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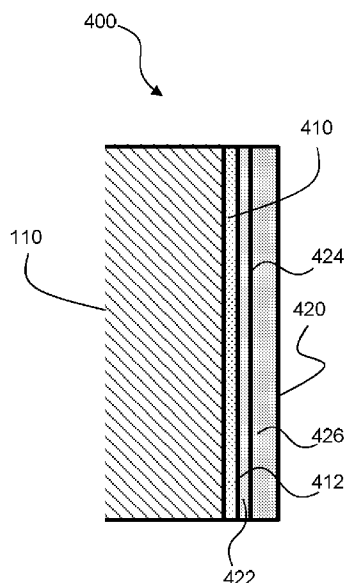


FIG. 4C

(57) Abstract: Methods of plating a metal on a substrate including coating a nanoporous metal-oxide layer on a surface of the substrate prior to metal plating. Methods may include coating a surface of the substrate with a slurry including colloidal metal-oxide precursor particles and aluminum oxide particles. After coating, the slurry may be calcinated on the surface of the substrate to form a nanoporous metal-oxide layer on the surface. Then, a metallic film may be plated on the nanoporous metal-oxide layer. The metallic film may be plated by an electroless plating method and/or an electroplating method. Articles, such as electronic interposers, may be made using the methods of plating a metal described herein.

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## **METHODS FOR INCREASING ADHESION BETWEEN METALLIC FILMS AND GLASS SURFACES AND ARTICLES MADE THEREFROM**

**[0001]** This application claims the benefit of priority to U.S. Provisional Application Serial No. 62/735,519 filed on September 24, 2018, the content of which is relied upon and incorporated herein by reference in its entirety.

Field

**[0002]** The present disclosure relates to methods for plating a metallic film on a glass or glass-ceramic substrate. In particular, the present disclosure relates to methods for plating a metallic film on a glass or glass-ceramic substrate that include coating a surface of the substrate with a nanoporous metal-oxide layer to improve adhesion between the metallic film and the substrate.

Background

**[0003]** Glass and glass-ceramic substrates have become an attractive alternative to silicon and organic fiber-reinforced polymer substrates for electronic applications. Glass and glass-ceramic substrates with vias are desirable for many applications, including interposers used as, for example, electrical interfaces, RF (radio frequency) filters, and RF switches. For example, 3D interposers with through package via (TPV) interconnects that connect a logic device on one side and a memory on the other side are useful in high bandwidth devices. Organic interposers suffer from poor dimensional stability across different temperatures. Silicon wafers are expensive and suffer from high dielectric loss due to their semiconducting properties. There is a trend, therefore, toward the use of glass or glass-ceramic as a superior substrate material due to its low dielectric constant, thermal stability, and low cost.

**[0004]** To create desired electrical properties, a glass or glass-ceramic substrate may be coated with a metallic material like copper. In case of interposers, the vias may be filled with a metallic material like copper. But metallic materials like copper do not adhere well to a glass or glass-ceramic material. A hermetic seal between copper and glass is desired

for some applications, and such a seal is difficult to obtain because of the poor adhesion between metallic materials and glass or glass ceramic materials.

[0005] Therefore, a continuing need exists for innovations in methods for adhering a metallic film, such a copper film, to glass and glass ceramic substrates.

#### *BRIEF SUMMARY*

[0006] The present disclosure is directed to methods of increasing the effective adhesion between a metallic material, such as copper, and a glass or glass ceramic substrate. The metallic material may be electrolessly plated and/or electroplated on a planar surface of a glass or glass-ceramic substrate, inside vias formed in the substrate, or both. Suitable adhesion between the plated metallic material and the glass or glass-ceramic substrate may be achieved by forming a nanoporous metal-oxide layer on the substrate by calcinating a slurry including metal-oxide particles and metal-oxide precursor articles. Subsequent electroless plating and/or electroplating of a metallic material on this nanoporous metal-oxide layer leads to strong and effective adhesion between the metallic material and the glass or glass-ceramic substrate due to penetration of the metallic material into the interior of the nanopores of the metal-oxide layer.

[0007] In a first aspect, a method of plating a metal on a substrate is described, the method including coating a surface of the substrate with a slurry including colloidal metal-oxide precursor particles and aluminum oxide particles; calcinating the slurry on the surface of the substrate to form a nanoporous metal-oxide layer on the surface of the substrate; and plating the nanoporous metal-oxide layer with a metal.

[0008] In a second aspect, the method of plating a metal substrate according to aspects of the preceding paragraph may include colloidal metal-oxide precursor particles that include at least one of: aluminum oxide precursor particles, silicon oxide precursor particles, titanium oxide precursor particles, cerium oxide precursor particles, and zirconium oxide precursor particles.

[0009] In a third aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include colloidal metal-oxide precursor particles that include aluminum oxide precursor particles.

- [0010] In a fourth aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include colloidal metal-oxide precursor particles that include aluminum oxide hydroxide particles.
- [0011] In a fifth aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include plating the nanoporous metal-oxide layer with a metal including copper.
- [0012] In a sixth aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include a substrate that is a glass or glass-ceramic substrate.
- [0013] In a seventh aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include a substrate that is a glass or glass-ceramic substrate having a via formed in the substrate and the surface of the substrate on which the nanoporous metal-oxide layer is formed may include an interior surface of the via. In some embodiments, the via may be a through via.
- [0014] In an eighth aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include a nanoporous metal-oxide layer having an average pore size in the range of 5 nanometers to 30 nanometers.
- [0015] In a ninth aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include a nanoporous metal-oxide layer having a pore volume in the range of 0.3 cubic centimeters per gram to 10 cubic centimeters per gram.
- [0016] In a tenth aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include aluminum oxide particles that include nanoparticles.
- [0017] In an eleventh aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include aluminum oxide particles having an average particle size in the range of 10 nanometers to 100 nanometers.
- [0018] In a twelfth aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include colloidal metal-oxide precursor particles having an average particle size in the range of 60 nanometers to 90 nanometers.
- [0019] In a thirteenth aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include aluminum oxide particles having an

average particle size and colloidal metal-oxide precursor particles having an average particle size, where the average particle size of the colloidal metal-oxide precursor particles is less than the average particle size of the aluminum oxide particles.

**[0020]** In a fourteenth aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include aluminum oxide particles having an average particle size and colloidal metal-oxide precursor particles having an average particle size, where the average particle size of the colloidal metal-oxide precursor particles is greater than the average particle size of the aluminum oxide particles.

**[0021]** In a fifteenth aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include a slurry having X wt% aluminum oxide particles and Y wt% colloidal metal-oxide precursor particles, where X is greater than or equal to Y.

**[0022]** In a sixteenth aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include a slurry where a weight percent ratio of the aluminum oxide particles to the colloidal metal-oxide precursor particles in the slurry is in the range of 3:1 to 20:1. In some embodiments, the weight percent ratio may be in the range of 3:1 to 10:1.

**[0023]** In a seventeenth aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include calcinating the slurry on the surface of the substrate by heating the slurry to a calcination temperature in the range of 300 degrees C to 650 degrees C.

**[0024]** In an eighteenth aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include plating the nanoporous metal-oxide layer with an electroless plating method.

**[0025]** In an nineteenth aspect, the method of plating a metal substrate according to aspects of the preceding paragraph may include charging the nanoporous metal-oxide layer prior to the electroless plating method. In some embodiments, charging the nanoporous metal-oxide layer may include treating the nanoporous metal-oxide layer with an aminosilane. In some embodiments, the aminosilane may include aminopropyltriethoxysilane.

**[0026]** In a twentieth aspect, the method of plating a metal substrate according to aspects of the preceding paragraph may include adsorbing palladium complexes into the

nanoporous metal-oxide layer after charging the nanoporous metal-oxide layer and prior to the electroless plating method.

[0027] In a twenty-first aspect, the method of plating a metal substrate according to aspects of either of the two preceding paragraphs may include plating the nanoporous metal-oxide layer with an electroplating method performed after the electroless plating method.

[0028] In a twenty-second aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include a plated metal that is capable of passing a 3N/cm tape test after being annealed at 350 degrees C for 30 minutes.

[0029] In a twenty-third aspect, the method of plating a metal substrate according to aspects of any of the preceding paragraphs may include a slurry including a pore former. In some embodiments, the pore former may include polyethylene glycol.

[0030] In a twenty-fourth aspect, a metal plated substrate made by the method according to aspects of any of the preceding paragraphs is described.

[0031] In a twenty-fifth aspect, a method of plating copper on a substrate is described, the method including coating a surface of the substrate with a slurry including colloidal aluminum oxide hydroxide particles and aluminum oxide particles; calcinating the slurry on the surface of the substrate to form a nanoporous metal-oxide layer on the surface of the substrate; charging the nanoporous metal-oxide layer, where the charging includes treating the nanoporous metal-oxide layer with an aminosilane; and plating the nanoporous metal-oxide layer with copper after charging the nanoporous metal-oxide layer.

[0032] In a twenty-sixth aspect, an article is described, the article including a glass or glass-ceramic substrate including a surface having a plurality of vias formed therein, each via having an interior surface; a nanoporous metal-oxide layer coated on the interior surface of each of the plurality of vias, the nanoporous metal-oxide layer including aluminum oxide and an average pore size in the range of 5 nanometers to 30 nanometers; and a metal plating disposed on the nanoporous metal-oxide layer in each of the plurality of vias.

[0033] In a twenty-seventh aspect, the article according to aspects of the preceding paragraph may include at least one via that is a through via.

[0034] In a twenty-eighth aspect, the article according to aspects of either of the two preceding paragraphs may include a metal plating that includes copper.

- [0035] In a twenty-ninth aspect, the article according to aspects of any of the three preceding paragraphs may include metal plating that fills each of the plurality of the vias.
- [0036] In a thirtieth aspect, the article according to aspects of any of the four preceding paragraphs may include a nanoporous metal-oxide layer that is coated on at least a portion of the surface of the glass or glass-ceramic substrate.
- [0037] In a thirty-first aspect, the article according to aspects of the preceding paragraph may include a metal plating that is disposed on the nanoporous metal-oxide layer coated on the surface of the glass or glass-ceramic substrate. In some embodiments, the metal plating disposed on the nanoporous metal-oxide layer coated on the surface of the glass or glass ceramic substrate may be capable of passing a 3N/cm tape test after being annealed at 350 degrees C for 30 minutes.

#### *BRIEF DESCRIPTION OF THE DRAWINGS*

- [0038] The accompanying figures, which are incorporated herein, form part of the specification and illustrate embodiments of the present disclosure. Together with the description, the figures further serve to explain the principles of and to enable a person skilled in the relevant art(s) to make and use the disclosed embodiments. These figures are intended to be illustrative, not limiting. Although the disclosure is generally described in the context of these embodiments, it should be understood that it is not intended to limit the scope of the disclosure to these particular embodiments. In the drawings, like reference numbers indicate identical or functionally similar elements.
- [0039] FIG. 1 shows a substrate having through vias according to some embodiments.
- [0040] FIG. 2 shows a substrate having blind vias according to some embodiments.
- [0041] FIG. 3 shows a flowchart of a method for depositing a metallic layer on a surface according to some embodiments.
- [0042] FIGS. 4A–4C show a region of the substrate of FIG. 1 as it appears at different process steps of the flow chart of FIG. 3.
- [0043] FIGS. 5A and 5B show mechanical interlocking of palladium catalyst and electroless copper according to some embodiments.
- [0044] FIG. 6 shows an article according to some embodiments.



