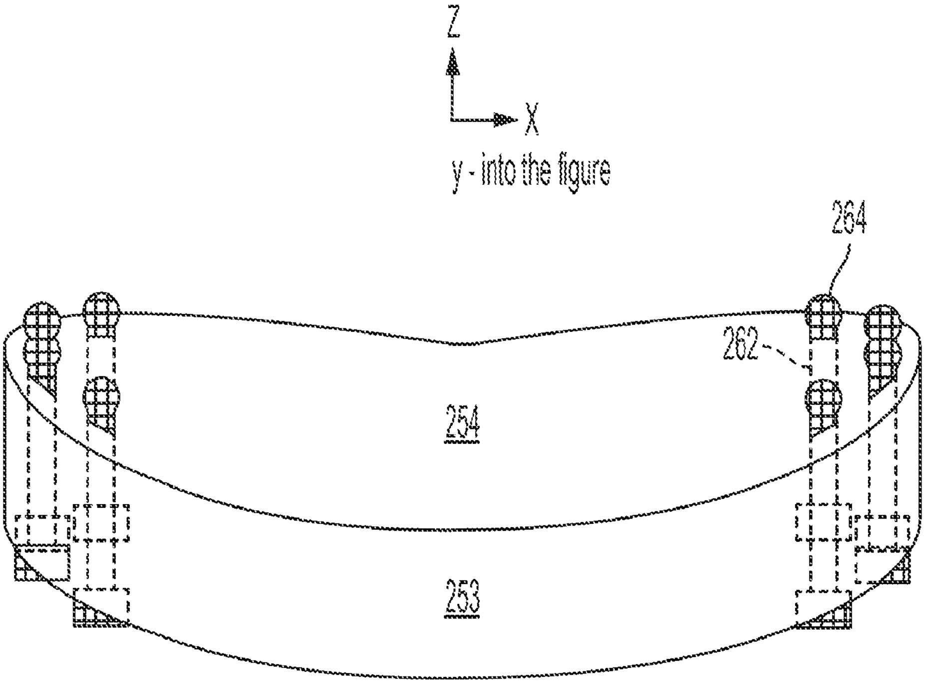


FIG. 11

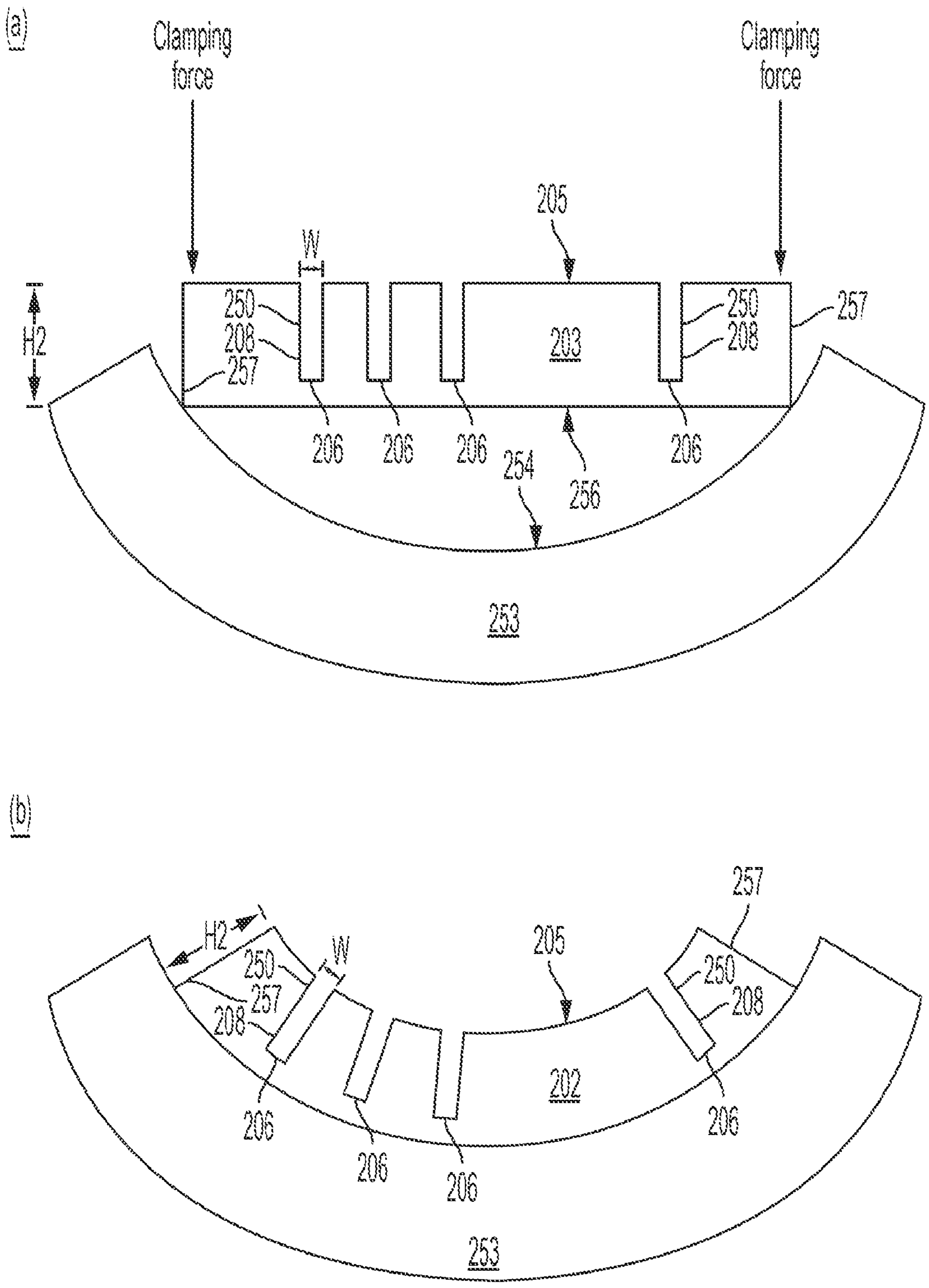

(a)
Clamping force
Clamping force
W
205
H2
250
208
257
203
250
208
257
206
206
206
206
254
256
253
(b)
257
H2
W
205
250
257
208
250
208
202
206
206
206
206
253