- [0045] FIG. 7 shows scanning electron microscope images of a spin-coated alumina AL20 coating.
- [0046] FIGS. 8A and 8B show scanning electron microscope images of an AL20 alumina coating.
- [0047] FIG. 9 shows a graph of particle size distribution for two slurries according to some embodiments.
- [0048] FIGS. 10A and 10B show scanning electron microscope images of a nanoporous aluminum oxide coating according to some embodiments.
- [0049] FIG. 11 shows a photograph of electroless copper formed on a glass substrate coated with an AL20 alumina coating.
- [0050] FIG. 12 shows a photograph of three samples with electroless copper plated on a glass substrate coated with an AL20 alumina coating after a 3N/cm tape test performed prior to annealing of the samples.
- [0051] FIG. 13 shows a photograph of three samples with electroless copper plated on a glass substrate coated with an AL20 alumina coating after a 3N/cm tape test performed after annealing of the samples at 350 degrees C.
- [0052] FIGS. 14A and 14B show scanning electron microscope images of an AL20 alumina coating on a glass substrate after a 3N/cm tape test performed after annealing of the samples at 350 degrees C.
- [0053] FIG. 15 shows a photograph of three samples of electroless copper plated on a glass substrate coated with a nanoporous aluminum oxide layer according to some embodiments.
- [0054] FIG. 16 shows a photograph of the three samples of FIG. 15 with electroplated copper deposited over the electroless copper according to some embodiments.
- [0055] FIG. 17 shows a scanning electron microscope image of an electroplated copper film deposited on an electroless copper film according to some embodiments.
- [0056] FIG. 18A and 18B show scanning electron microscope images of electroless and electroplated copper deposited on a nanoporous aluminum oxide layer according to some embodiments.
- [0057] FIG. 19A shows a TEM/EDX image of a cross-section of a substrate coated with a nanoporous aluminum oxide layer and plated with copper according to some embodiments. FIG. 19B shows the palladium content in the image of FIG. 19A. FIG. 19C shows the

copper content in the image of FIG. 19A. FIG. 19D shows the aluminum content in the image of FIG. 19A. FIG. 19E shows the silicon content in the image of FIG. 19A.

#### *DETAILED DESCRIPTION*

**[0058]** The following examples are illustrative, but not limiting, of the present disclosure. Other suitable modifications and adaptations of the variety of conditions and parameters normally encountered in the field, and which would be apparent to those skilled in the art, are within the spirit and scope of the disclosure.

**[0059]** Glass and glass ceramic substrates with vias are desirable for a number of applications. These vias typically need to be fully or conformally filled with conducting metallic materials, such as copper, to provide an electrical pathway through and/or within the substrate. The chemical inertness and low intrinsic roughness of glass and glass-ceramic materials, however, results in poor adhesion between a metallic material and the glass or glass-ceramic materials on surfaces of a glass or glass-ceramic substrate. For example, the chemical inertness and low intrinsic roughness may result in poor adhesion between a metallic material and interior surfaces of vias. Also, lack of adhesion between a metallic material and a glass or glass-ceramic substrate could lead to reliability issues such as cracking, delamination, and a path for moisture and other contaminants along the glass-metal interface. These reliability issues can result in undesirable electrical properties.

**[0060]** Described herein are methods to improve metallization of a glass or glass-ceramic substrate. In particular, described herein are methods to improve the effective adhesion between a metallic material, such as copper, and glass or glass-ceramic materials defining a surface of a substrate, including interior surfaces of vias. Improved effective adhesion between a metallic material and a glass or glass-ceramic, both inside vias and on other surfaces of a glass or glass-ceramic substrate, may be achieved with a nanoporous metal-oxide interlayer. This nanoporous metal-oxide interlayer may be a nanoporous aluminum oxide (alumina,  $\text{Al}_2\text{O}_3$ ) interlayer.

**[0061]** Nanoporous metal-oxide interlayers according to embodiments of the present application may increase the adhesion of a metallic material to a glass or glass-ceramic surface by creating a mechanical interlock between the glass or glass-ceramic surface and

a plated metallic material. In particular, the nanoporous structure of the metal-oxide interlayer with re-entrant geometries serves to create a mechanical interlock between the plated metallic material and the glass or glass-ceramic substrate. By creating nanoporous structures having desirable pore structures, a high degree of interlocking can be achieved, which results in strong adhesion between a plated metallic material and a glass or glass-ceramic surface.

**[0062]** The nanoporous interlayer may be made by coating all or a portion of a glass or glass-ceramic substrate with a slurry including colloidal metal-oxide precursor particles and metal-oxide particles (e.g., alumina particles) followed by calcination at a high temperature. These coating and calcination processes create sufficient adhesion between the nanoporous interlayer and the substrate. In some embodiments, the metal-oxide particles may be nanoparticles.

**[0063]** The combination of colloidal metal-oxide precursor particles and metal-oxide particles within a slurry creates a desired pore structure for the nanoporous interlayer. Mixtures of these two components in the slurry allow for the formation of desirable pore sizes, pore volumes, and/or pore geometries in the nanoporous interlayer. Appropriately controlled pore sizes, pore volumes, and/or pore geometries leads to suitable adhesion and interlocking between a glass or glass-ceramic material and a plated metallic material. In some embodiments, the plated metallic material may be adhered to the glass or glass-ceramic substrate such that plated metallic material is capable of passing a 3N/cm tape test after being annealing at 350 degrees C for 30 minutes.

**[0064]** As described and referred to herein, a “3N/cm tape test” is conducted according to ASTM 3359 using a tape having a specific adhesion strength of 3 N/cm when bonded to a conductive metal that is copper.

**[0065]** As used herein, “nanoporous” means a porous material having an average pore size in the range of 1 nanometer (nm) to 100 nanometers. A nanoporous structure includes a plurality of interconnected tunnels or “nanopores.” The nanoporous structures described herein are generally open structures, meaning that there is a path of travel from anywhere within a nanopore to the surface of the material. The nanoporous structures are open because of the manner in which they are formed. While the nanoporous layers

described herein are generally interconnected, it is possible that portions of the nanoporous network may be isolated from each other.

**[0066]** The “size” of a nanopore is the average dimension of a cross-section of the pore in a plane normal to the direction of the pore. So, if a cylindrical nanopore intersects a surface, the “size” of the nanopore is the diameter of the circle. For non-circular cross-sections, the “size” of the cross-section is the diameter of a circle having the same area as the cross-section. In some embodiments, an average (mean) nanopore size may be measured by obtaining a high-resolution scanning electron microscope (SEM) image, measuring the area of all visible nanopores in a 100 x 100 nm area, calculating the diameter of a circle with equivalent area for each visible nanopore, and calculating the average of these diameters. Where the nanopores are circular in shape, the same result may be obtained by directly measuring the diameter of each nanopore. In some embodiments, an average (mean) nanopore size may be measured by Barrett-Joyner-Halenda (BJH) nitrogen adsorption and desorption. Unless indicated otherwise, an average (mean) nanopore size discussed herein is measured by Barrett-Joyner-Halenda (BJH) nitrogen adsorption and desorption.

**[0067]** As used herein a “pore volume” is the ratio of a porous material’s open volume (volume occupied by pores, measured in cubic centimeters (cc)) to the porous material’s total mass (measured in grams (g)). Unless indicated otherwise, a porous material’s pore volume discussed herein is measured by BJH nitrogen adsorption and desorption.

**[0068]** As used herein, “nanoparticle” means a particle having at least one dimension in the range of 1 nanometer to 100 nanometers in size. The size of a nanoparticle may be measured by scanning electron microscopy or a dynamic light scattering (DLS) particle size analyzer. An average particle size of a batch of particles may be measured by measuring a sample of the particles using scanning electron microscopy or a DLS particle size analyzer, or may be calculated from the Brunauer–Emmett–Teller (BET) surface area of the sample. Unless indicated otherwise, the size of a nanoparticle discussed herein is measured by scanning electron microscopy and an average particle size of a batch of particles discussed herein is calculated from the Brunauer–Emmett–Teller (BET) surface area of the sample.

- [0069] As used herein, a “colloidal” particle means a particle that is dispersed and insoluble in a solution in which it mixed.
- [0070] As used herein, “metal-oxide precursor particle” means a particle that is a source particle for a metal-oxide particle. A metal-oxide precursor particle is capable of undergoing a chemical change that transforms it into a metal-oxide particle. The chemical change may be induced by the application of energy, such as heat. Exemplary metal-oxide precursor particles include oxide hydroxide particles, oxide acetate particles, and oxide nitrate particles.
- [0071] As used herein, “slurry” means a mixture including a solvent and particles that are insoluble in the solvent. The solvent may be aqueous or non-aqueous.
- [0072] As used herein, “calcination” or “calcinating” or “calcinated” means the heating of a substance to high temperature for the purpose of removing volatile ingredients and/or oxidizing the substance.
- [0073] As used herein, a “via” is an opening in a substrate. In some embodiments, a via may extend all the way through the substrate, in which case it is a “through via.” In some embodiments, a via may extend only partially through the substrate, in which case it is a “blind via.”
- [0074] FIG. 1 shows a cross-section of an article 100 according to some embodiments. Article 100 includes a substrate 110 having a first surface 112, a second surface 114, and a thickness 116 measured from first surface 112 to second surface 114. One or more vias 124 are formed in substrate 110 and extend from first surface 112 to second surface 114. Vias 124 are through vias. Each via 124 includes an interior surface 126 defining the shape of the via 124. Vias 124 may have an internal dimension 128 in the range of 10 microns to 20 microns, for example.
- [0075] Internal dimension 128 of vias 124 is defined by the smallest lateral distance between opposing interior surfaces 126 on a plane parallel to first surface 112. For example, for vias 124 with a circular cross-sectional shape, internal dimension 128 is the diameter of the circle, for vias 124 with an elliptical cross-sectional shape, internal dimension 128 is the diameter of the ellipse along the ellipse’s minor axis, and for vias 124 with a square cross-sectional shape, internal dimension 128 is the width or length of the square.

[0076] FIG. 2 shows a cross-section of an article 200 according to some embodiments. Article 200 includes a substrate 110 having a first surface 112, a second surface 114, and a thickness 116 measured from first surface 112 to second surface 114. One or more vias 224 are formed in substrate 110 and extend from first surface 112 towards second surface 114 without reaching second surface 114. Vias 224 are blind vias. Each via 224 includes an interior surface 226 defining the shape of the via 224. Vias 224 may have the same cross-sectional shapes and sizes as vias 124. But since vias 224 are blind vias, interior surface 226 includes a closed bottom surface 228 located between first surface 112 and second surface 114.