FIG. 12

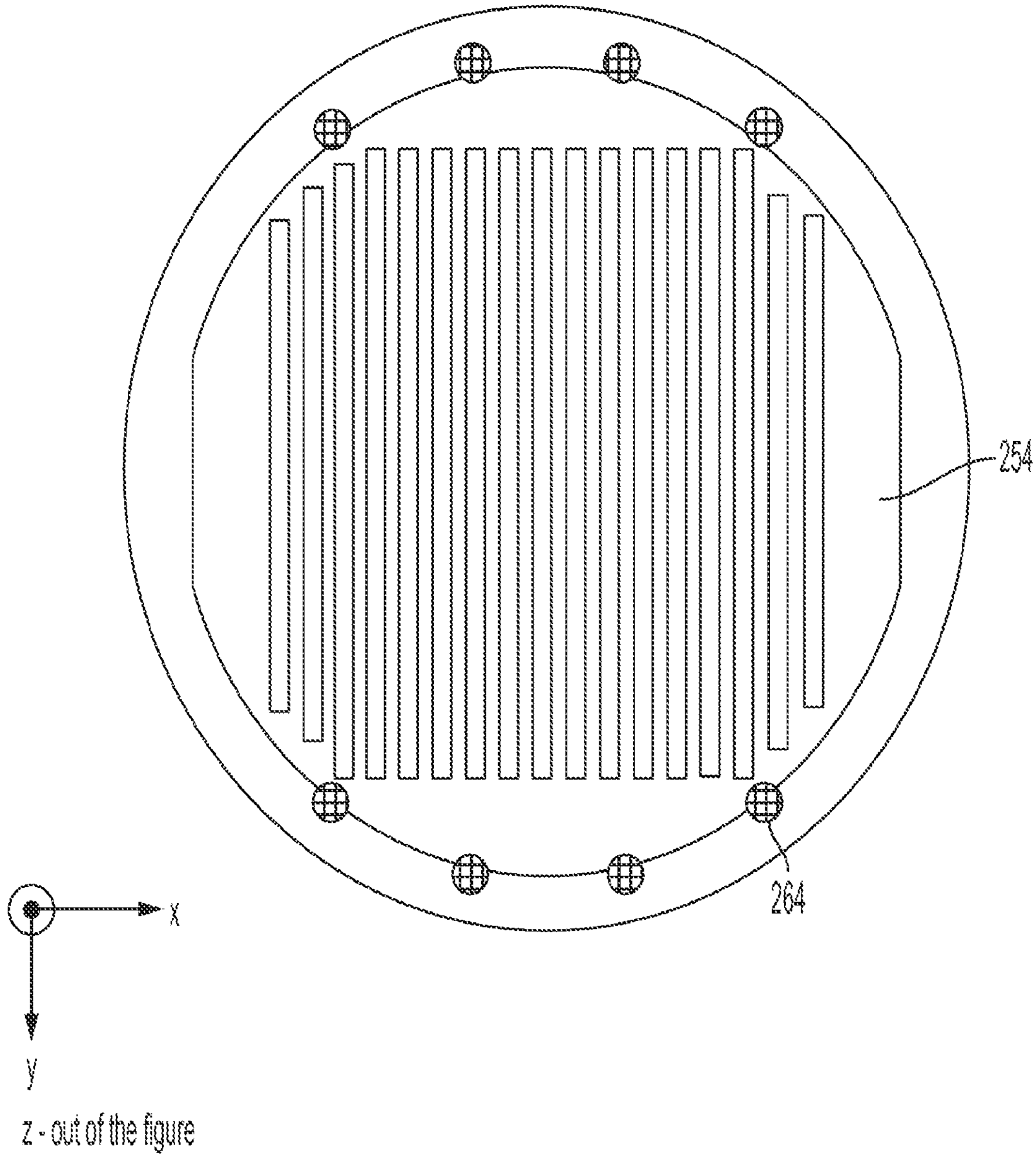


FIG. 13

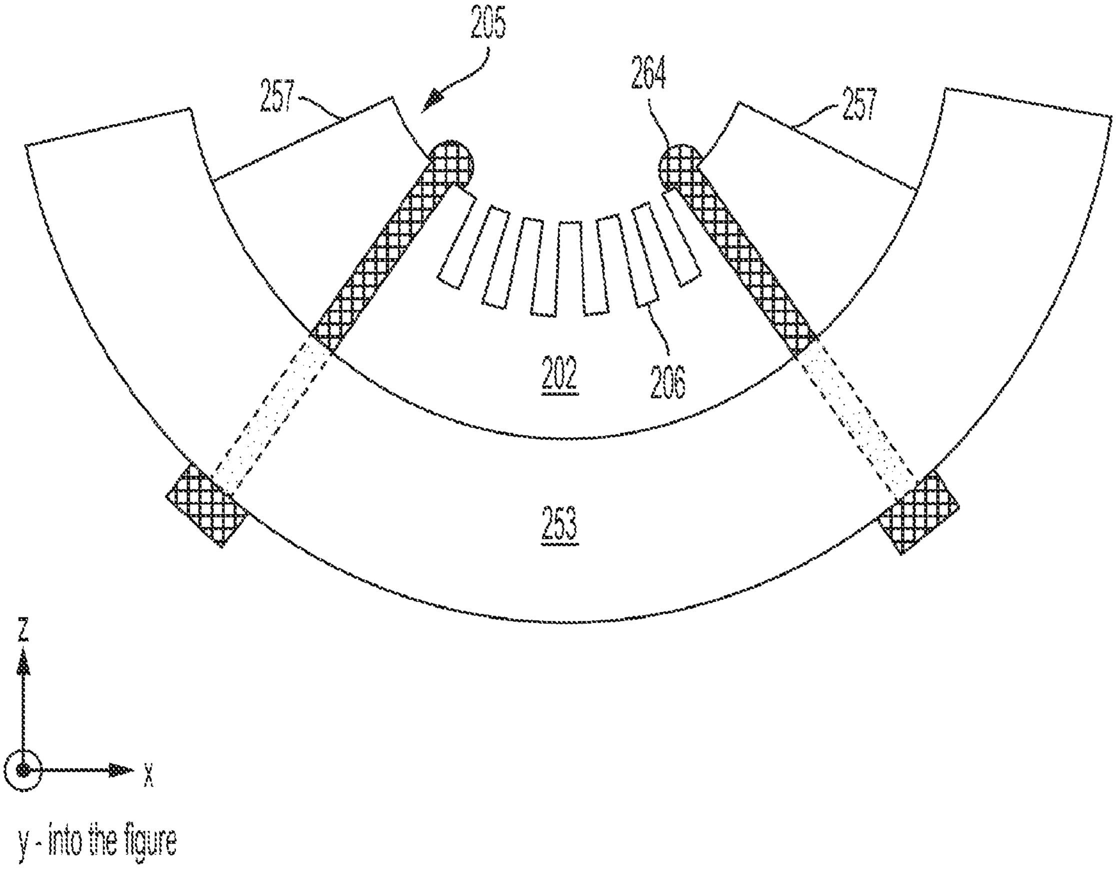


FIG. 14

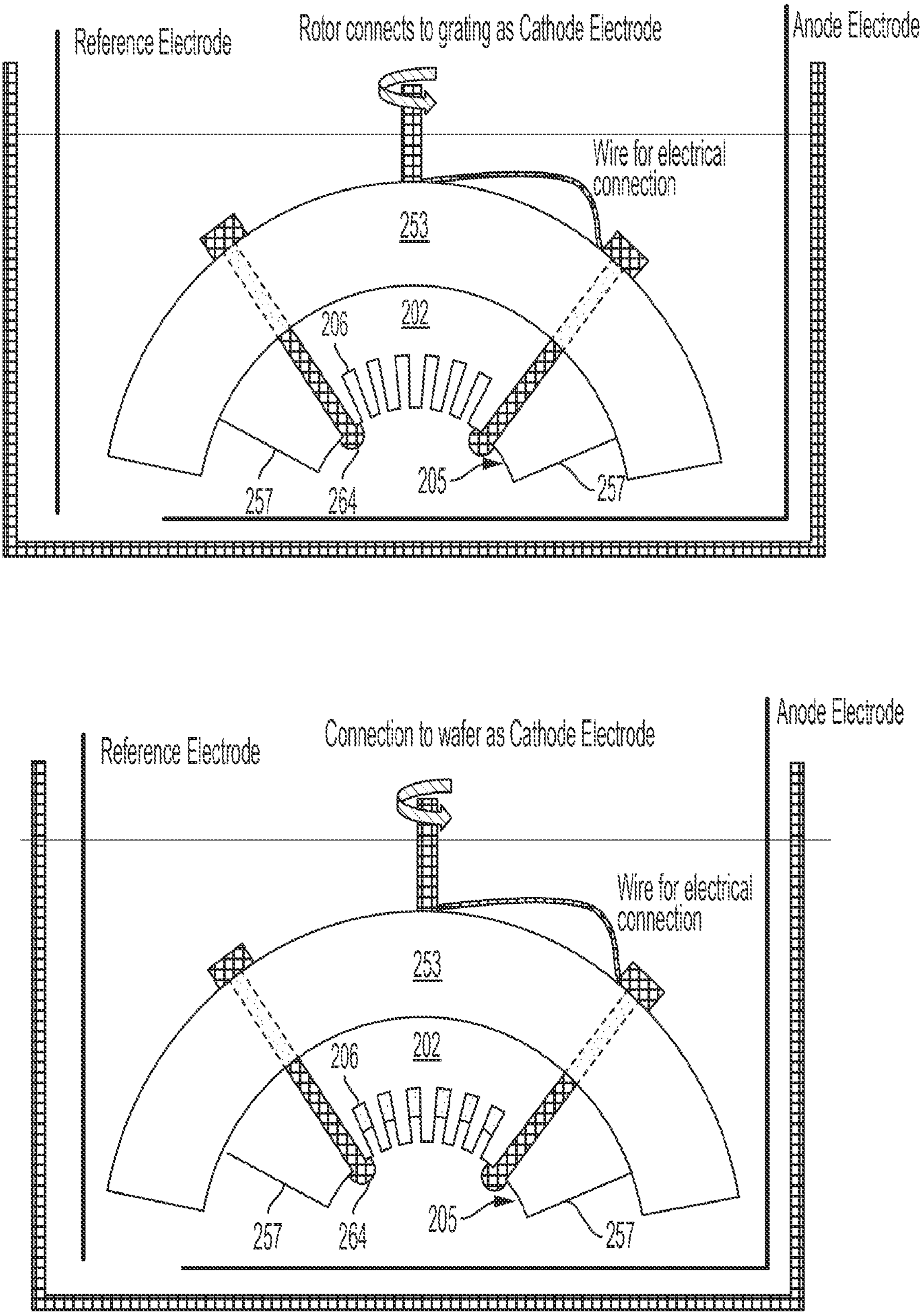

Reference Electrode
Rotor connects to grating as Cathode Electrode
Anode Electrode
Wire for electrical connection
253
202
206
257
264
205
257
Reference Electrode
Connection to wafer as Cathode Electrode
Anode Electrode
Wire for electrical connection
253
202
206
257
264
205
257

FIG. 15

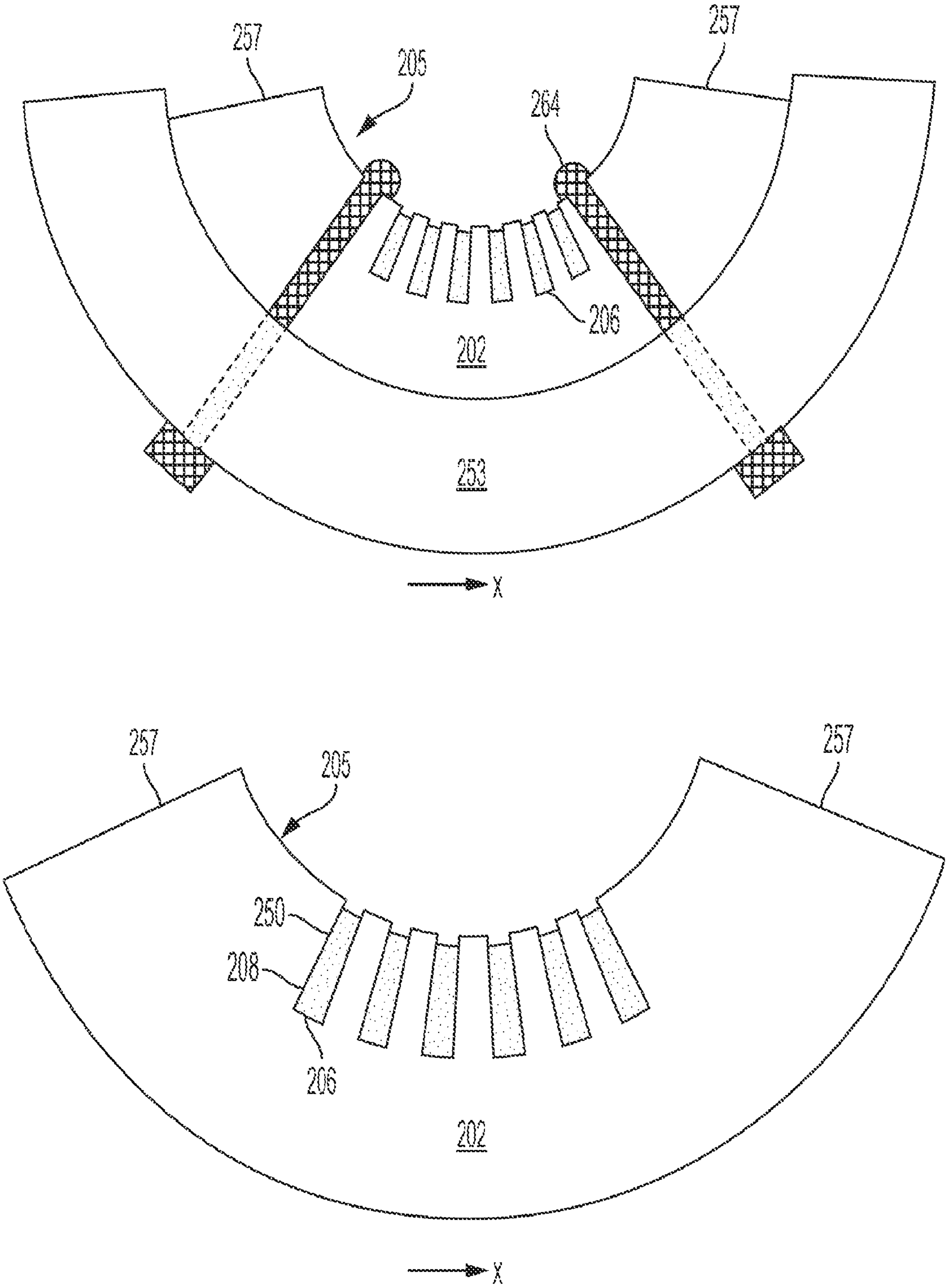


FIG. 16

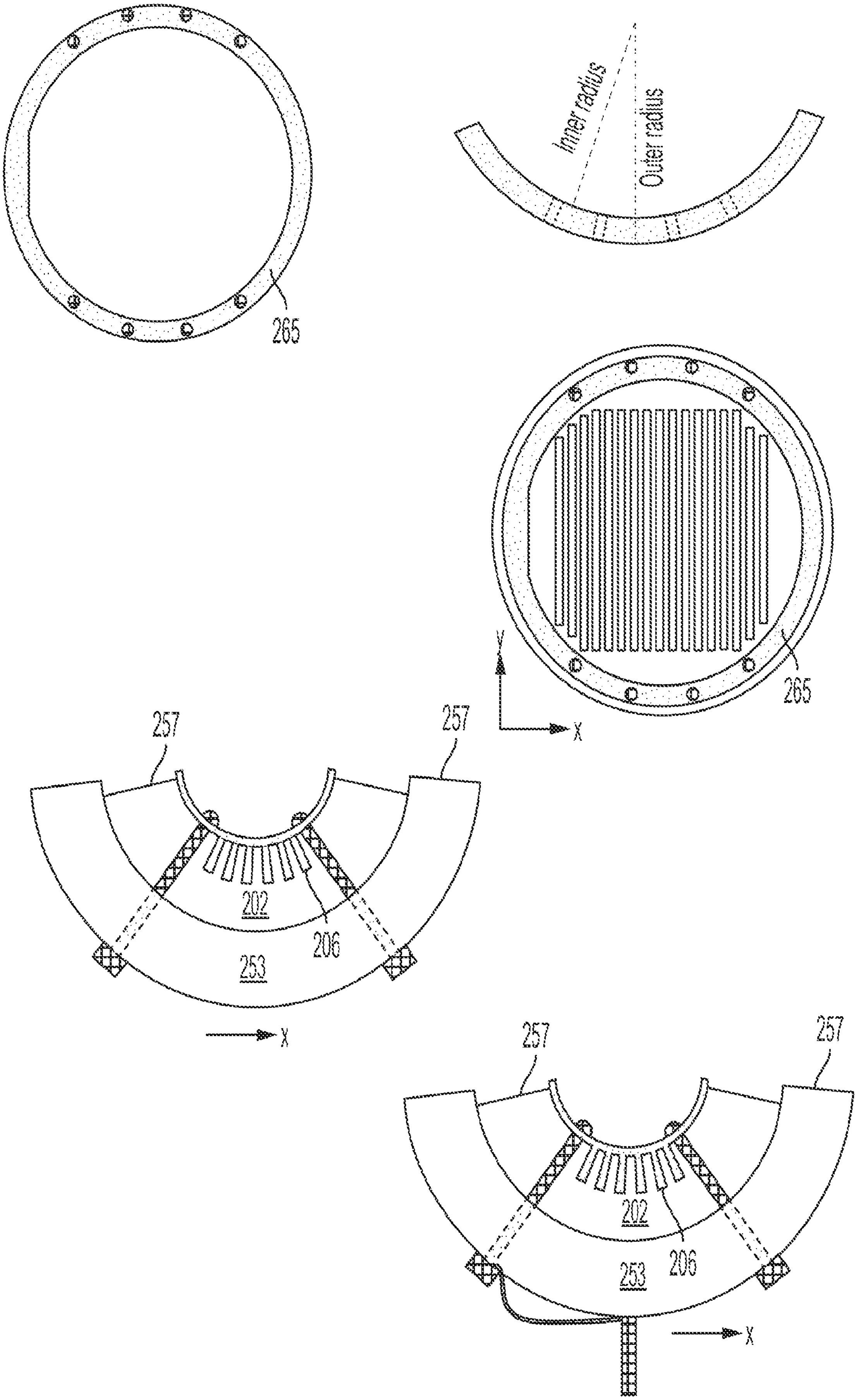

Inner radius
Outer radius
265
265
y
x
257
257
202
206
253
x
257
257
202
206
253
x

FIG. 17

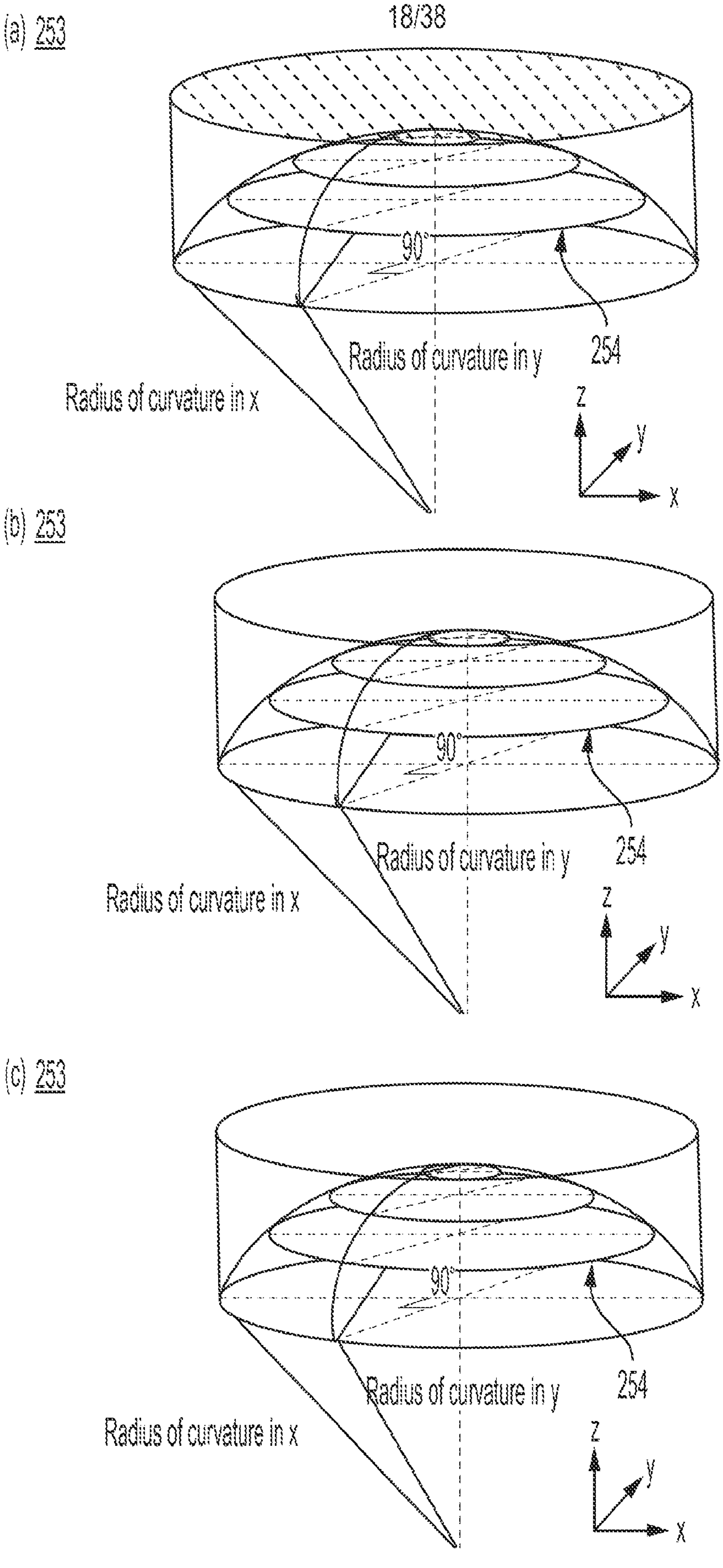

(a) 253
90°
254
Radius of curvature in y
Radius of curvature in x
z
y
x
(b) 253
90°
254
Radius of curvature in y
Radius of curvature in x
z
y
x
(c) 253
90°
254
Radius of curvature in y
Radius of curvature in x
z
y
x