[0077] While FIGS. 1 and 2 show specific via configurations, various other via configurations may be used. By way of non-limiting example, vias having an hourglass shape, a barbell shape, beveled edges, or a variety of other geometries may be used instead of the cylindrical geometries shown in FIGS. 1 and 2. Vias may be substantially cylindrical, for example having a waist (point along the via with the smallest diameter) with a diameter that is at least 70%, at least 75%, or at least 80% of the diameter of an opening of the via on the first or second surface. Other via geometries may be used. Vias may have any suitable aspect ratio. For example, vias may have an aspect ratio of 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1, 9:1, 10:1, or any range having any two of these values as endpoints, or any open-ended range having any of these values as a lower bound. An aspect ratio for a via is the ratio of substrate 110 thickness 116 to a via internal dimension 128.

[0078] In some embodiments, article 100 may be an interposer with through-glass vias 124 and/or blind vias 224. These through-glass vias 124 and/or blind vias 224 may be fabricated by any suitable method. One method is to form a damage track in substrate 100 with a laser, followed by etching. Exemplary methods are described in U.S. Pat. No. 9,656,909, U.S. App. No. 62/588,615, and U.S. Pat. App. Pub. No. 2015/0166395, each of which is incorporated herein by reference in its entirety. Another method is to modify photosensitive glass with a laser, followed by etching.

[0079] FIG. 3 shows a flowchart of a method 300 for plating a metal on a substrate according to some embodiments. A method according to embodiments of the present application may include all or some of the steps shown in FIG. 3. Steps shown in method

300 are not exhaustive; other steps can be performed before, after, or between any of the described steps. In the following description, article 100 is used to illustrate the steps of method 300. However, method 300 may be applied to any article or substrate discussed herein (e.g., article 200).

**[0080]** In step 310, a surface of substrate 110 is coated with a slurry including colloidal metal-oxide precursor particles and aluminum oxide particles. The surface of substrate 110 coated with the slurry may be all or a portion of first surface 112, all or a portion of second surface 114, and/or all or a portion of interior surfaces 126 of vias 124. In some embodiments, only interior surfaces 126 of vias 124 may be coated with slurry. In such embodiments, any slurry coated on first surface 112 and/or second surface 114 during coating of interior surfaces 126 is removed. Suitable coating methods include, but are not limited to, wash-coating, spin-coating, and dip-coating. The coating time may be in the range of 10 seconds to 10 minutes.

**[0081]** In some embodiments the slurry may include an aqueous solvent, such as DI (deionized) water. In some embodiments, slurry may include a non-aqueous. In some embodiments, slurry may include an aqueous solvent and a non-aqueous solvent.

**[0082]** Colloidal metal-oxide precursor particles, aluminum oxide particles, and solvent are present at desired weight percentages (wt%) in the slurry. In some embodiments, the slurry may include solvent at a weight percent in the range of 75 wt% to 99 wt%, including subranges. For example, the slurry may include 75 wt%, 76 wt%, 77 wt%, 78 wt%, 79 wt%, 80 wt%, 81 wt%, 82 wt%, 83 wt%, 84 wt%, 85 wt%, 86 wt%, 87 wt%, 88 wt%, 89 wt%, 90 wt%, 91 wt%, 92 wt%, 93 wt%, 94 wt%, 95 wt%, 96 wt%, 97 wt%, 98 wt%, or 99 wt% solvent, or solvent at a weight percent within any range having any two of these values as endpoints.

**[0083]** In some embodiments, the slurry may include colloidal metal-oxide precursor particles at a weight percent in the range of 0.5 wt% to 10 wt%, including subranges. For example, the slurry may include 0.5 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 6 wt%, 7 wt%, 8 wt%, 9 wt%, or 10 wt% colloidal metal-oxide precursor particles, or colloidal metal-oxide precursor particles at a weight percent within any range having any two of these values as endpoints. In some embodiments, the slurry may include aluminum oxide particles at a weight percent in the range of 0.5 wt% to 10 wt%, including subranges. For

example, the slurry may include 0.5 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 6 wt%, 7 wt%, 8 wt%, 9 wt%, or 10 wt% aluminum oxide particles, or aluminum oxide particles at a weight percent within any range having any two of these values as endpoints.

**[0084]** In some embodiments, the wt% of aluminum oxide particles in the slurry may be greater than the wt% of colloidal metal-oxide precursor particles in the slurry. In some embodiments, the wt% of aluminum oxide particles in the slurry may be less than the wt% of colloidal metal-oxide precursor particles in the slurry. In some embodiments, the wt% of aluminum oxide particles in the slurry may be equal to the wt% of colloidal metal-oxide precursor particles in the slurry.

**[0085]** In some embodiments, the weight ratio of aluminum oxide particles to colloidal metal-oxide precursor particles in the slurry may be in the range of 1:1 to 20:1, including subranges. For example, the weight ratio of aluminum oxide particles to colloidal metal-oxide precursor particles in the slurry may be 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1, 9:1, 10:1, 11:1, 12:1, 13:1, 14:1, 15:1, 16:1, 17:1, 18:1, 19:1, or 20:1, or within any range having any two these values as endpoints. In some embodiments, the weight ratio of aluminum oxide particles to colloidal metal-oxide precursor particles in the slurry may be in the range of 3:1 to 20:1. In some embodiments, the weight ratio of aluminum oxide particles to colloidal metal-oxide precursor particles in the slurry may be in the range of 3:1 to 10:1.

**[0086]** In some embodiments, the aluminum oxide particles in the slurry may be nanoparticles (gamma( $\gamma$ )-aluminum oxide particles). In some embodiments, the aluminum oxide particles may have an average particle size in the range of 10 nanometers to 100 nanometers, including subranges. For example, the aluminum oxide particles may have an average particle size of 10 nanometers, 20 nanometers, 25 nanometers, 30 nanometers, 40 nanometers, 50 nanometers, 60 nanometers, 70 nanometers, 75 nanometers, 80 nanometers, 90 nanometers, or 100 nanometers, or within any range having any two of these values as endpoints.

**[0087]** The colloidal metal-oxide precursor particles in the slurry may include, but are not limited to, aluminum oxide precursor particles, silicon oxide precursor particles, titanium oxide precursor particles, cerium oxide precursor particles, zirconium oxide precursor particles, or a combination of two or more of these types of metal-oxide



precursor particles. In some embodiments, the metal-oxide precursor particles may be nanoparticles. In some embodiments, the colloidal metal-oxide precursor particles may have an average particle size in the range of 50 nanometers to 100 nanometers, including subranges. For example, the aluminum oxide particles may have an average particle size of 50 nanometers, 55 nanometers, 60 nanometers, 65 nanometers, 70 nanometers, 75 nanometers, 80 nanometers, 85 nanometers, 90 nanometers, 95 nanometers, or 100 nanometers, or within any range having any two of these values as endpoints. In some embodiments, the colloidal metal-oxide precursor particles may have an average particle size in the range of 60 nanometers to 90 nanometers.

**[0088]** In some embodiments, the average particles size of aluminum oxide particles in the slurry and the average size of the colloidal metal-oxide precursor particles in the slurry may be different. In some embodiments, the average particle size of the colloidal metal-oxide precursor particles may be less than the average particle size of the aluminum oxide particles. In some embodiments, the average particle size of the colloidal metal-oxide precursor particles may be greater than the average particle size of the aluminum oxide particles. In some embodiments, the average particle size of the colloidal metal-oxide precursor particles may be equal to the average particle size of the aluminum oxide particles.

**[0089]** In some embodiments, the colloidal aluminum oxide precursor particles may include colloidal aluminum oxide hydroxide (also called boehmite or alumina hydrate) particles. In some embodiments, the colloidal aluminum oxide hydroxide particles may be NYACOL<sup>®</sup> Colloidal Alumina manufactured by Nyacol Nano Technologies, Inc. In some embodiments, the colloidal aluminum oxide hydroxide particles may be NYACOL<sup>®</sup> AL20 Colloidal Alumina manufactured by Nyacol Nano Technologies, Inc. In some embodiments, the colloidal aluminum oxide hydroxide particles may be DISPERAL<sup>®</sup> colloidal boehmite alumina manufactured by Sasol. In some embodiments, the colloidal aluminum oxide hydroxide particles may be DISPERAL<sup>®</sup> P2 colloidal boehmite alumina manufactured by Sasol.

**[0090]** In some embodiments, the colloidal titanium oxide precursor particles may include colloidal titanium oxide particles with hydroxyl groups on the surface (i.e., colloidal titanium oxide hydroxide ). In some embodiments, the colloidal titanium oxide

precursor particles may be NYACOL<sup>®</sup> Colloidal Titanium Dioxide manufactured by Nyacol Nano Technologies, Inc. In some embodiments, the colloidal titanium oxide precursor particles may be NYACOL<sup>®</sup> TiSol A Colloidal Titanium Dioxide manufactured by Nyacol Nano Technologies, Inc.

**[0091]** In some embodiments, the colloidal cerium oxide precursor particles may include colloidal cerium acetate or cerium nitrite. In some embodiments, the colloidal cerium oxide particles may be NYACOL<sup>®</sup> Colloidal Cerium Oxide manufactured by Nyacol Nano Technologies, Inc. In some embodiments, the colloidal cerium oxide precursor particles may be NYACOL<sup>®</sup> CeO<sub>2</sub>(AC) manufactured by Nyacol Nano Technologies, Inc.

**[0092]** In some embodiments, the colloidal silicon oxide precursor particles may include colloidal silica particles with hydroxyl groups on the surface (i.e., colloidal silicon oxide hydroxide ). For example, the colloidal silicon oxide precursor particles may include LUDOX<sup>®</sup> colloidal silica.

**[0093]** In some embodiments, the colloidal zirconium oxide precursor particles may include colloidal zirconia particles with hydroxyl groups on the surface (i.e., colloidal zirconium oxide hydroxide ) or colloidal zirconium acetate. In some embodiments, the colloidal zirconium oxide particles may be NYACOL<sup>®</sup> Colloidal Zirconia manufactured by Nyacol Nano Technologies, Inc.

**[0094]** In some embodiments, the slurry may include a pore former to control the formation of pores in a nanoporous metal-oxide layer during calcination. In some embodiments, the pore former may include polyethylene glycol (PEG). In some embodiments, the slurry may include 8 wt% to 32 wt% pore former by weight of solids in the slurry, including subranges. For example, the slurry may include 8 wt%, 10 wt%, 16 wt%, 20 wt%, 24 wt%, 30 wt%, or 32 wt% pore former by weight of solids in the slurry, or pore former at a weight percent within any range having any two of these values as endpoints.

**[0095]** In step 320, the coating of slurry is calcinated on a surface of substrate 110 to form a nanoporous metal-oxide layer on the surface of substrate 110. Calcination is performed by applying heat to the coating of slurry. During calcination, the coating of slurry may be heated to a calcination temperature in the range of 300 degrees C to 650

degrees C, including subranges. For example, the coating of slurry may be heated to a temperature of 300 degrees C, 350 degrees C, 400 degrees C, 450 degrees C, 500 degrees C, 550 degrees C, 600 degrees C, or 650 degrees C during calcination, or within any range having any two of these values as endpoints. In some embodiments, the coating of slurry may be heated to a temperature in the range of 400 degrees C to 500 degrees C. A calcination temperature may be measured by a thermal couple disposed in the oven.

**[0096]** Calcination of the coating of slurry at the calcination temperature may be performed for a time in the range of 5 minutes to 6 hours, including subranges. For example, calcination may be performed for 5 minutes, 30 minutes, 1 hour, 2 hours, 3 hours, 4 hours, 5 hours, 6 hours, or within any range having any two of these values as end points. In some embodiments, calcination may be performed for a time in the range of 30 minutes to 5 hours. In some embodiments, the temperature ramp rate for a calcination process may be in the range of 20 degrees C/hour to 300 degrees C/hour, including subranges. For example, the temperature ramp rate may be 20 degrees C/hour, 50 degrees C/hour, 100 degrees C/hour, 150 degrees C/hour, 200 degrees C/hour, 250 degrees C/hour, 300 degrees C/hour, or a ramp rate within in range having any two of these values as endpoints. In some embodiments, calcination may be performed in an oven. In some embodiments, calcination may be performed on a hot plate. For example, calcination may be performed directly on a hot plate with a set temperature of 300 degrees C for 5 minutes

**[0097]** In some embodiments, the coating of slurry on substrate 110 may be dried prior to calcinating the slurry. In some embodiments, drying may be performed at a temperature in the range of room temperature (23 degrees C) to 110 degrees C. In some embodiments, drying may be performed a time in the range of 5 minutes to 1 hour. In some embodiments, drying may include flowing nitrogen gas over the coating of slurry.

**[0098]** In step 330, the nanoporous metal-oxide layer may be charged to ensure a suitable cationic charge state of the glass surface for catalyst adsorption in step 340. The palladium complexes adsorbed in step 340 typically exist in anionic form and, therefore, their adsorption on the nanoporous metal-oxide layer can be enhanced by cationic surface groups such as protonated amines. A suitable number of palladium complexes can provide a sufficient number of nucleation sites within the nanoporous layer to seed

deposition of a metal material during electroless plating. By providing a suitable amount of nucleation sites, a suitable bond strength between a plated metallic film and a nanoporous metal-oxide layer can be achieved, which facilitates the adhesion between the metallic film and surfaces of substrate 110.

**[0099]** Charging the nanoporous metal-oxide layer may include treating the nanoporous metal-oxide layer with an aminosilane, such as aminopropyltriethoxysilane (APTES). In some embodiments, treating the nanoporous metal-oxide layer with APTES may include soaking the nanoporous metal-oxide layer in 1.0 vol% APTES solution (95 mL methanol, 4 mL H<sub>2</sub>O, and 1 mL APTES) at room temperature for 15 minutes. In some embodiments, charging the nanoporous metal-oxide layer may include treating the nanoporous metal-oxide layer with cationic polymers. In some embodiments, the treated the nanoporous metal-oxide layer may be dried after step 330. For example, the treated the nanoporous metal-oxide layer may be dried in an oven at approximately 120 degrees C for 30 minutes.

**[0100]** In step 340, palladium complexes may be adsorbed on the nanoporous metal-oxide layer. This palladium complex adsorption step may include treatment of the nanoporous metal-oxide layer with K<sub>2</sub>PdCl<sub>4</sub> (potassium tetrachloropalladate), ionic palladium, and/or a Sn/Pd (tin/palladium) colloidal solution. If K<sub>2</sub>PdCl<sub>4</sub> or ionic palladium are used in step 340, step 340 may include reduction of the K<sub>2</sub>PdCl<sub>4</sub> or ionic palladium into metallic palladium. In such embodiments, the reduction of K<sub>2</sub>PdCl<sub>4</sub> or ionic palladium forms palladium particles. Such a reduction may be performed by reacting the K<sub>2</sub>PdCl<sub>4</sub> or ionic palladium with dimethylaminoborane (DMAB). If a Sn/Pd colloidal solution is used in step 340, the palladium is already in Pd<sup>0</sup> form with a tin shell around it. The tin shell can be removed by acid etching.

**[0101]** This treatment in step 340 results in the adsorption of metallic palladium particles (Pd<sup>0</sup> particles) on surfaces of the nanoporous metal-oxide layer, including interior surfaces defining the porous structure of nanoporous metal-oxide layer. The adsorbed palladium particles may have an average particle size smaller than the average pore size of the nanoporous metal-oxide layer. In some embodiments, the adsorbed palladium particles may have an average particle size in the range of 1 nanometer to 10 nanometers, including subranges. For example, the adsorbed palladium particles may have an average

particle size of 1 nanometer, 2 nanometers, 3 nanometers, 4 nanometers, 5 nanometers, 6 nanometers, 7 nanometers, 8 nanometers, 9 nanometers, 10 nanometers, or within any range having any two of these values as endpoints.

**[0102]** The surface roughness and/or high porosity of the nanoporous metal-oxide layer on substrate 110 leads to more palladium catalyst inside the nanoporous metal-oxide layer after step 340, particularly if the cationic surface treatment of step 330 is used. More palladium catalyst leads to more metallic material inside the nanoporous metal-oxide layer, thus creating strong mechanical interlocking between the nanoporous metal-oxide layer and a plated metallic film. In some embodiments, a different catalyst material may be used in step 340 to catalyze the nanoporous metal-oxide layer prior to metallic plating.

**[0103]** In steps 350 and 360, the nanoporous metal-oxide layer is plated with a metal to form a metallic film, which is adhered to surfaces of substrate 110 via the nanoporous metal-oxide layer. Step 350 includes an electroless plating method for plating metal on the nanoporous metal-oxide layer. The electroless plating method may fill pores of the nanoporous metal-oxide layer with a metallic material and coat an exterior surface of the nanoporous metal-oxide layer (e.g., exterior surface 412 shown in FIG. 4C) with a metallic film. Filling the pores of the nanoporous metal-oxide layer with the metallic material mechanically interlocks the metallic film to surfaces of substrate 110. In some embodiments, the metal plated in step 350 may include copper. Other metallic materials that may be plated in step 350 include, but are not limited to, silver, gold, ruthenium, rhodium, palladium, osmium, iridium and platinum.

**[0104]** The thickness of the metallic film plated in step 350 may be about 100 nanometers to about 200 nanometers. In some embodiments, the thickness of the metallic film formed in step 350 may be in the range of 50 nanometers to 250 nanometers, including subranges. For example, the thickness of the metallic film formed in step 350 may be 50 nanometers, 75 nanometers, 100 nanometers, 125 nanometers, 150 nanometers, 175 nanometers, 200 nanometers, 225 nanometers, or 250 nanometers, or within any range having any two of these values as endpoints.

**[0105]** Step 360 includes an electroplating method for plating metal on an exterior surface of the metallic film deposited in step 350 (e.g., exterior surface 424 of film 422

shown in FIG. 4C). The electroplating method may form a film (e.g., film 426) on the top surface of the electrolessly plated film. In some embodiments, the metal plated in step 360 may include copper. Other metallic materials that may be plated in step 360 include, but are not limited to, silver, gold, ruthenium, rhodium, palladium, osmium, iridium and platinum.

**[0106]** Step 360 may be performed if a metallic film thicker than that formed in step 350 is desired. Electroless plating has certain advantages, such as the ability to plate onto an initially non-conductive surface. But, electroless plating can be slow when thick layers are desired. Once an initial film of electroless metal is deposited to form a conductive surface, electroplating may be used to more quickly plate a thicker film of metal. In some embodiments, electroless plating alone may be used to plate the metallic film. In such embodiments, step 360 may not be included, and step 350 may be used to deposit a metallic film with a desired thickness.

**[0107]** The thickness of the metallic film plated in step 360 may be greater than 1 micron (micrometer,  $\mu\text{m}$ ). In some embodiments, the thickness of the metallic film formed in step 360 may be in the range of 1 micron to 100 microns, including subranges. For example, the thickness of the metallic film formed in step 360 may be 1 micron, 5 microns, 10 microns, 20 microns, 30 microns, 40 microns, 50 microns, 60 microns, 70 microns, 80 microns, 100 microns, or within a range having any two of these values as endpoints. In embodiments not including step 360, the metallic film plated in step 350 may have any of these thicknesses.

**[0108]** In some embodiments, the metallic film formed in step 350 and/or step 360 may completely fill vias 124 of substrate 110. For example, FIG. 6 shows metal plating 620 completely filling vias 124 of article 600. In other words, the metallic film may completely fill the volume defined by the interior surfaces 126 of vias 124. In some embodiments, the metallic film formed in step 350 and/or step 360 may not completely fill vias 124 of substrate 110. In other words, a portion of the volume defined by the interior surfaces 126 of vias 124 may remain open after plating of the metallic film. By controlling the thickness of the metallic film formed in 350 and/or step 360, the degree at which the vias are filled can be controlled.

- [0109] FIGS. 4A–4C illustrate how substrate 110 is processed during various steps of method 300. Specifically, FIGS. 4A–4C show region 400 of FIG. 1 and how an interior surface 126 of a via 124 is processed during various steps of method. Other surfaces, such as first surface 112 and second surface 114 may be processed in the same way. Further, while FIGS. 4A – 4C show a single via 124, all vias 124 of substrate may be processed as shown in FIGS. 4A–4C. Although FIGS. 4A–4C show a specific substrate geometry, any substrate geometry for which metallization is desired may be used.
- [0110] FIG. 4A shows interior surface 126 of a via 124 prior to coating interior surface 126 with a slurry. FIG. 4B shows a nanoporous metal-oxide layer 410 coated on interior surface 126 of via 124. As discussed in regards to steps 310 and 320, nanoporous metal-oxide layer 410 is formed by coating a slurry on interior surface 126 and calcinating the slurry to create a nanoporous metal-oxide layer 410 having a desired porous structure (pore size, distribution, and geometry).
- [0111] In some embodiments, nanoporous metal-oxide layer 410 may have an average pore size in the range of 5 nanometers to 30 nanometers, including subranges. For example, nanoporous metal-oxide layer 410 may have an average pore size of 5 nanometers, 7.5 nanometers, 10 nanometers, 12.5 nanometers, 15 nanometers, 17.5 nanometers, 20 nanometers, 22.5 nanometers, 25 nanometers, 27.5 nanometers, or 30 nanometers, or within any range having any two of these values as endpoints. In some embodiments, nanoporous metal-oxide layer 410 may have an average pore size in the range of 5 nanometers to 10 nanometers, including subranges. For example, nanoporous metal-oxide layer 410 may have an average pore size of 5 nanometers, 5.5 nanometers, 6 nanometers, 6.5 nanometers, 7 nanometers, 8.5 nanometers, 9 nanometers, 9.5 nanometers, or 10 nanometers, or within any range having any two of these values as endpoints. In some embodiments, nanoporous metal-oxide layer 410 may have an average pore size in the range of 6 nanometers to 8 nanometers, including subranges. For example, nanoporous metal-oxide layer 410 may have an average pore size of 6 nanometers, 6.25 nanometers, 6.5 nanometers, 6.75 nanometers, 7 nanometers, 7.25 nanometers, 7.5 nanometers, 7.75 nanometers, or 8 nanometers, or within any range having any two of these values as endpoints.