FIG. 18

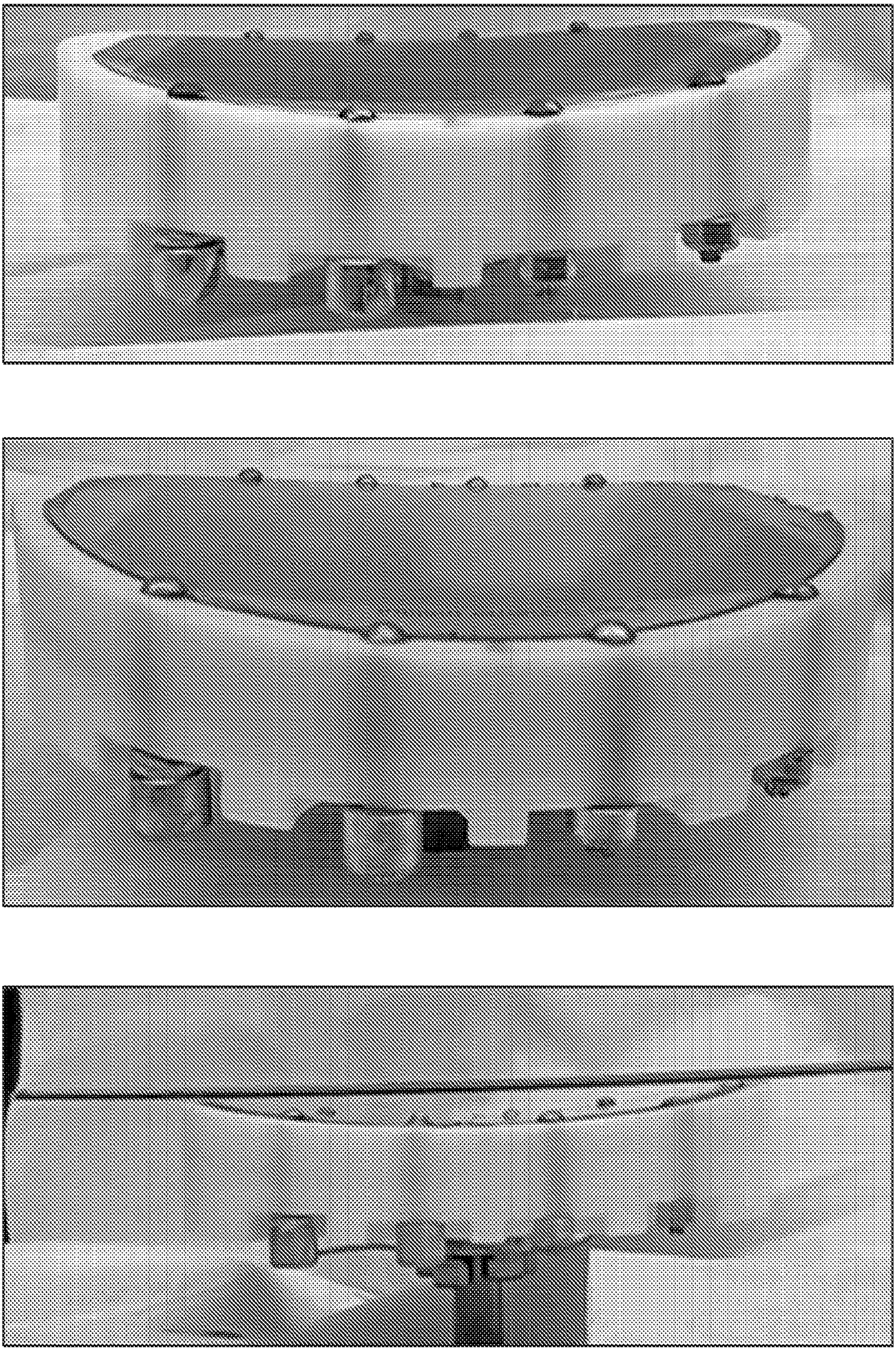


FIG. 19

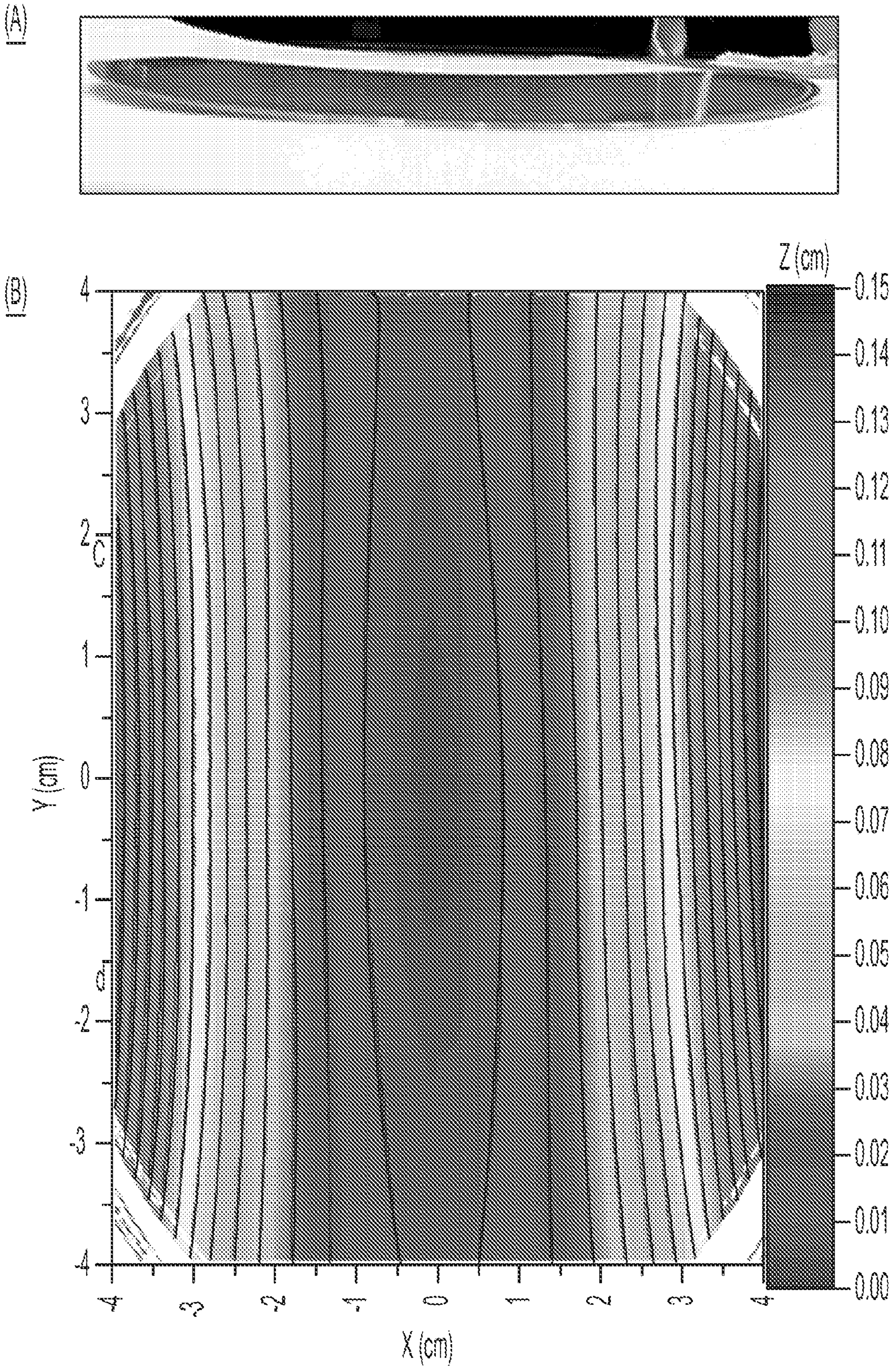

(A)
(B)
Z (cm)
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Y (cm)
4
3
2
1
0
-1
-2
-3
-4
C
X (cm)
-4
-3
-2
-1
0
1
2
3
4

FIG. 20

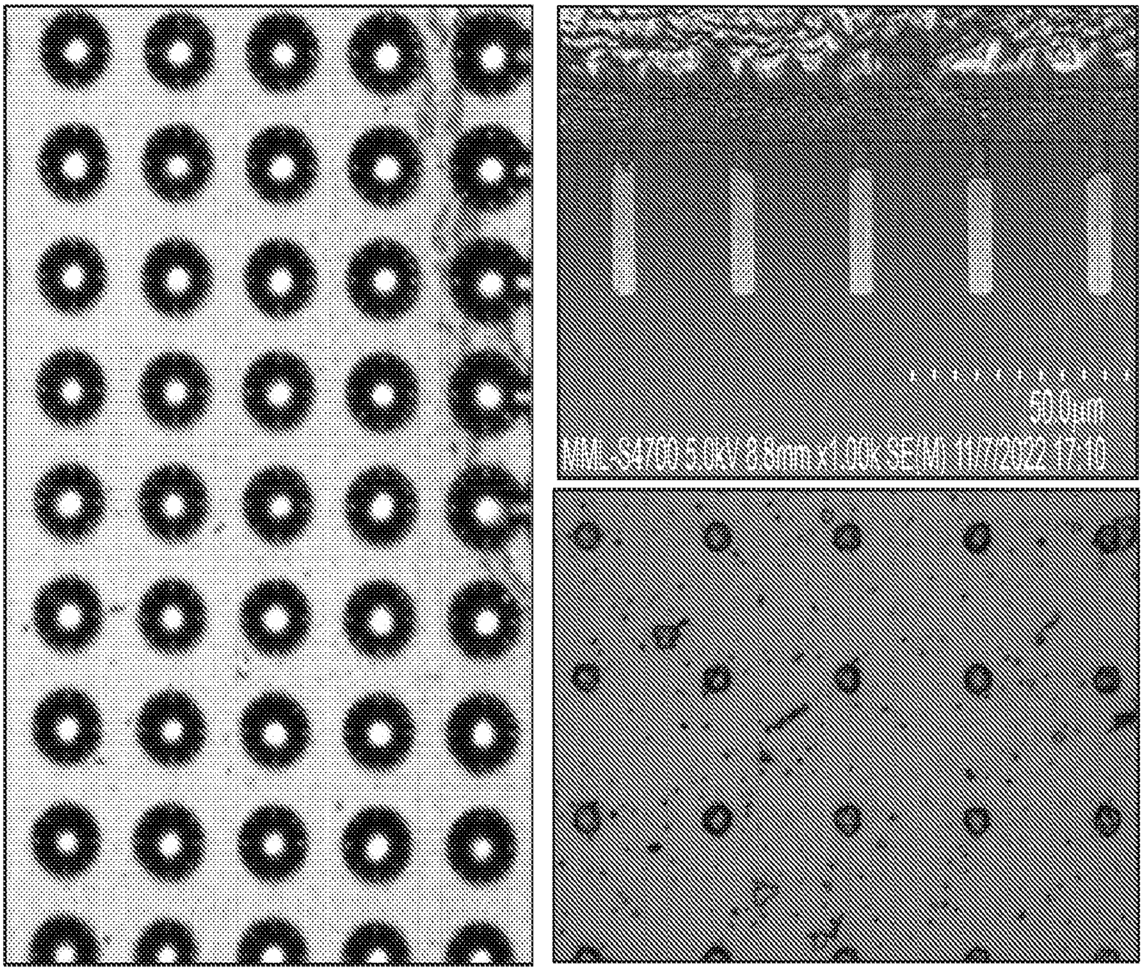


FIG. 21

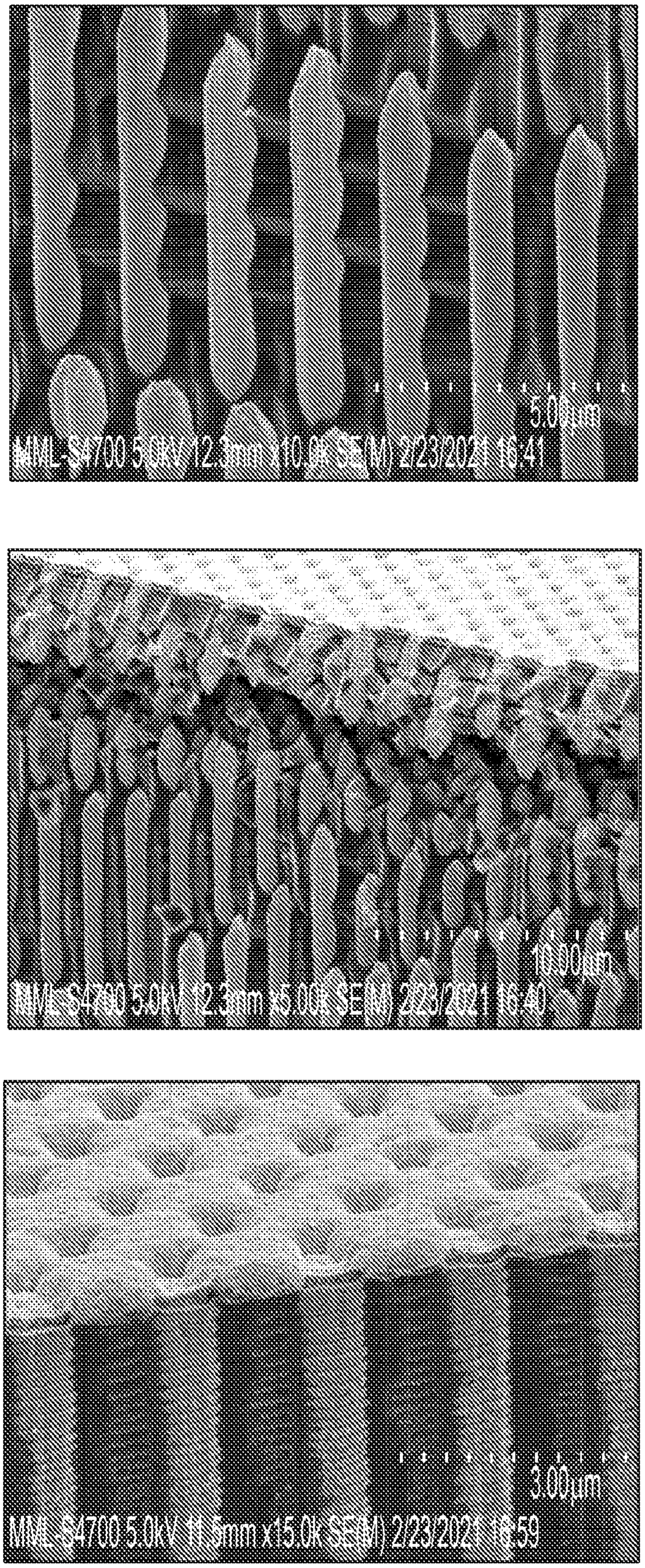

5.00μm
MML-S4700 5.0kV 12.3mm x10.0k SE(M) 2/23/2021 16:41
10.00μm
MML-S4700 5.0kV 12.3mm x5.00k SE(M) 2/23/2021 16:40
3.00μm
MML-S4700 5.0kV 11.5mm x15.0k SE(M) 2/23/2021 16:59