**[0112]** In some embodiments, nanoporous metal-oxide layer 410 may have a pore volume in the range of 0.3 cubic centimeters per gram (cc/g) to 10 cubic centimeters per gram (cc/g), including subranges. For example, nanoporous metal-oxide layer 410 may have a pore volume of 0.3 cc/g, 0.5 cc/g, 1 cc/g, 2 cc/g, 3 cc/g, 4 cc/g, 5 cc/g, 6 cc/g, 7 cc/g, 8 cc/g, 9 cc/g, or 10 cc/g, or within any range having any two these values as endpoints. In some embodiments, nanoporous metal-oxide layer 410 may have a pore volume in the range of 0.3 cc/g to 0.6 cc/g, including subranges. For example, nanoporous metal-oxide layer 410 may have a pore volume of 0.3 cc/g, 0.35 cc/g, 0.4 cc/g, 0.45 cc/g, 0.5 cc/g, 0.55 cc/g, or 0.6 cc/g, or within any range having any two these values as endpoints.

**[0113]** In some embodiments, nanoporous metal-oxide layer 410 may have a thickness in the range of 10 nanometers to 200 nanometers, including subranges. For example, the thickness of nanoporous metal-oxide layer 410 may be 10 nanometers, 20 nanometers, 30 nanometers, 40 nanometers, 50 nanometers, 60 nanometers, 70 nanometers, 80 nanometers, 90 nanometers, 100 nanometers, 110 nanometers, 120 nanometers, 130 nanometers, 140 nanometers, 150 nanometers, 160 nanometers, 170 nanometers, 180 nanometers, 190 nanometers, 200 nanometers, or within a range having any two of these values as endpoints. In some embodiments, the thickness of nanoporous metal-oxide layer 410 may be in the range of 50 nanometers to 150 nanometers.

**[0114]** FIG. 4C shows exterior surface 412 of nanoporous metal-oxide layer 410 plated with metallic film 420 after step 350 and/or step 360. Metallic film 420 includes electrolessly plated metallic film 422 plated on an exterior surface 412 of nanoporous metal-oxide layer 410 and electroplated metallic film 426 plated on an exterior surface 424 of electrolessly plated metallic film 422. In embodiments where only electroless plating is used, metallic film 420 will only include electrolessly plated metallic film 422 plated at a desired thickness.

**[0115]** FIGS. 5A and 5B illustrate the processing of nanoporous metal-oxide layer 410 during catalyzation with palladium particles in step 340 and electroless plating in step 350. FIG. 5A shows Pd<sup>0</sup> particles 500 penetrated into nanopores 510 of nanoporous metal-oxide layer 410 and adsorbed onto surfaces 512 of the nanopores 510. FIG. 5B



shows nanopores 510 filed with electrolessly plated metal 520 (e.g., copper) after step 350.

[0116] FIG. 6 shows an article 600 according to some embodiments. Article 600 includes substrate 110 with a plurality of vias 124 formed in first surface 112, each via 124 having an interior surface 126. A nanoporous metal-oxide layer 610 is coated on the interior surface 126 of each of the plurality of vias 124. Nanoporous metal-oxide layer 610 may be the same as or similar to nanoporous metal-oxide layer 410. Disposed on nanoporous metal-oxide layer 610 in each of the plurality of vias 124 is a metal plating 620. Metal plating may be a plated metallic film the same as or similar to metallic film 420. In some embodiments, the metal plating 620 may include copper. In some embodiments, article 600 may be an electrical interposer, such as a 3D (three-dimensional) interposer.

[0117] In some embodiments, as shown in FIG. 6, nanoporous metal-oxide layer 610 may be coated on at least a portion of first surface 112 of substrate 110. In some embodiments, nanoporous metal-oxide layer 610 may be coated on at least a portion of second surface 114 of substrate 110. In some embodiments, metal plating 620 may be disposed on all portions of article 600 coated with nanoporous metal-oxide layer 610. In some embodiments, metal plating 620 may be disposed on at least a portion of nanoporous metal-oxide layer 610 coated on first surface 112. In some embodiments, metal plating 620 may be disposed on at least a portion of nanoporous metal-oxide layer 610 coated on second surface 114. In some embodiments, metal plating 620 disposed on nanoporous metal-oxide layer 610 coated on first surface 112 and/or second surface 114 of substrate 110 may be capable of passing a 3N/cm tape test after being annealed at 350 degrees C for 30 minutes.

[0118] The following examples illustrate the effectiveness of nanoporous metal-oxide layers according to embodiments of the present application. In particular, the following examples illustrate the effectiveness of nanoporous metal-oxide layers made from a slurry including colloidal metal-oxide precursor particles and aluminum oxide particles according to embodiments discussed herein.

Example 1: Spin-coated AL20 Coating

[0119] In this example, two 6 inch diameter by 0.7 millimeter (mm) thick Eagle XG® (EXG) glass wafers were spin-coated with as-received 1:1 diluent to AL20 solution

purchased from Nano Technologies, Inc. after soaking for 1 minute. In other words, the wafers were spin coated with a slurry including only colloidal metal-oxide precursor particles (aluminum oxide hydroxide particles). The first wafer was spun at 500 rotations per minute (rpm) for 30 seconds and at 1000 rpm for 15 seconds and then at 300 rpm for 15 seconds. The second wafer was spun at 1000 rpm for 30 seconds, and again at 1000 rpm for 15 seconds, and then at 300 rpm for 15 seconds. The coated wafers were baked on hot plate at 300 degrees C for 3 minutes. The spin-coated EXG wafers had a uniform nanoporous alumina layer with a thickness of 318 nm, as shown in SEM images 700 of FIG. 7. It was found that lower rpm spinning and ramp improved the uniformity of the AL20 coating.

**[0120]** After APTES treatment for 15 minutes, the coated wafers were baked in an oven for 30 minutes. Then, the wafers were soaked in a  $K_2PdCl_4$  solution for 2 minutes and dried. APTES treatment included soaking the coated wafers in a 1.0 vol% APTES solution (95 mL methanol, 4 mL  $H_2O$  and 1 mL APTES) at room temperature for 15 minutes.

**[0121]** After drying, the samples were electrolessly plated with a copper film. The electroless copper thickness was 47 nanometers. After electroless plating, a copper film was electroplated on the electrolessly plated copper film. The electroplating was performed using an electric resistance of 1.5 ohms per centimeter squared ( $ohm/cm^2$ ). The electroplated copper film thickness was 2.5 microns.

**[0122]** After electroplating, the adhesion force was measured by a peel test to be greater than 3.7 N/cm. However, all the samples failed a 3N/cm tape test after electroplating of 2.5 microns of copper film.

#### Example 2: Wash-coated AL20 Coating

**[0123]** In this example, two 6 inch diameter by 0.7 mm thick EXG glass wafers were wash-coated with a slurry of as-received 1:1 diluent to AL20 solution purchased from Nano Technologies, Inc. Both samples were then baked to calcinate the slurry on the wafers. After baking, the first sample was APTES treated, catalyzed with palladium particles, and electrolessly plated with a copper film. APTES treatment included soaking the first sample in a 1.0 vol% APTES solution (95 mL methanol, 4 mL  $H_2O$  and 1 mL APTES) at room temperature for 15 minutes. The second wafer was processed in the

same way as the first, the exception that APTES treatment was not performed on the second sample. The wash-coated wafers had a nanoporous metal-oxide layer with a thickness of 48 nanometers, as shown in SEM images 800 and 850 of FIGS. 8A and 8B.

**[0124]** The first wafer showed a full coverage copper film but with some surface texture. The second wafer had a discontinuous copper film. This example shows that APTES treatment can improve electroless plating of a metallic film on a nanoporous metal-oxide layer.

Example 3: Dip-coated Alumina Nanoparticle-AL20 Coating

**[0125]** In this example, 12 pieces of 2 inch by 2 inch by 0.7 mm thick EXG glass substrates were dip-coated with two different aqueous slurries containing a mixture of gamma( $\gamma$ )-alumina particles (aluminum oxide nanoparticles) and as-received AL20. In other words, the substrates were dip-coated with a slurry including both metal oxide particles and colloidal metal-oxide precursor particles. The first slurry included 5 wt% gamma-alumina particles and 5 wt% AL20 and the second slurry included 1 wt% gamma-alumina particles and 1 wt% AL20. Two different withdraw speeds, 50 mm/minute and 250 mm/minute, were chosen for each slurry.

**[0126]** The gamma-alumina particles had a Brunauer–Emmett–Teller (BET) surface area of 173.8 meters squared per gram ( $\text{m}^2/\text{g}$ ), which led to an average calculated particle size of 10 nanometers. SEM analysis indicated that the gamma-alumina particles had particle size of around 50 nanometers. Dynamic light scattering data indicated that the two slurries had similarly wide particle size distribution in the range of 30 nanometers to 2 microns, as shown in graph 900 of FIG. 9.

**[0127]** After drying in 120 degrees C for 1 hour, the samples were calcinated in an oven at 400 degrees C for 1 hour with a heating and cooling rate of 60 degrees C/hour. The thickness of nanoporous metal-oxide layers formed on the substrates were measured by SEM to be in the range of about 15 nanometers to about 83 nanometers. The SEM images 1000 and 1050 of FIGS. 10A and 10B show an exemplary 83.8 nanometer thick nanoporous metal-oxide layer.

**[0128]** After calcination, half of the nanoporous metal-oxide layers were treated with APTES and the other half were not. APTES treatment included soaking the substrates in a 1.0 vol% APTES solution (95 mL methanol, 4 mL  $\text{H}_2\text{O}$  and 1 mL APTES) at room

temperature for 15 minutes. Then, all the nanoporous metal-oxide layers were catalyzed using a  $K_2PdCl_4$  solution that was reduced with DMAB. And after catalyzation, the nanoporous metal-oxide layers were electrolessly plated with a metallic film.

[0129] The test results for four of the substrates, two coated with the 5 wt%/5 wt% slurry and two coated with the 1 wt%/1 wt% slurry, are shown below in Table 1. As shown in Table 1, a higher concentration slurry and a faster withdraw speed resulted in a thicker nanoporous metal-oxide layer. Also, a higher concentration slurry and a faster withdraw speed resulted in a higher surface roughness for a nanoporous metal-oxide layer. The thicker nanoporous layers of samples #4-9 and #4-10 appeared more uniform than the thinner nanoporous layers of samples #4-11 and #4-12.

Sample	Slurry	Withdrawal speed, mm/minute	Nanoporous layer thickness, nm	Surface roughness Ra, nm
#4-9	5% $\gamma$ -alumina+5%AL20	50	63	11.9
#4-10	5% $\gamma$ -alumina+5%AL20	250	83	39.1
#4-11	1% $\gamma$ -alumina+1%AL20	50	15	1.7
#4-12	1% $\gamma$ -alumina+1%AL20	250	30	3.7

**Table 1: Comparison of different substrates dip-coated with alumina nanoparticle-AL20 slurries**

[0130] Furthermore, as with Example 2, it was found that APTES treatment significantly improves the coverage of a copper film on a nanoporous metal-oxide layer. With APTES treatment full coverage of a copper film was achieved. This example illustrates the ability to form suitable nanoporous metal-oxide layers by calcinating a coating of slurry including both metal oxide particles and colloidal metal-oxide precursor particles.

Example 4: Dip-coated AL20 Coating with Copper Plating

[0131] In this example, 2 inch by 2 inch by 0.7 mm thick EXG glass substrates were dip-coated with four diluted AL20 slurries with 1:1, 1:3, 1:6, and 1:12 AL20 to water dilution ratios. In other words, the wafers were coated with slurries including only colloidal metal-oxide precursor particles (aluminum oxide hydroxide particles) at different dilution ratios. First, each substrate was dip-coated using the same process and the same withdrawal speed of 50 mm/minute. Then, after drying in an oven at 120 degrees C for 1

hour, the substrates were coated again with the same dip-coating process followed by drying in an oven at 120 degrees C.

[0132] After drying, the coated substrates were calcined in an oven at 400 degrees C for 1 hour with a heating and cooling rate of 60 degrees C/hour. Table 2 below lists the nanoporous metal-oxide layer thickness of the calcined AL20 coating samples measured by SEM.

Sample	Ratio of AL20 to DI water by weight	AL20 coating thickness, nm	Sheet resistance, ohm/cm <sup>2</sup>
#10-2	1:1	415	1.11
#23-1	1:3	149	1.13
#23-2	1:6	73	1.16
#23-3	1:12	50	1.25

**Table 2: Comparison of different substrates dip-coated with AL20 slurries**

[0133] The calcined nanoporous metal-oxide layers then went through a cleaning process, and then were soaked in a 1.0 vol% APTES solution (95 mL methanol, 4 mL H<sub>2</sub>O and 1 mL APTES) at room temperature for 15 min. After a gentle rinse with DI water three times, the substrates were placed in an oven at 120 degrees C for 30 minutes to dry. After drying, the treated nanoporous metal-oxide layers were soaked in a K<sub>2</sub>PdCl<sub>4</sub> solution at 45 degrees C for 3 minutes, followed by reduction into metallic palladium particles at room temperature by DMAB.

[0134] Electroless copper plating was conducted in an electroless plating bath at 34 degrees C for 2 minutes. FIG. 11 shows an exemplary photograph 1100 of one of the plated samples showing that a full coverage copper film was formed on each nanoporous metal-oxide layer. After drying the substrates with a nitrogen spray gun, the substrates were annealed in a vacuum oven at 250 degrees C for 30 minutes. Immediately after drying, the sheet resistance of the copper films was measured with a single point measurement. The measured sheet resistance, measured in ohm per square centimeter (ohm/cm<sup>2</sup>), of each sample is listed in Table 2.

[0135] The electroless-plated samples were then placed in a 1M (molar) CuSO<sub>4</sub> (copper sulfate) solution for electroplating with a 50 mA (milliampere) current for 1 hour. After manually drying the samples with a nitrogen spray gun, a 3N/cm tape test was conducted on each sample. All the samples passed the test. Photograph 1200 of FIG. 12 shows three of the tested samples (#23-1, #23-2, and #23-3) after the 3N/cm tape test. But, when the

3N/cm tape test was repeated after annealing the samples in vacuum oven at 350 degrees C for 30 minutes with a ramp rate of 3 C/min, all samples failed the test. Photograph 1300 in FIG. 13 shows the electroplated copper removed from samples #23-1, #23-2, and #23-3 by the tape.

[0136] Upon examination of the surface morphology of the samples, it was discovered that failure of the sample in the second 3N/cm tape test was due to weak bonding between the electroplated copper film and the nanoporous alumina layer formed by calcinating the coating of slurries including only colloidal metal-oxide precursor particles. FIG. 14A shows an SEM image 1400 of the surface morphology of sample #23-1 with 60 degree tilt. In image 1400 it can be seen that the electroplated copper film has been removed from the nanoporous alumina layer by the tape. SEM image 1450 in FIG. 14B is a zoomed-in image of the interface between the nanoporous alumina layer and nanoporous alumina layer in image 1400 showing the removal of the electroplated copper film.

Example 5: Dip-coated Alumina Nanoparticle and AL20 Coating with Copper Plating

[0137] In this example, three 2 inch by 2 inch by 0.7 mm thick EXG glass substrates were dip-coated with a slurry having 5% wt% gamma( $\gamma$ )-alumina particles (aluminum oxide nanoparticles) and 5 wt% as-received AL20 at a withdrawal speed of 50 mm/min. The diluent for the slurry was DI water. After drying in an oven at 120 degrees C for 1 hour, the samples were coated again with the same slurry followed by drying at 120 degrees C. The dried samples were then calcined at three different temperature profiles, 400 degrees C for 1 hour, 400 degrees C for 6 hours, and 550 degrees C for 1 hour, respectively, to form nanoporous metal-oxide layers on the glass substrates.

[0138] After calcination, the samples were cleaned and then soaked in a 1.0 vol% APTES solution (95 mL methanol, 4 mL H<sub>2</sub>O and 1 mL APTES) at room temperature for 15 minutes. After a gentle rinse with DI water three times, the samples were placed in an oven at 120 degrees C for 30 minutes. Then, the samples were soaked in a K<sub>2</sub>PdCl<sub>4</sub> solution at 45 degrees C for 3 minutes, followed by reduction into metallic palladium particles at room temperature by DMAB.

[0139] After catalyzation, the samples were placed in an electroless plating bath at 34 degrees C for 2 minutes to electrolessly plate a copper film on the nanoporous metal-

oxide layers. After manually drying the samples with a nitrogen spray gun, the samples were annealed in a vacuum oven at 250 degrees C for 30 minutes. The sheet resistance was immediately measured with single point measurement. Each of the samples showed a sheet resistance in the range of 0.9 to 1.1 ohm per square centimeter ( $\text{ohm}/\text{cm}^2$ ).

Photograph 1500 in FIG. 15 shows all three samples after electroless plating.

[0140] The electrolessly-plated samples were then placed in a 1M (molar)  $\text{CuSO}_4$  solution for electroplating with a 50 mA current for 1 hour to electroplate copper on the electrolessly-plated copper film. Photograph 1600 in FIG. 16 shows all three samples after electroplating. And FIG. 17 shows an SEM image 1700 of the surface morphology of an electroplated copper film deposited on an electrolessly-plated film for one of the samples. Image 1700 shows electroplated copper crystals having a size in the range of 3 microns to 5 microns. These electroplated copper crystals are significantly larger than the electrolessly-plated copper crystals underneath the electroplated copper crystals. Also, the electroplated copper crystals are more densely deposited than the electrolessly-plated copper crystals. As shown in SEM images 1800 and 1850 of FIGS. 18A and 18B, respectively, the electrolessly-plated copper film was about 100 nanometers thick to about 200 nanometers thick and the electroplated copper film was about 6 microns thick.

[0141] After manually drying the samples with a nitrogen spray gun, a 3 N/cm tape test was conducted on each sample. All samples passed the 3 N/cm tape test. After this first 3 N/cm tape test, the samples were annealed in a vacuum oven at 350 degrees C for 30 minutes with a ramp rate of 3 degrees C / minute. Then, the 3 N/cm tape test was repeated on all the samples. Unlike the samples of Example 4, all samples passed the second N/cm tape test.

[0142] FIGS. 19A–19E show TEM/EDX (transmission electron microscopy energy-dispersive X-ray spectroscopy) images 1900, 1910, 1920, 1930, and 1940 of a cross-section of the sample calcined at 400 degrees C for 1 hour. Image 1900 shows locations of palladium, copper, aluminum, and silicon in the cross-section. Image 1910 shows the location of palladium in the cross-section. Image 1920 shows the location of copper in the cross-section. Image 1930 shows the location of aluminum in the cross-section. Image 1940 shows the location of silicon in the cross-section.

- [0143] The images in FIGS. 19A–19E show that the sample had a sandwich structure with a nanoporous aluminum oxide layer 1904 disposed between a copper film 1906 and a EXG glass substrate 1902. The presence of palladium and copper inside the nanoporous aluminum oxide layer 1904 is shown in shown in images 1910 and 1920. The porosity of nanoporous aluminum oxide layer 1904 on the glass substrate 1902 in combination with cationic surface treatment led to a high concentration of palladium catalyst on the nanoporous aluminum oxide layer 1904 as well as mechanical interlocking between the nanoporous aluminum oxide layer 1904 and the copper film 1906.
- [0144] By comparing Examples 4 and 5, it can be seen that metal-oxide layers formed by calcinating a coating of slurry having both colloidal metal-oxide precursor particles and aluminum oxide particles results in improved mechanical interlocking and tape test performance compared to metal-oxide layers formed by calcinating a slurry having only colloidal metal-oxide precursor particles. After annealing, the samples of Example 4 failed the 3N/cm tape test, whereas the samples of Example 5 passed the 3N/cm tape test after annealing.
- [0145] To evaluate differences between the samples of Example 4 and Example 5, the pore size and the pore volume of the nanoporous aluminum oxide layers on the samples were measured. BJH nitrogen adsorption and desorption analysis showed that the mean pore size of the Alumina Nanoparticle-AL20 layers of Example 5 was 7.25 nanometers and the mean pore size of the AL20 layers of Example 4 was 4.29 nanometers. The pore volume of the Alumina Nanoparticle-AL20 layers of Example 5 was 0.45 cc/g and the pore volume of the AL20 layers of Example 4 was 0.37 cc/g. Without being bound by theory, it is believed the larger pore size and higher porosity of the Alumina Nanoparticle-AL20 layers of Example 5 led to better mechanical interlock and thus higher adhesion between the plated copper and the glass substrate compared to the AL20 layers of Example 4, which failed after electroplating and annealing.
- [0146] Examples of suitable glass or glass substrates described herein include soda lime glass, alkali aluminosilicate glass, alkali containing borosilicate glass and alkali aluminoborosilicate glass. In some variants, the glass may be free of lithia. As used herein the term “glass” is meant to include any material made at least partially of glass, including glass and glass-ceramics. “Glass-ceramics” include materials produced through



controlled crystallization of glass. In embodiments, glass-ceramics have about 30% to about 90% crystallinity. Non-limiting examples of glass ceramic systems that may be used include  $\text{Li}_2\text{O} \times \text{Al}_2\text{O}_3 \times n\text{SiO}_2$  (i.e. LAS system),  $\text{MgO} \times \text{Al}_2\text{O}_3 \times n\text{SiO}_2$  (i.e. MAS system), and  $\text{ZnO} \times \text{Al}_2\text{O}_3 \times n\text{SiO}_2$  (i.e. ZAS system).

**[0147]** While various embodiments have been described herein, they have been presented by way of example, and not limitation. It should be apparent that adaptations and modifications are intended to be within the meaning and range of equivalents of the disclosed embodiments, based on the teaching and guidance presented herein. It therefore will be apparent to one skilled in the art that various changes in form and detail can be made to the embodiments disclosed herein without departing from the spirit and scope of the present disclosure. The elements of the embodiments presented herein are not necessarily mutually exclusive, but may be interchanged to meet various situations as would be appreciated by one of skill in the art.

**[0148]** Embodiments of the present disclosure are described in detail herein with reference to embodiments thereof as illustrated in the accompanying drawings, in which like reference numerals are used to indicate identical or functionally similar elements. References to “one embodiment,” “an embodiment,” “some embodiments,” “in certain embodiments,” etc., indicate that the embodiment described may include a particular feature, structure, or characteristic, but every embodiment may not necessarily include the particular feature, structure, or characteristic. Moreover, such phrases are not necessarily referring to the same embodiment. Further, when a particular feature, structure, or characteristic is described in connection with an embodiment, it is submitted that it is within the knowledge of one skilled in the art to affect such feature, structure, or characteristic in connection with other embodiments whether or not explicitly described.