FIG. 22

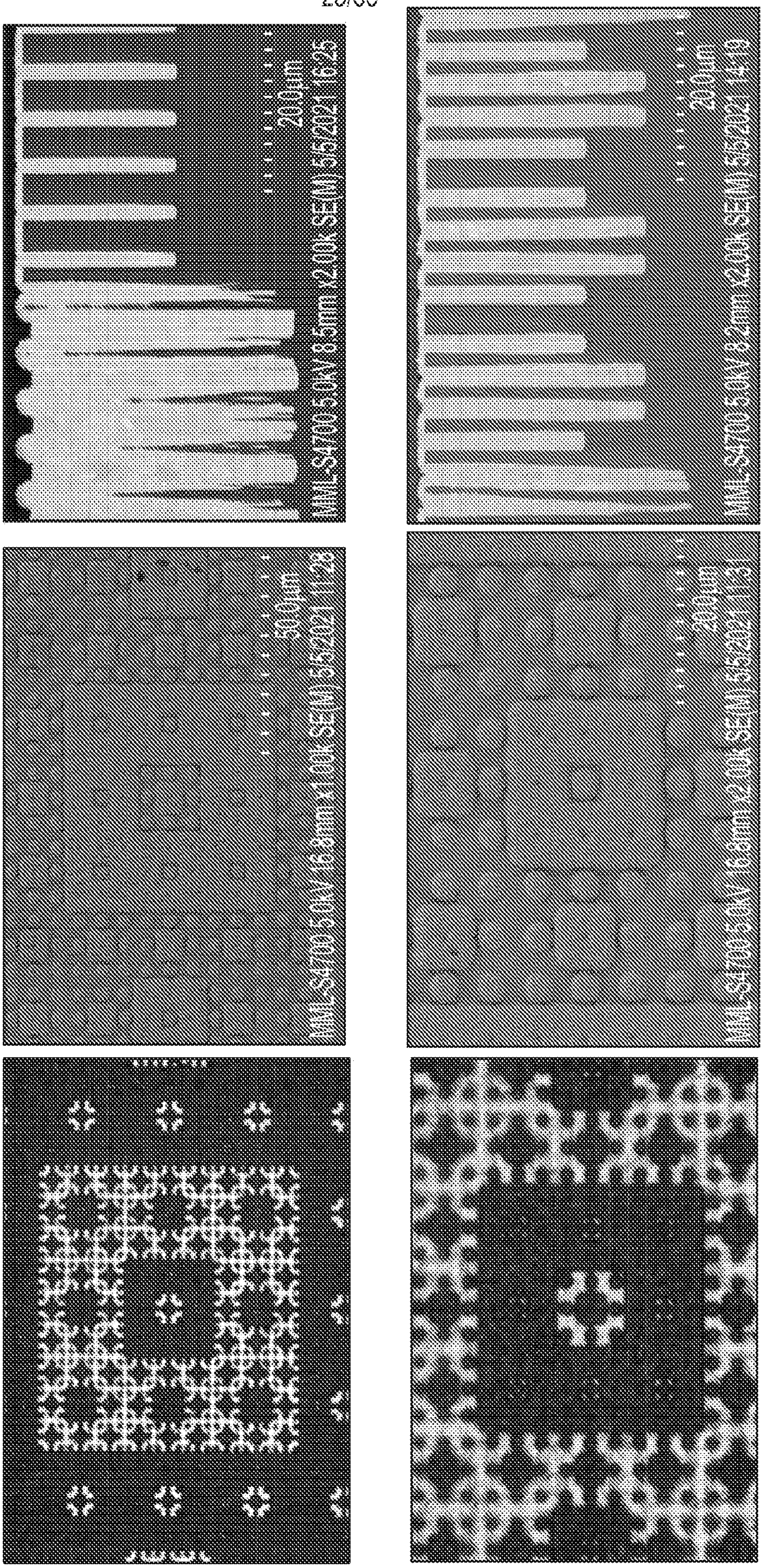

20.0um
MML-S4700 5.0kV 8.5mm x2.00k SE(M) 5/5/2021 16:25
20.0um
MML-S4700 5.0kV 8.2mm x2.00k SE(M) 5/5/2021 14:19
50.0um
MML-S4700 5.0kV 16.8mm x1.00k SE(M) 5/5/2021 11:26
20.0um
MML-S4700 5.0kV 16.8mm x2.00k SE(M) 5/5/2021 11:31

FIG. 23

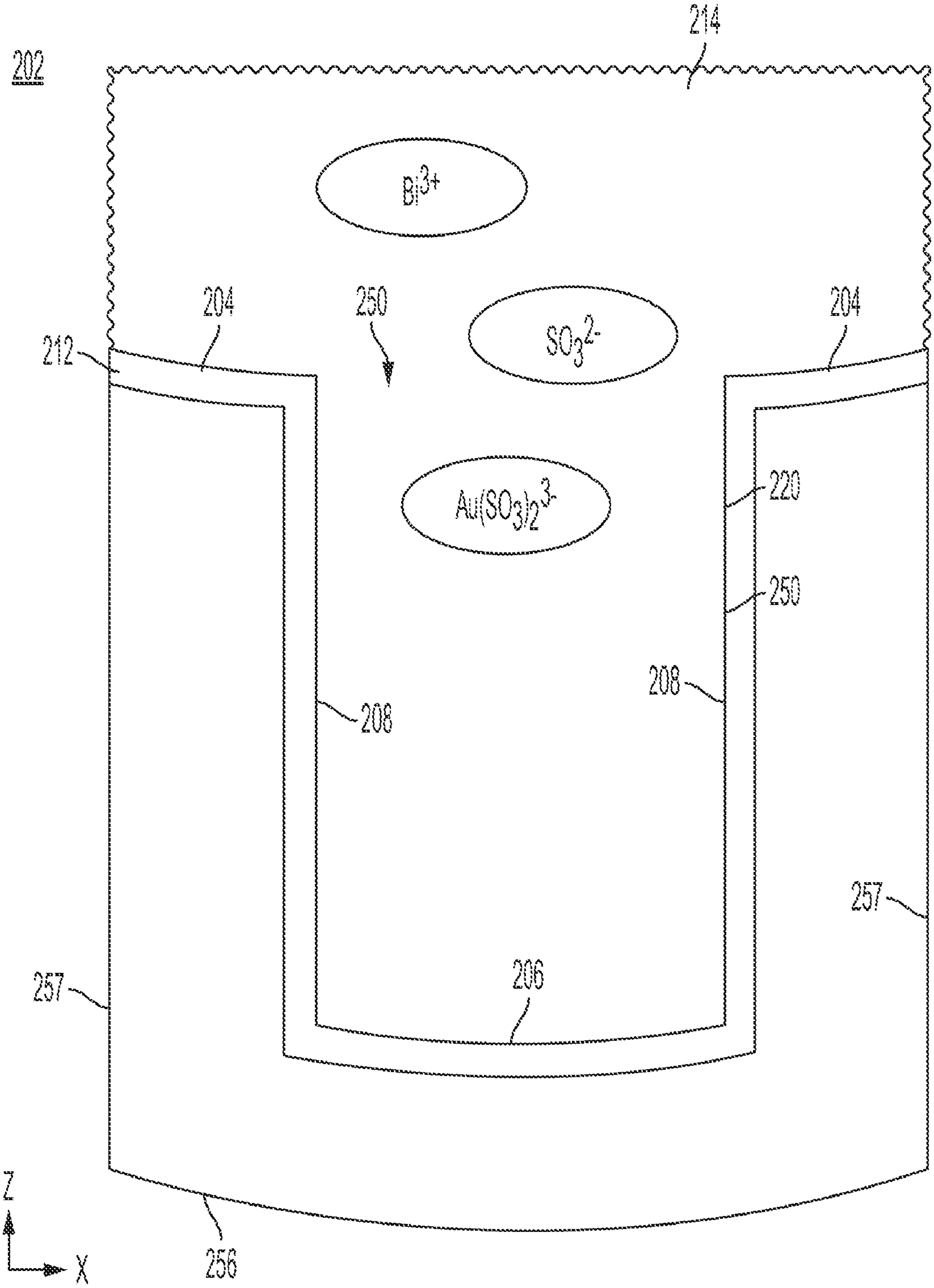

202
214
Bi^{3+}
204
250
SO_3^{2-}
204
212
$Au(SO_3)_2^{3-}$
220
250
208
208
257
257
206
Z
X
256

FIG. 24

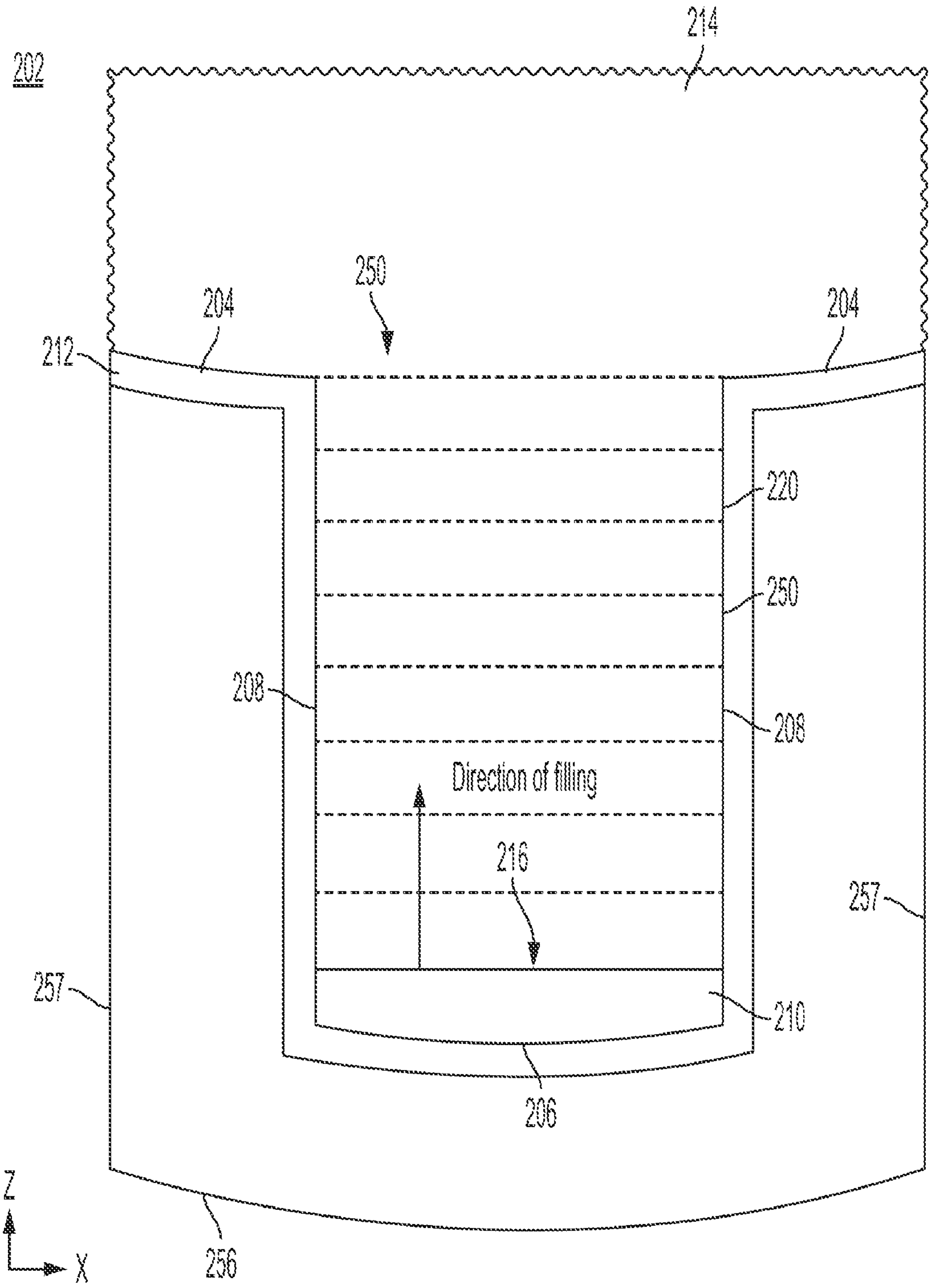
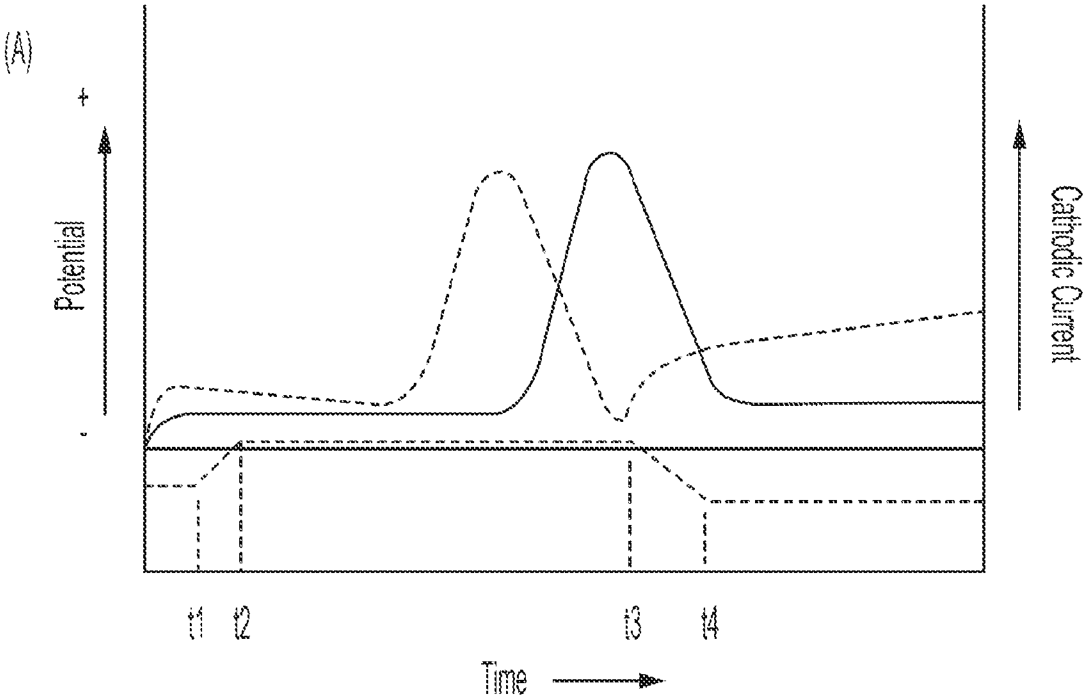
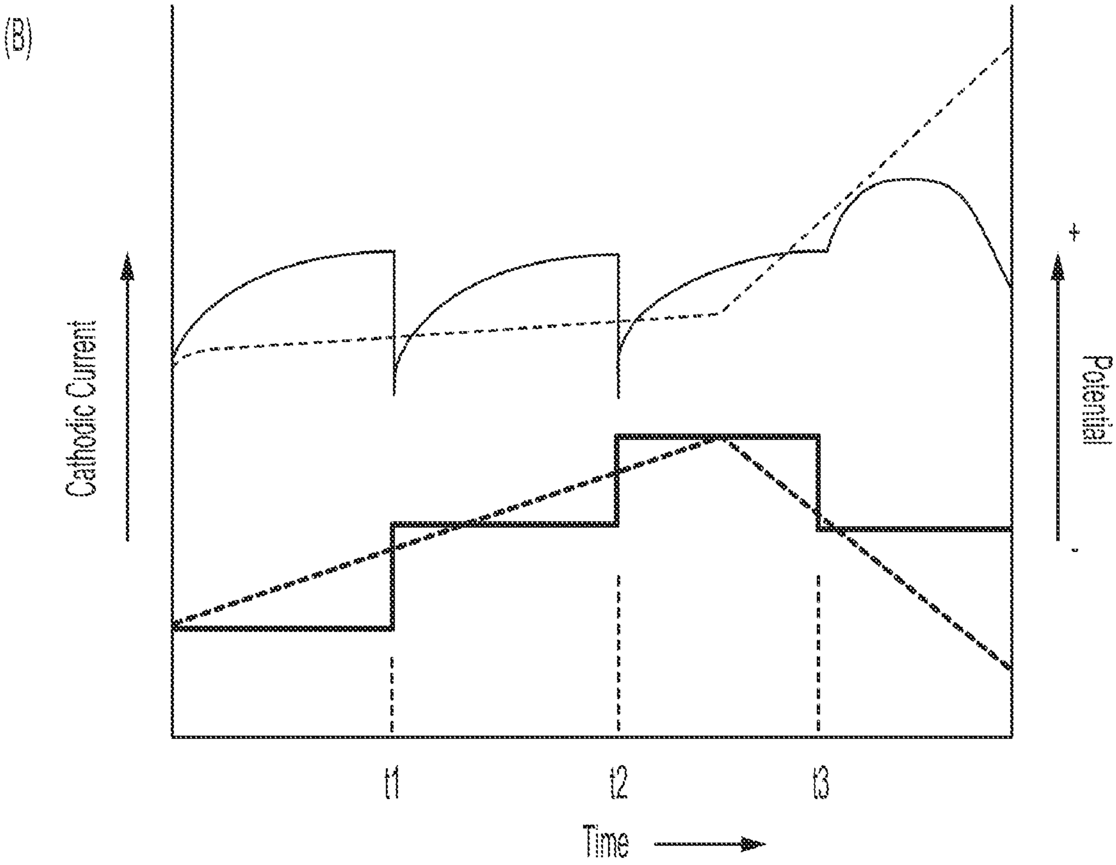

202
214
250
204
204
212
220
250
208
208
Direction of filling
216
257
257
210
206
256
Z
X

FIG. 25

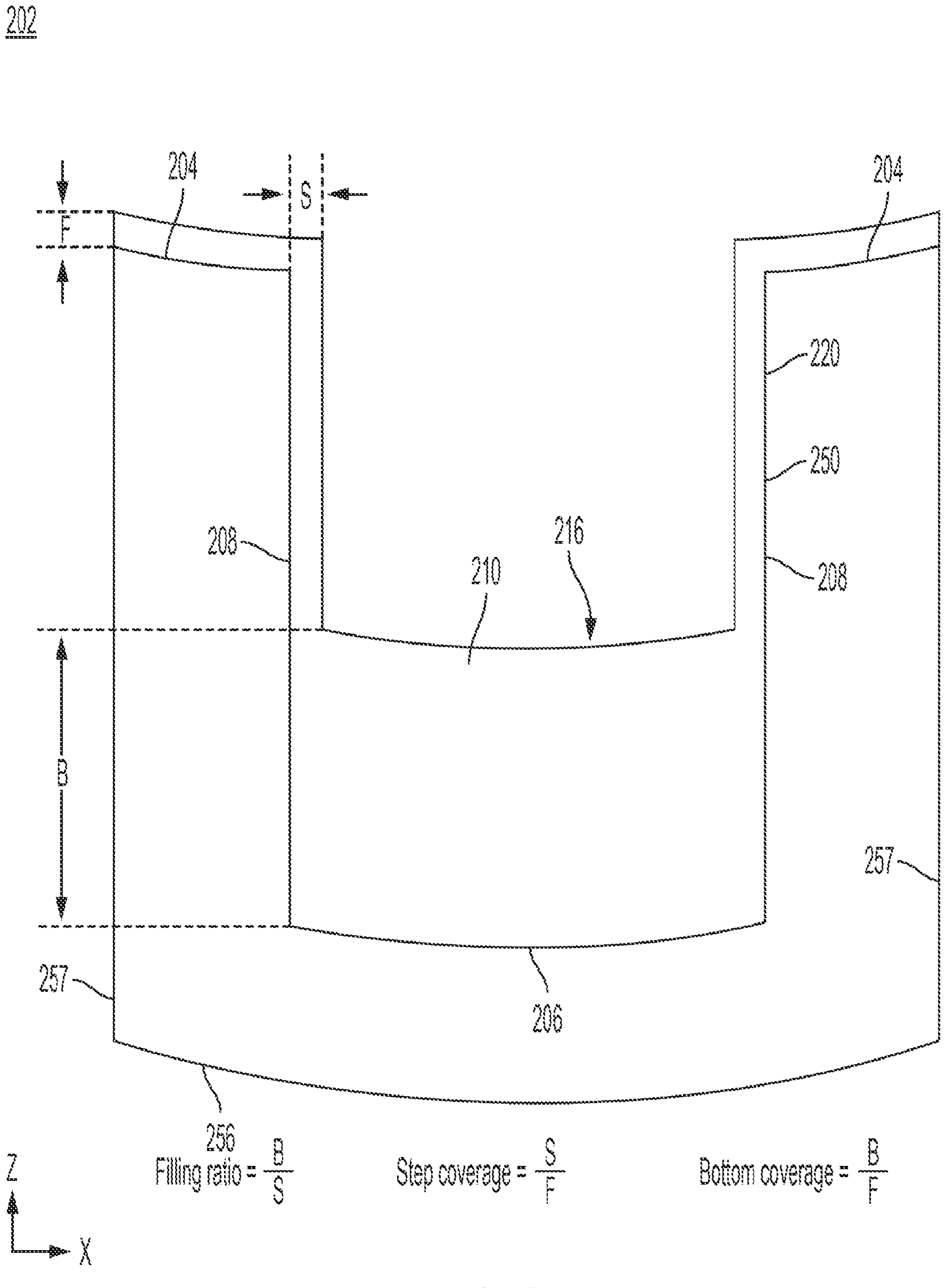


Potentiostatic (———) and Potentiodynamic (- - - - -) Control



Galvanostatic (———) and Galvanodynamic (- - - - -) Control

FIG. 26



Filling ratio = $\frac{B}{S}$ Step coverage = $\frac{S}{F}$ Bottom coverage = $\frac{B}{F}$

FIG. 27

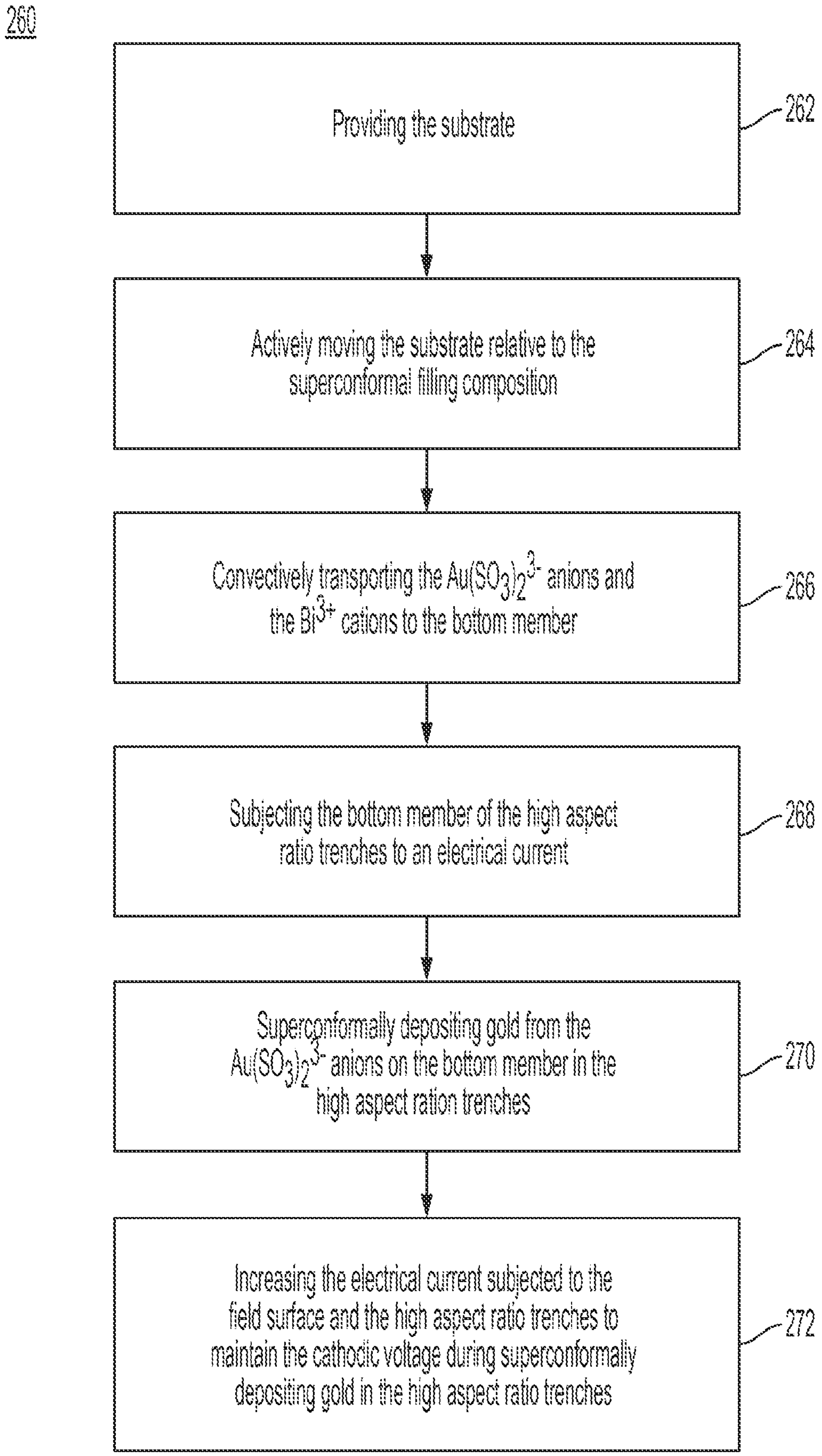

260
Providing the substrate
262
Actively moving the substrate relative to the superconformal filling composition
264
Convectively transporting the $Au(SO_3)_2^{3-}$ anions and the Bi^{3+} cations to the bottom member
266
Subjecting the bottom member of the high aspect ratio trenches to an electrical current
268
Superconformally depositing gold from the $Au(SO_3)_2^{3-}$ anions on the bottom member in the high aspect ration trenches
270
Increasing the electrical current subjected to the field surface and the high aspect ratio trenches to maintain the cathodic voltage during superconformally depositing gold in the high aspect ratio trenches
272