**[0149]** The examples are illustrative, but not limiting, of the present disclosure. Other suitable modifications and adaptations of the variety of conditions and parameters normally encountered in the field, and which would be apparent to those skilled in the art, are within the spirit and scope of the disclosure.

**[0150]** The term “or,” as used herein, is inclusive; more specifically, the phrase “A or B” means “A, B, or both A and B.” Exclusive “or” is designated herein by terms such as “either A or B” and “one of A or B,” for example.

- [0151] The indefinite articles “a” and “an” to describe an element or component means that one or at least one of these elements or components is present. Although these articles are conventionally employed to signify that the modified noun is a singular noun, as used herein the articles “a” and “an” also include the plural, unless otherwise stated in specific instances. Similarly, the definite article “the,” as used herein, also signifies that the modified noun may be singular or plural, again unless otherwise stated in specific instances.
- [0152] As used in the claims, “comprising” is an open-ended transitional phrase. A list of elements following the transitional phrase “comprising” is a non-exclusive list, such that elements in addition to those specifically recited in the list may also be present. As used in the claims, “consisting essentially of” or “composed essentially of” limits the composition of a material to the specified materials and those that do not materially affect the basic and novel characteristic(s) of the material. As used in the claims, “consisting of” or “composed entirely of” limits the composition of a material to the specified materials and excludes any material not specified.
- [0153] The term “wherein” is used as an open-ended transitional phrase, to introduce a recitation of a series of characteristics of the structure.
- [0154] Where a range of numerical values is recited herein, comprising upper and lower values, unless otherwise stated in specific circumstances, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the claims be limited to the specific values recited when defining a range. Further, when an amount, concentration, or other value or parameter is given as a range, one or more preferred ranges or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether such pairs are separately disclosed. Finally, when the term “about” is used in describing a value or an end-point of a range, the disclosure should be understood to include the specific value or end-point referred to. Whether or not a numerical value or end-point of a range recites “about,” the numerical value or end-point of a range is intended to include two embodiments: one modified by “about,” and one not modified by “about.”

- [0155]** As used herein, the term “about” means that amounts, sizes, formulations, parameters, and other quantities and characteristics are not and need not be exact, but may be approximate and/or larger or smaller, as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art.
- [0156]** The terms “substantial,” “substantially,” and variations thereof as used herein are intended to note that a described feature is equal or approximately equal to a value or description. For example, a “substantially planar” surface is intended to denote a surface that is planar or approximately planar. Moreover, “substantially” is intended to denote that two values are equal or approximately equal. In some embodiments, “substantially” may denote values within about 10% of each other, such as within about 5% of each other, or within about 2% of each other.
- [0157]** The present embodiment(s) have been described above with the aid of functional building blocks illustrating the implementation of specified functions and relationships thereof. The boundaries of these functional building blocks have been arbitrarily defined herein for the convenience of the description. Alternate boundaries can be defined so long as the specified functions and relationships thereof are appropriately performed.
- [0158]** It is to be understood that the phraseology or terminology used herein is for the purpose of description and not of limitation. The breadth and scope of the present disclosure should not be limited by any of the above-described exemplary embodiments, but should be defined in accordance with the following claims and their equivalents.

## WHAT IS CLAIMED IS:

1. A method of plating a metal on a substrate, the method comprising:  
coating a surface of the substrate with a slurry, the slurry comprising:  
colloidal metal-oxide precursor particles, and  
aluminum oxide particles;  
calcinating the slurry on the surface of the substrate to form a nanoporous metal-oxide layer on the surface of the substrate; and  
plating the nanoporous metal-oxide layer with a metal.
2. The method of claim 1, wherein the colloidal metal-oxide precursor particles comprise at least one of: aluminum oxide precursor particles, silicon oxide precursor particles, titanium oxide precursor particles, cerium oxide precursor particles, and zirconium oxide precursor particles.
3. The method of claim 1 or claim 2, wherein the colloidal metal-oxide precursor particles comprise aluminum oxide precursor particles.
4. The method of any of claims 1–3, wherein the colloidal metal-oxide precursor particles comprise aluminum oxide hydroxide particles.
5. The method of any of claims 1–4, wherein the metal comprises copper.
6. The method of any of claims 1–5, wherein the substrate is a glass or glass-ceramic substrate.
7. The method of any of claims 1–5, wherein the substrate is a glass or glass-ceramic substrate comprising a via formed in the substrate and wherein the surface is an interior surface of the via.
8. The method of claim 7, wherein the via is a through via.

9. The method of any of claims 1–8, wherein the nanoporous metal-oxide layer comprises an average pore size in the range of 5 nanometers to 30 nanometers.

10. The method of any of claims 1–9, wherein the nanoporous metal-oxide layer comprises a pore volume in the range of 0.3 cubic centimeters per gram to 10 cubic centimeters per gram.

11. The method of any of claims 1–10, wherein the aluminum oxide particles comprise nanoparticles.

12. The method of any of claims 1–11, wherein the aluminum oxide particles comprise an average particle size in the range of 10 nanometers to 100 nanometers.

13. The method of any of claims 1–12, wherein the colloidal metal-oxide precursor particles comprise an average particle size in the range of 60 nanometers to 90 nanometers.

14. The method of any of claims 1–13, wherein the aluminum oxide particles comprise an average particle size, wherein the colloidal metal-oxide precursor particles comprise an average particle size, and wherein the average particle size of the colloidal metal-oxide precursor particles is less than the average particle size of the aluminum oxide particles.

15. The method of any of claims 1–13, wherein the aluminum oxide particles comprise an average particle size, wherein the colloidal metal-oxide precursor particles comprise an average particle size, and wherein the average particle size of the colloidal metal-oxide precursor particles is greater than the average particle size of the aluminum oxide particles.

16. The method of any of claims 1–15, wherein the slurry comprises X wt% aluminum oxide particles and Y wt% colloidal metal-oxide precursor particles, and wherein X is greater than or equal to Y.

17. The method of any of claims 1–16, wherein a weight percent ratio of the aluminum oxide particles to the colloidal metal-oxide precursor particles in the slurry is in the range of 3:1 to 20:1.

18. The method of claim 17, wherein the weight percent ratio is in the range of 3:1 to 10:1.

19. The method of any of claims 1–18, wherein calcinating the slurry on the surface of the substrate comprises heating the slurry to a calcination temperature in the range of 300 degrees C to 650 degrees C.

20. The method of any of claims 1–19, wherein plating the nanoporous metal-oxide layer comprises an electroless plating method.

21. The method of claim 20, further comprising charging the nanoporous metal-oxide layer prior to the electroless plating method.

22. The method of claim 21, wherein charging the nanoporous metal-oxide layer comprises treating the nanoporous metal-oxide layer with an aminosilane.

23. The method of claim 22, wherein the aminosilane comprises aminopropyltriethoxysilane.

24. The method of any of claims 21–23, further comprising adsorbing palladium complexes into the nanoporous metal-oxide layer after charging the nanoporous metal-oxide layer and prior to the electroless plating method.

25. The method of any of claims 20–24, wherein plating the nanoporous metal-oxide layer further comprises an electroplating method performed after the electroless plating method.

26. The method of any of claims 1–25, wherein the plated metal is capable of passing a 3N/cm tape test after being annealed at 350 degrees C for 30 minutes.

27. The method of any of claims 1–26, wherein the slurry comprises a pore former.
28. The method of claim 27, wherein the pore former comprises polyethylene glycol.
29. A metal plated substrate made by the method of any of claims 1–28.
30. A method of plating copper on a substrate, the method comprising:  
coating a surface of the substrate with a slurry, the slurry comprising:  
colloidal aluminum oxide hydroxide particles, and  
aluminum oxide particles;  
calcinating the slurry on the surface of the substrate to form a nanoporous metal-oxide layer on the surface of the substrate;  
charging the nanoporous metal-oxide layer, wherein the charging comprises  
treating the nanoporous metal-oxide layer with an aminosilane; and  
plating the nanoporous metal-oxide layer with copper after charging the nanoporous metal-oxide layer.
31. An article, comprising:  
a glass or glass-ceramic substrate comprising a surface having a plurality of vias formed therein, each via having an interior surface;  
a nanoporous metal-oxide layer coated on the interior surface of each of the plurality of vias, the nanoporous metal-oxide layer comprising aluminum oxide and an average pore size in the range of 5 nanometers to 30 nanometers; and  
a metal plating disposed on the nanoporous metal-oxide layer in each of the plurality of vias.
32. The article of claim 31, wherein a least one of the vias is a through via.
33. The article of claim 31 or claim 32, wherein the metal plating comprises copper.

34. The article of any of claims 31–33, wherein the metal plating fills each of the plurality of the vias.

35. The article of any of claims 31–34, wherein the nanoporous metal-oxide layer is coated on at least a portion of the surface of the glass or glass-ceramic substrate.

36. The article of claim 35, wherein the metal plating is disposed on the nanoporous metal-oxide layer coated on the surface of the glass or glass-ceramic substrate.

37. The article of claim 36, wherein the metal plating disposed on the nanoporous metal-oxide layer coated on the surface of the glass or glass ceramic substrate is capable of passing a 3N/cm tape test after being annealed at 350 degrees C for 30 minutes.