FIG. 28

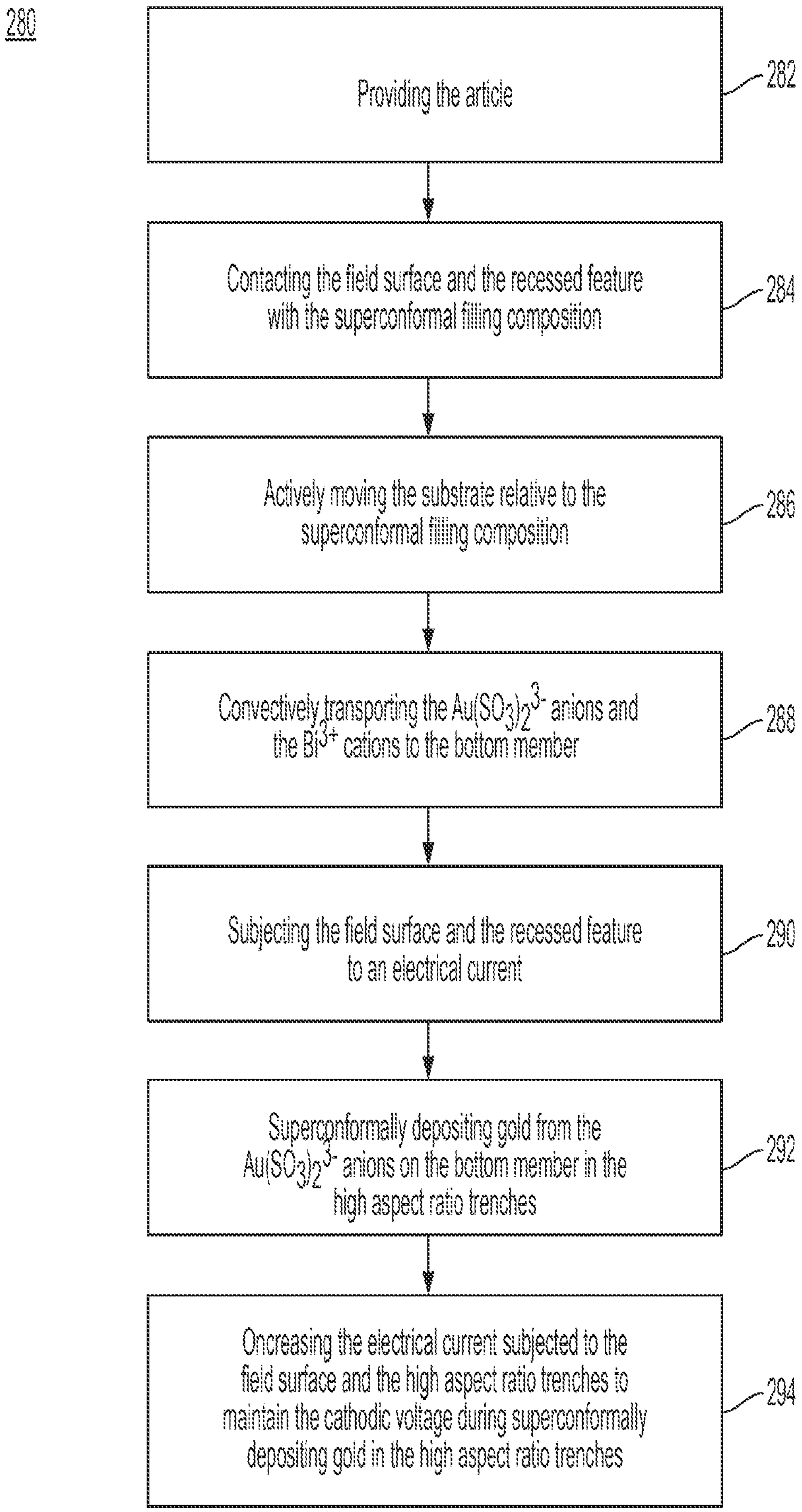

280
Providing the article
282
Contacting the field surface and the recessed feature with the superconformal filling composition
284
Actively moving the substrate relative to the superconformal filling composition
286
Convectively transporting the $Au(SO_3)_2^{3-}$ anions and the Bi^{3+} cations to the bottom member
288
Subjecting the field surface and the recessed feature to an electrical current
290
Superconformally depositing gold from the $Au(SO_3)_2^{3-}$ anions on the bottom member in the high aspect ratio trenches
292
Oncreasing the electrical current subjected to the field surface and the high aspect ratio trenches to maintain the cathodic voltage during superconformally depositing gold in the high aspect ratio trenches
294

FIG. 29

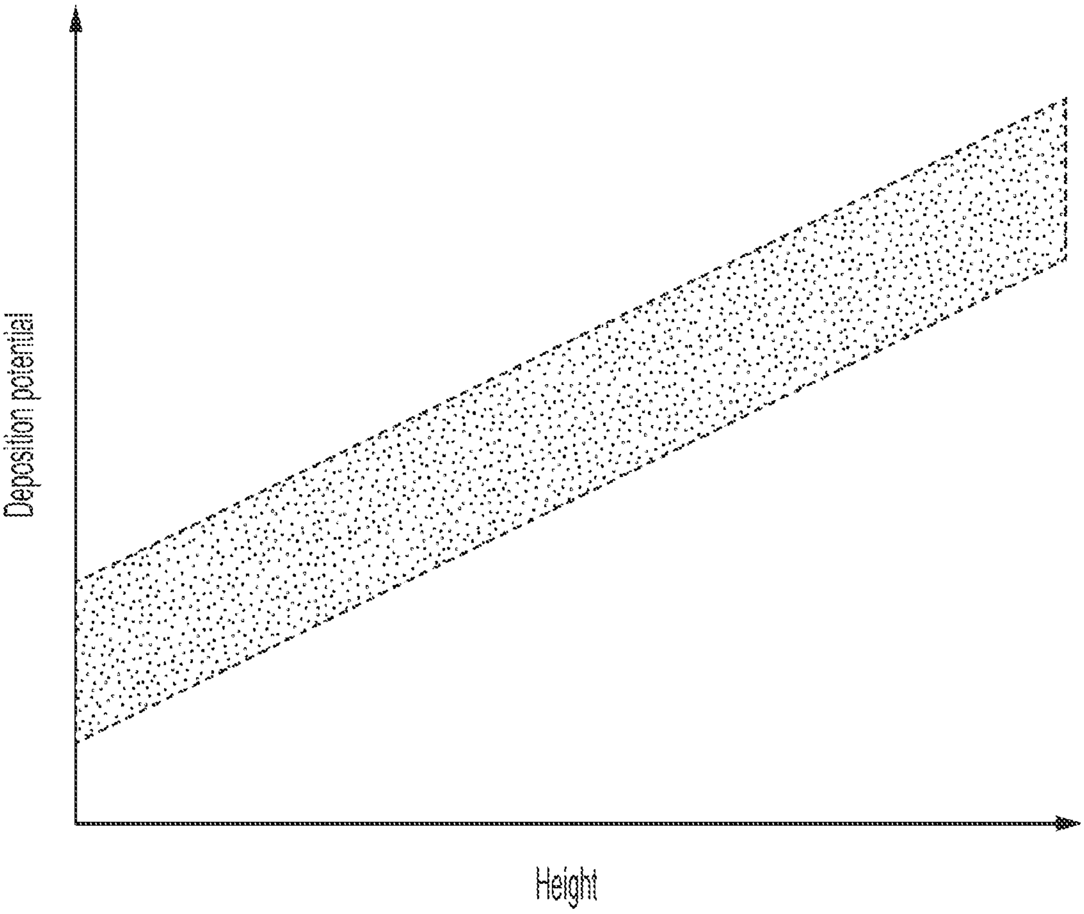


FIG. 30

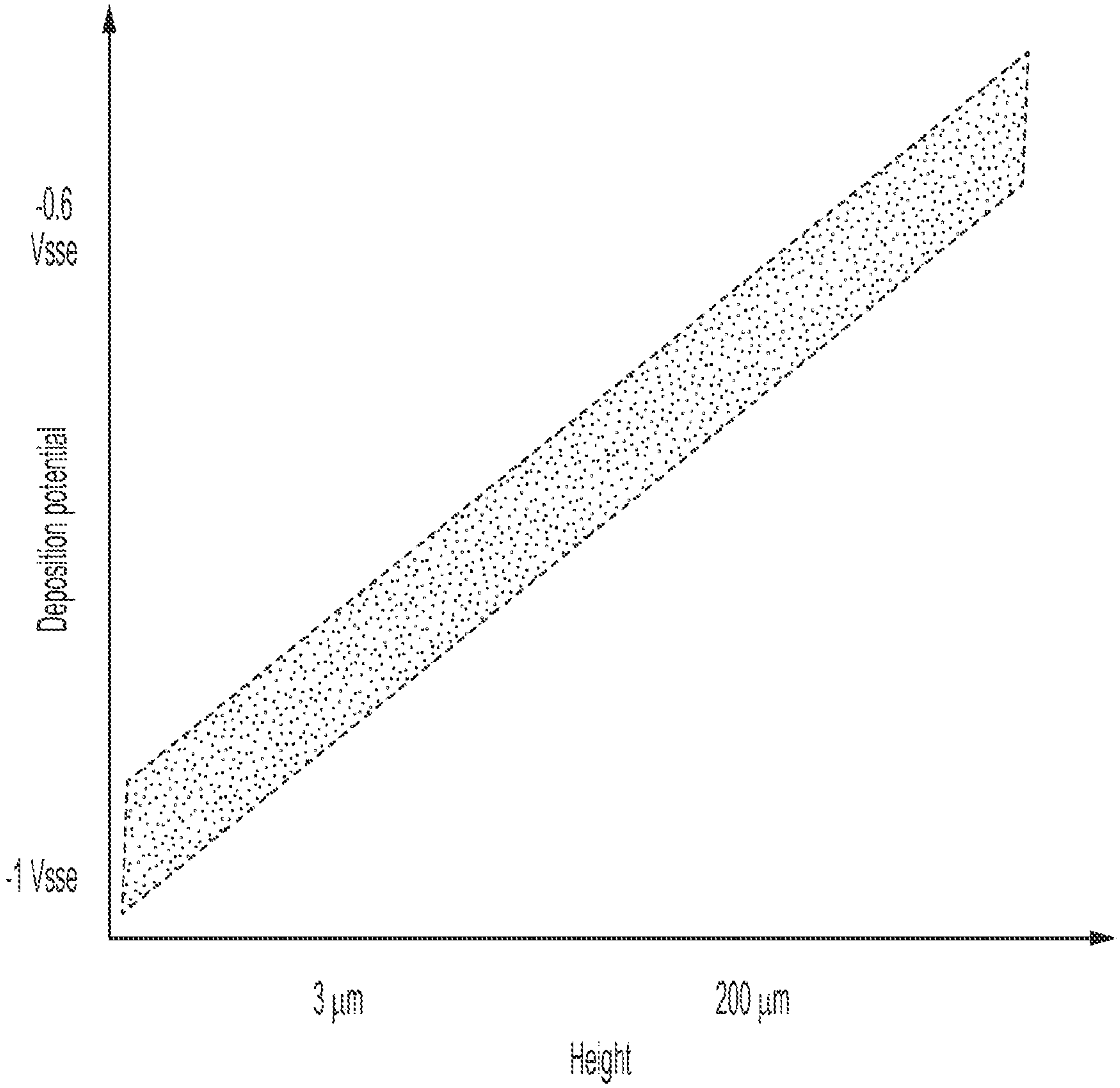


FIG. 31

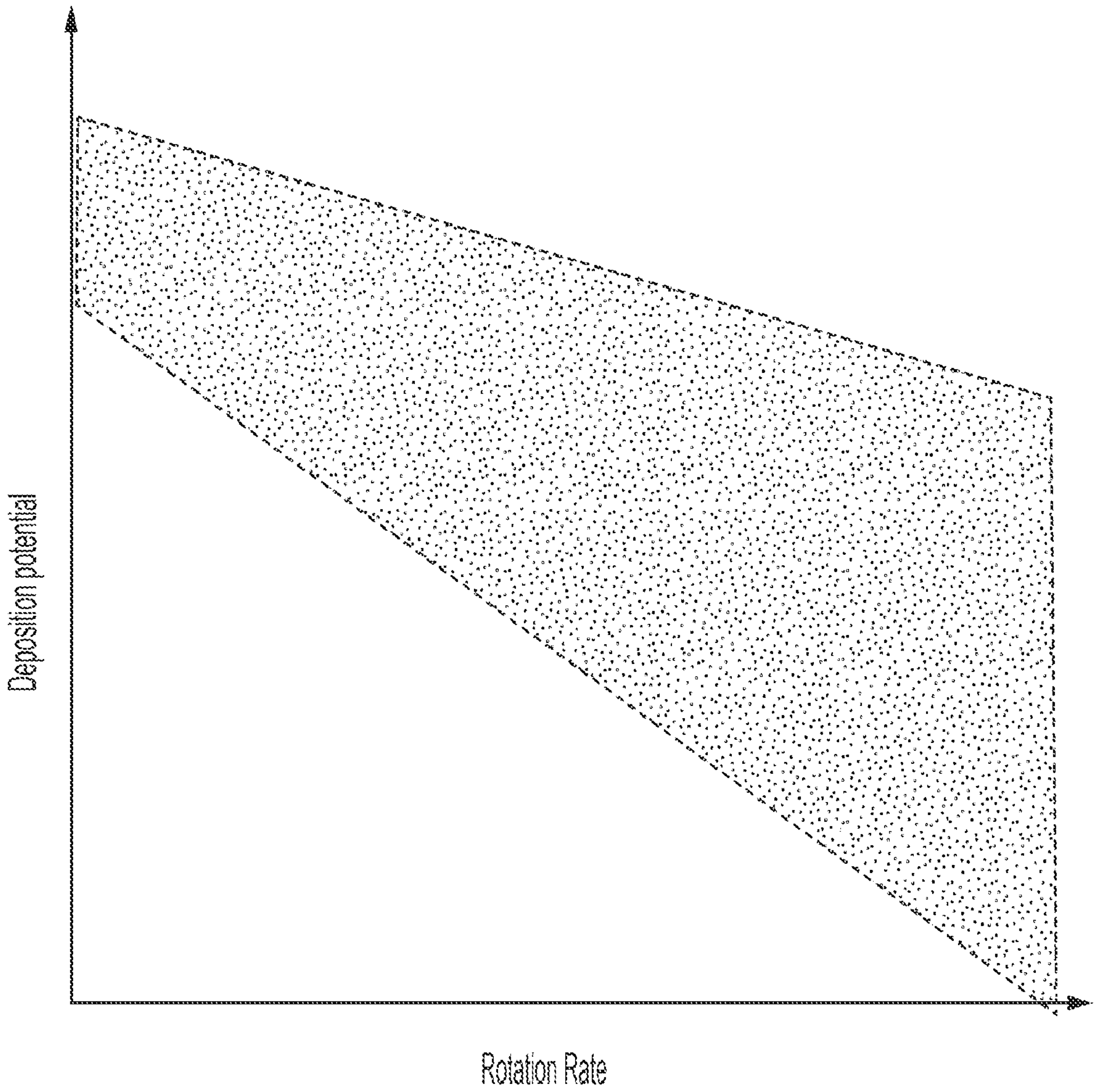


FIG. 32

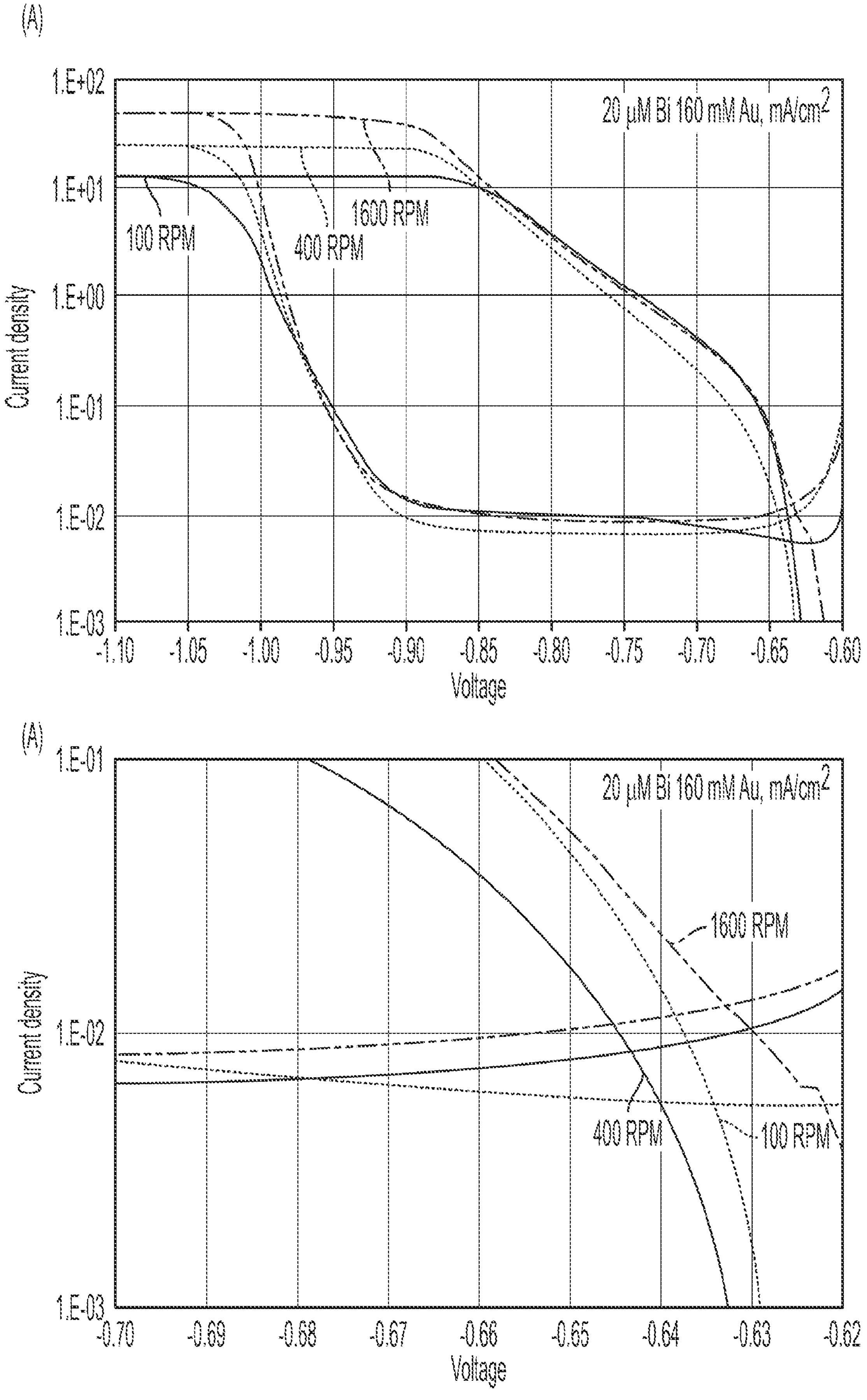

(A)
20 μM Bi 160 mM Au, mA/cm^2
1.E+02
1.E+01
1.E+00
1.E-01
1.E-02
1.E-03
Current density
100 RPM
400 RPM
1600 RPM
-1.10
-1.05
-1.00
-0.95
-0.90
-0.85
-0.80
-0.75
-0.70
-0.65
-0.60
Voltage
(A)
20 μM Bi 160 mM Au, mA/cm^2
1.E-01
1.E-02
1.E-03
Current density
1600 RPM
400 RPM
100 RPM
-0.70
-0.69
-0.68
-0.67
-0.66
-0.65
-0.64
-0.63
-0.62
Voltage

FIG. 33

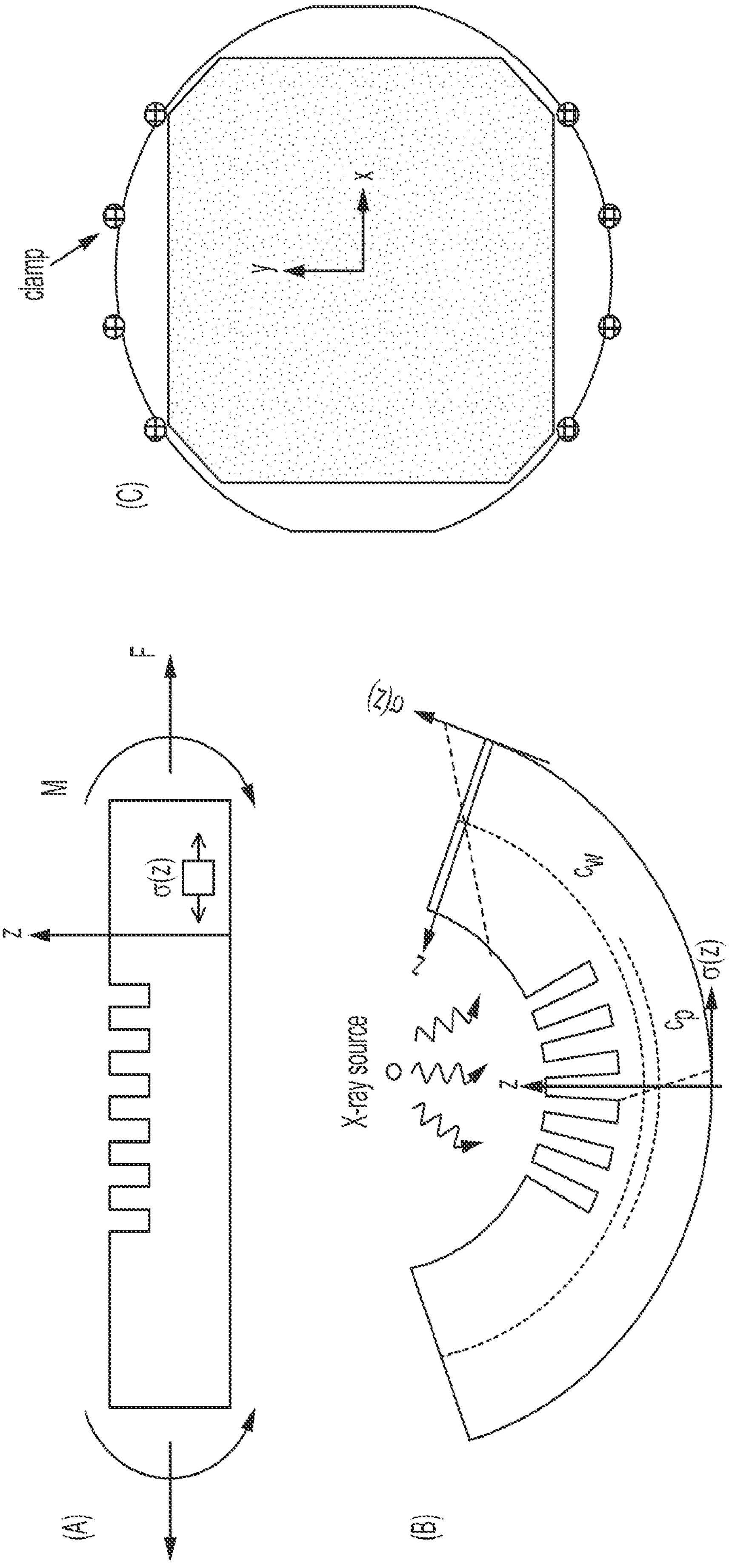


FIG. 34

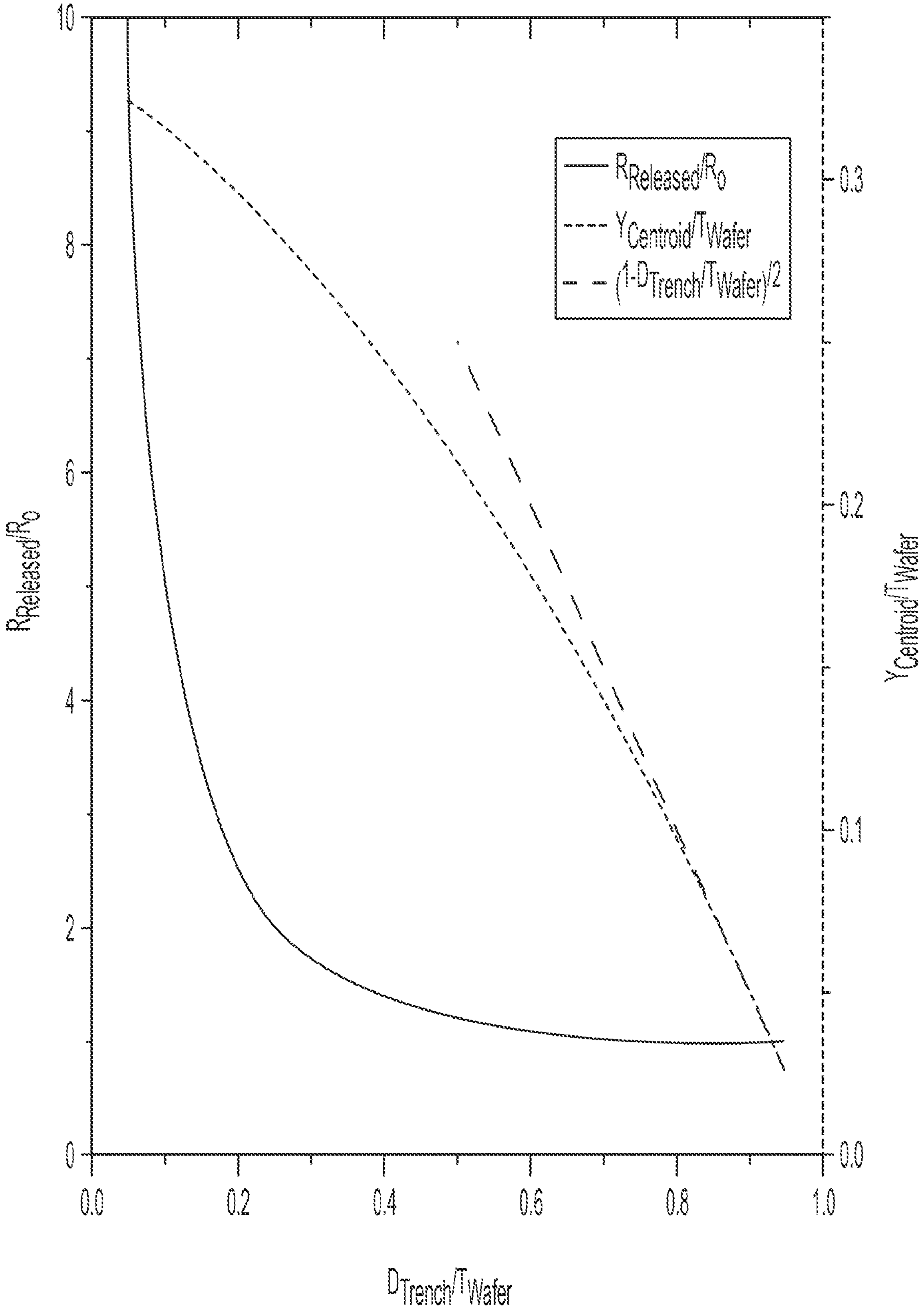

$R_{Released}/R_O$
$Y_{Centroid}/T_{Wafer}$
$(1-D_{Trench}/T_{Wafer})/2$
10
8
6
4
2
0
0.3
0.2
0.1
0.0
0.0
0.2
0.4
0.6
0.8
1.0
D_{Trench}/T_{Wafer}

FIG. 35

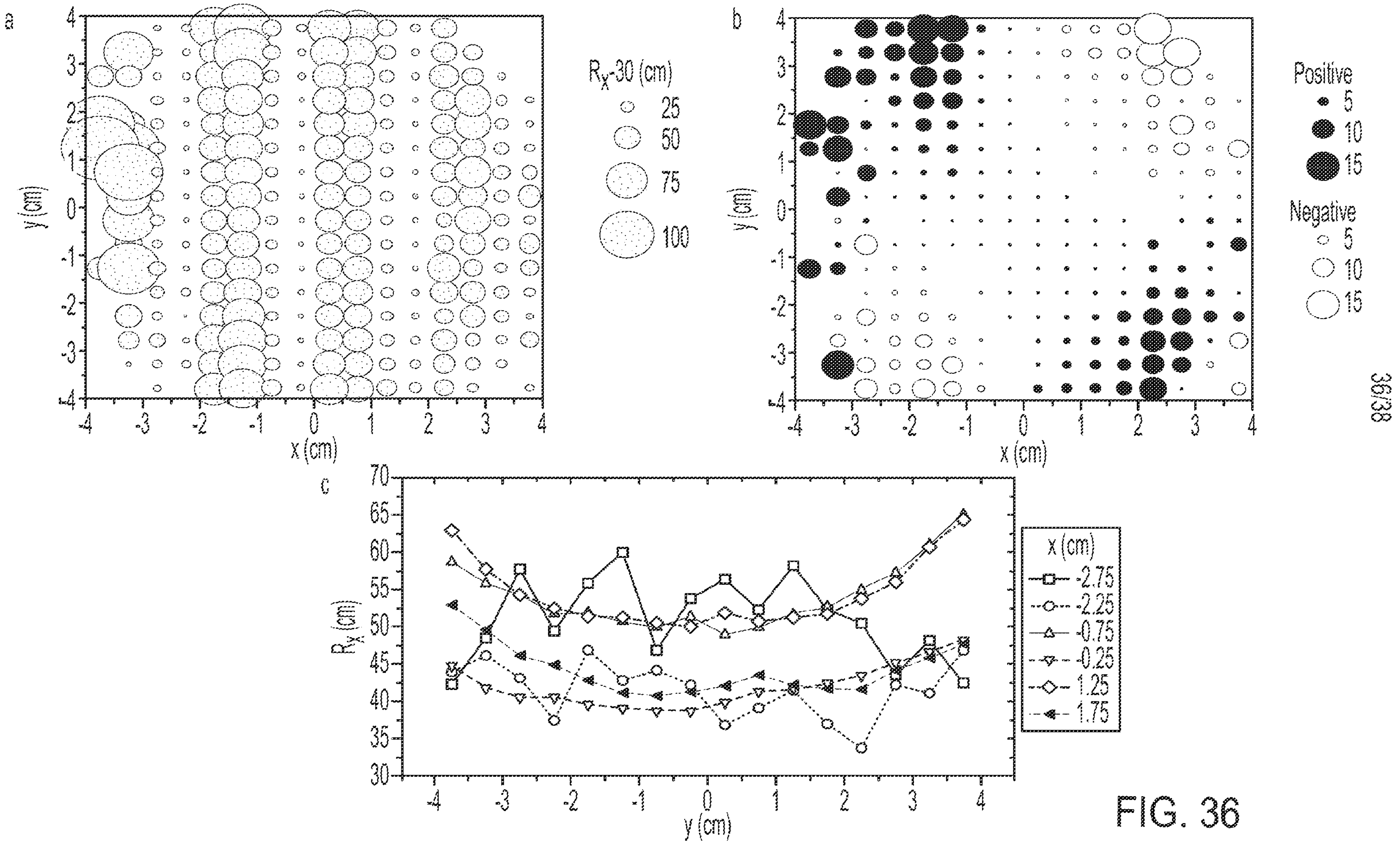

a
y (cm)
4
3
2
1
0
-1
-2
-3
-4
-4
-3
-2
-1
0
1
2
3
4
x (cm)
R_x-30 (cm)
25
50
75
100
b
y (cm)
x (cm)
Positive
5
10
15
Negative
5
10
15
c
R_x (cm)
70
65
60
55
50
45
40
35
30
y (cm)
x (cm)
-2.75
-2.25
-0.75
-0.25
1.25
1.75

FIG. 36

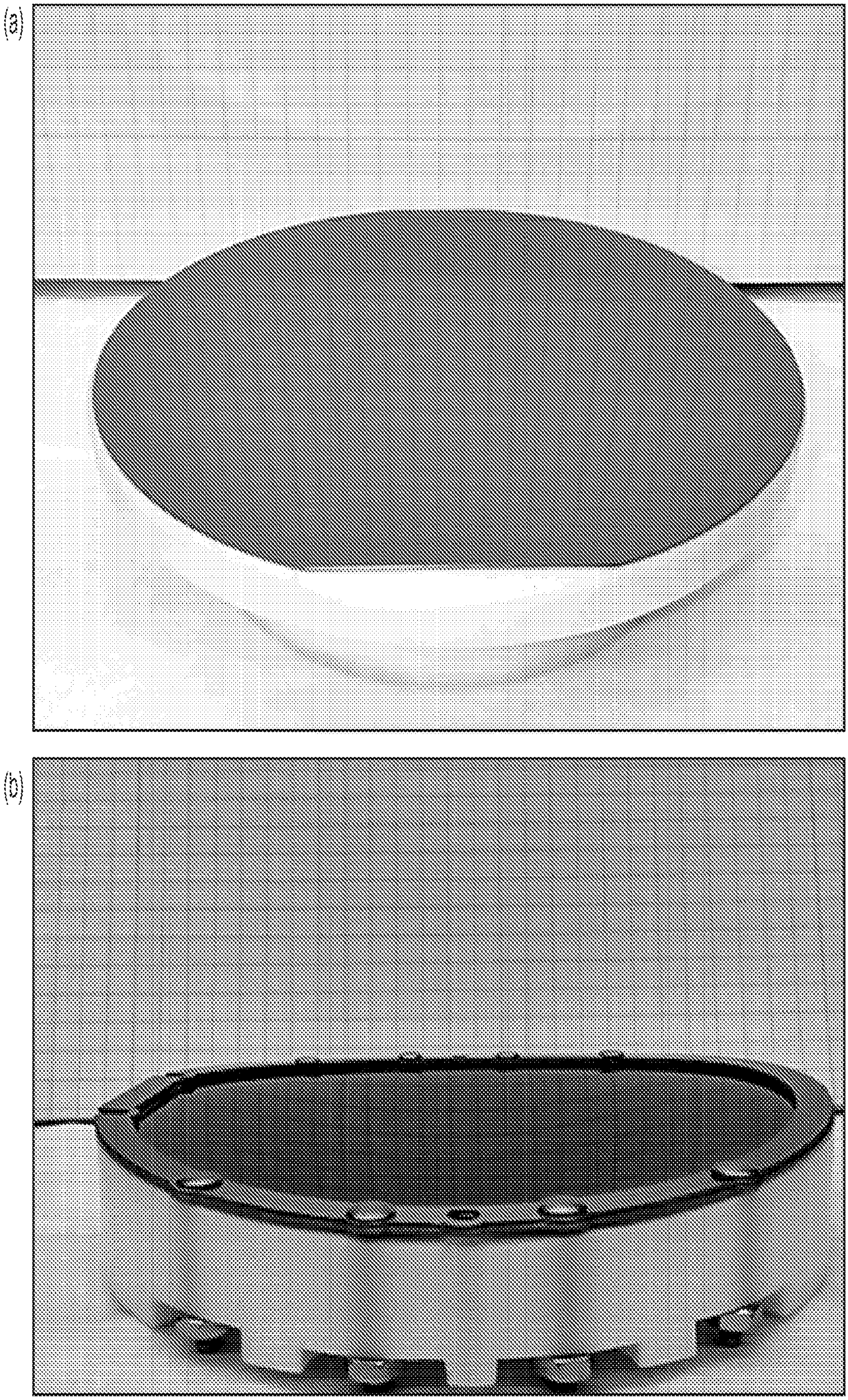


FIG. 37

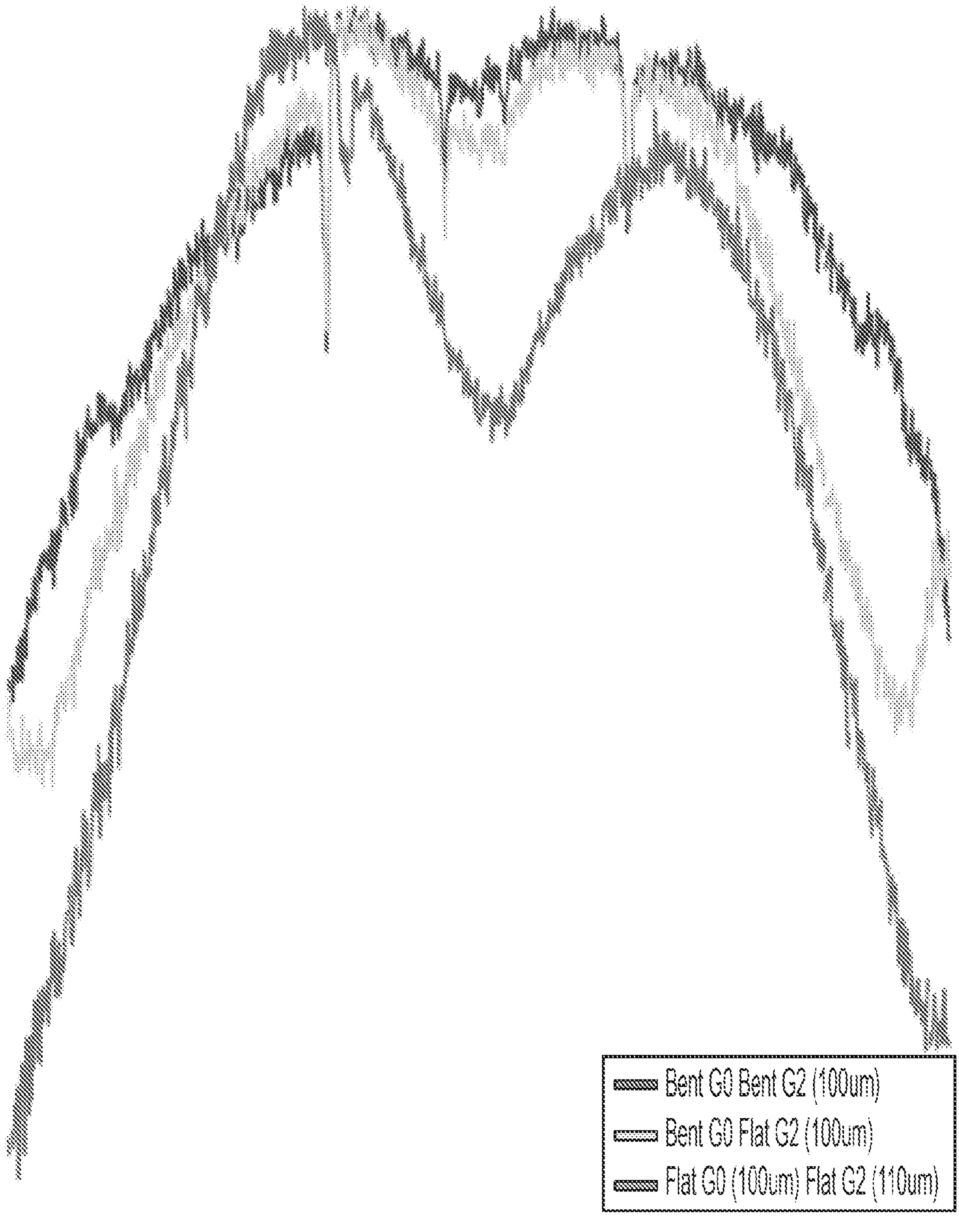

Bent G0 Bent G2 (100um)
Bent G0 Flat G2 (100um)
Flat G0 (100um) Flat G2 (110um)

FIG. 38

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/026727

A. CLASSIFICATION OF SUBJECT MATTER
INV. G02B5/18 G21K1/06
ADD.

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)
G02B H05G G21K

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2011/052800 A1 (SETOMOTO YUTAKA [JP] ET AL) 3 March 2011 (2011-03-03) paragraph [0023] - paragraph [0044]; claims 1, 2; figures 1A-1G	1-9, 11-14 15-17
X	US 2016/265125 A1 (YOKOYAMA MITSURU [JP]) 15 September 2016 (2016-09-15) paragraph [0014] - paragraph [0028]; figures 1, 2	18-32
A	US 2015/316494 A1 (TESHIMA TAKAYUKI [JP] ET AL) 5 November 2015 (2015-11-05) claim 1	1-32
A	US 2012/002785 A1 (KANEKO YASUHISA [JP]) 5 January 2012 (2012-01-05) claim 4	1-32
	-/--	

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

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"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 3 October 2023	Date of mailing of the international search report 11/10/2023
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 Le Masson, Nicolas

1

International application No
PCT/US2023/026727

C(Continuation). **DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2020/301051 A1 (JOSELL DANIEL [US] ET AL) 24 September 2020 (2020-09-24) claims 8-10 -----	15-17
A	WO 2017/036729 A1 (SCHERRER INST PAUL [CH]) 9 March 2017 (2017-03-09) claim 20 -----	1-32

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2023/026727

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011052800 A1	03-03-2011	JP 5597066 B2	01-10-2014
		JP 2011069818 A	07-04-2011
		US 2011052800 A1	03-03-2011
US 2016265125 A1	15-09-2016	EP 3054455 A1	10-08-2016
		JP 6436089 B2	12-12-2018
		JP WO2015060093 A1	09-03-2017
		US 2016265125 A1	15-09-2016
		WO 2015060093 A1	30-04-2015
US 2015316494 A1	05-11-2015	JP 2015221192 A	10-12-2015
		US 2015316494 A1	05-11-2015
US 2012002785 A1	05-01-2012	JP 2012013530 A	19-01-2012
		US 2012002785 A1	05-01-2012
US 2020301051 A1	24-09-2020	US 2020301051 A1	24-09-2020
		US 2023037933 A1	09-02-2023
WO 2017036729 A1	09-03-2017	NONE	