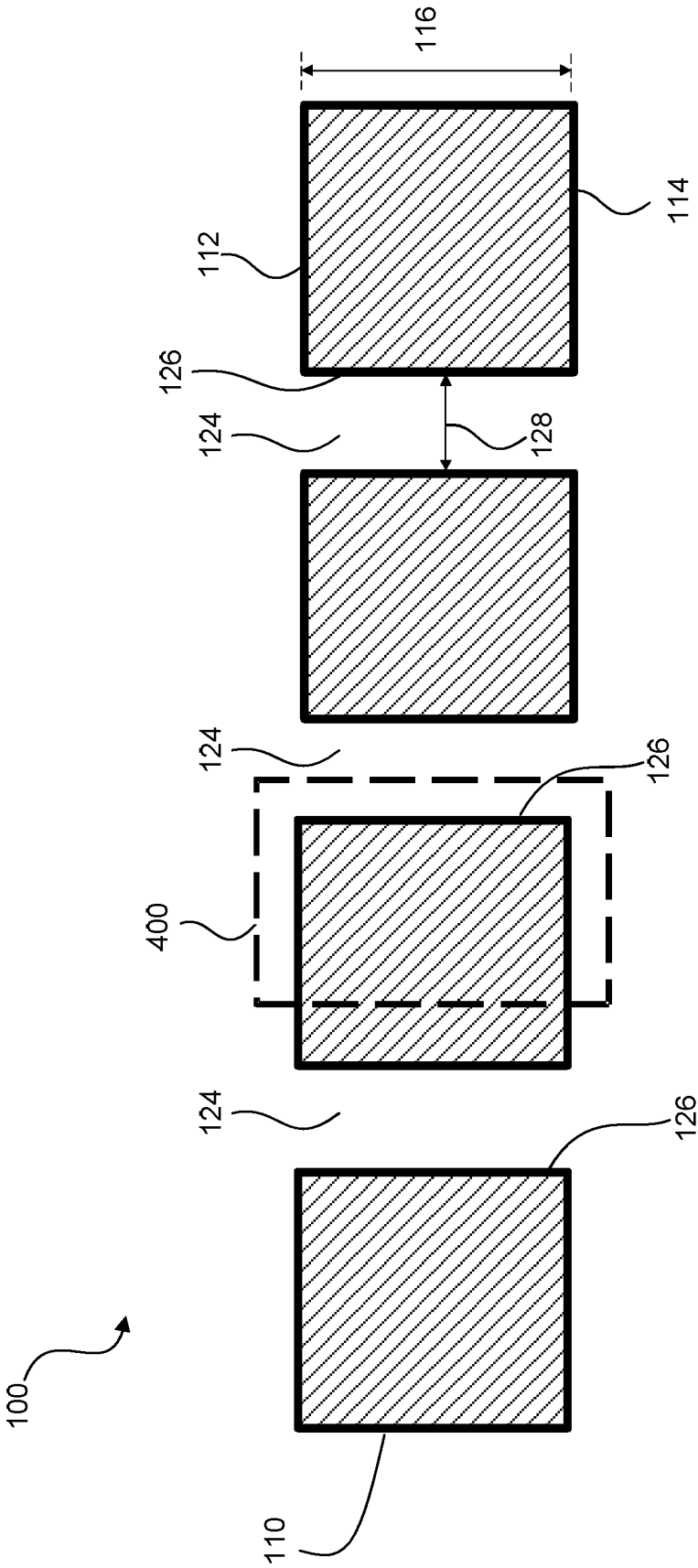


FIG. 1

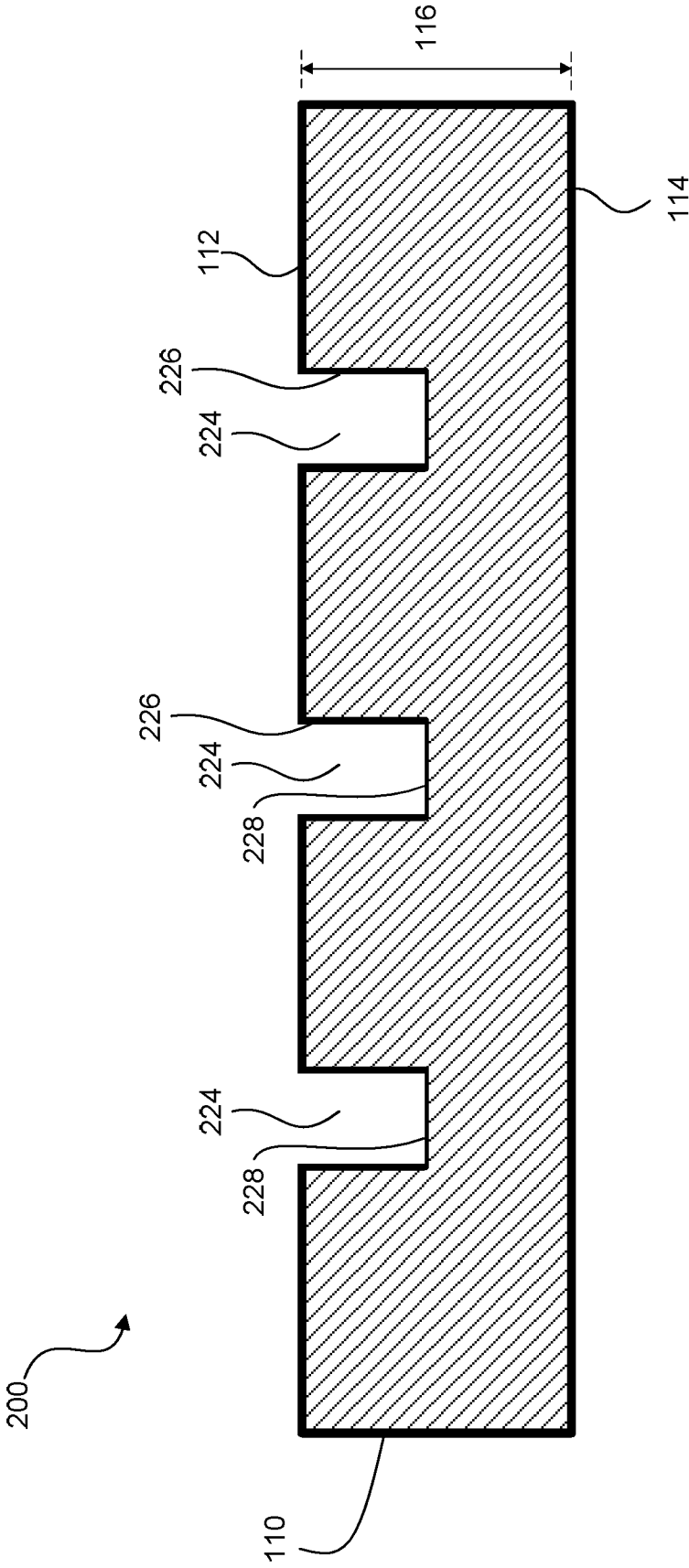
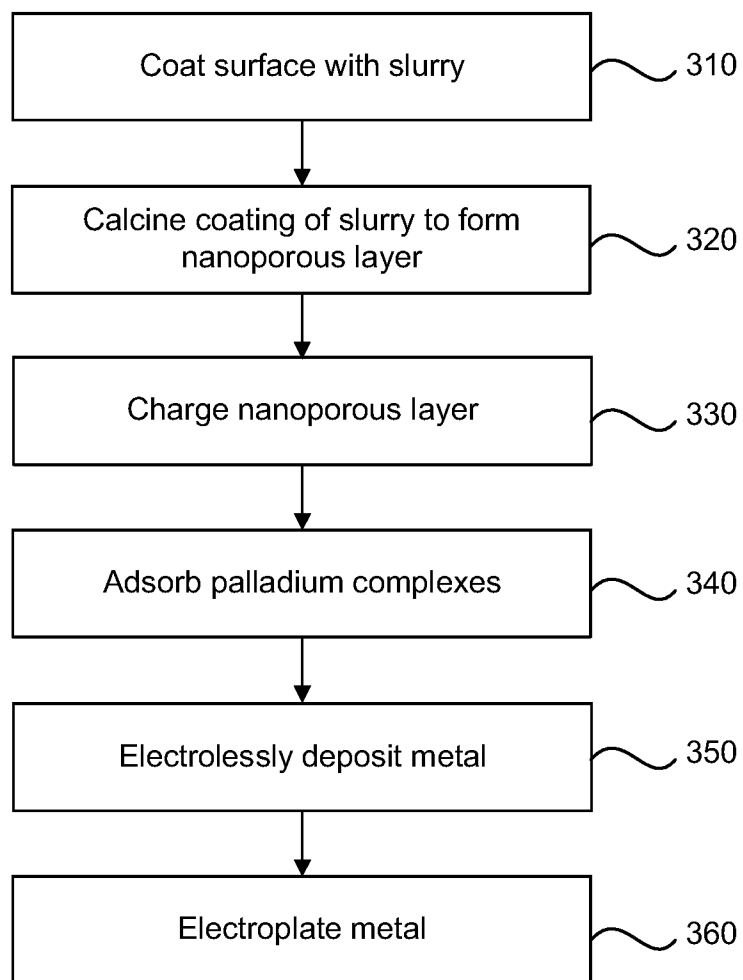


FIG. 2

3/19

300

**FIG. 3**

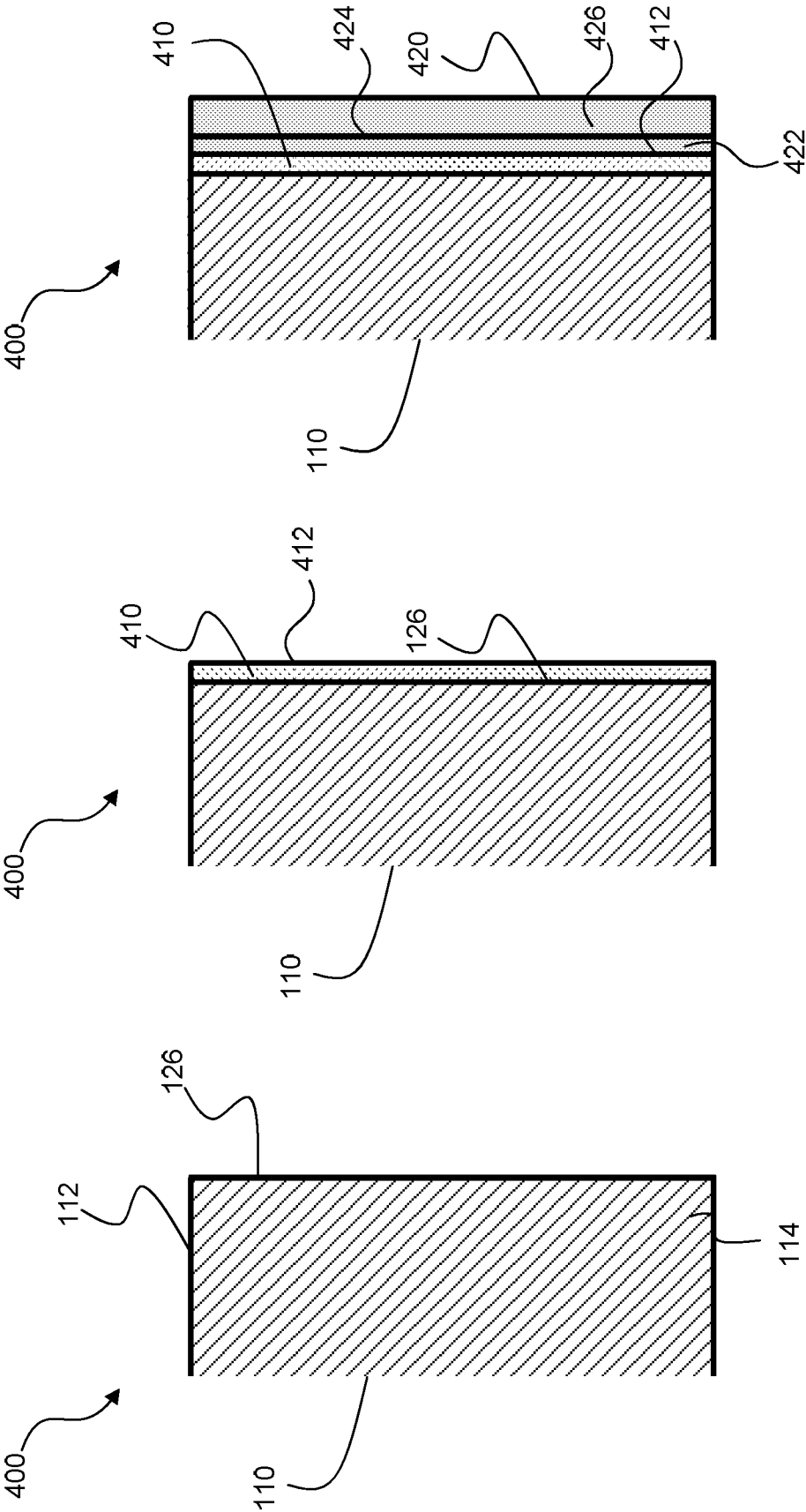
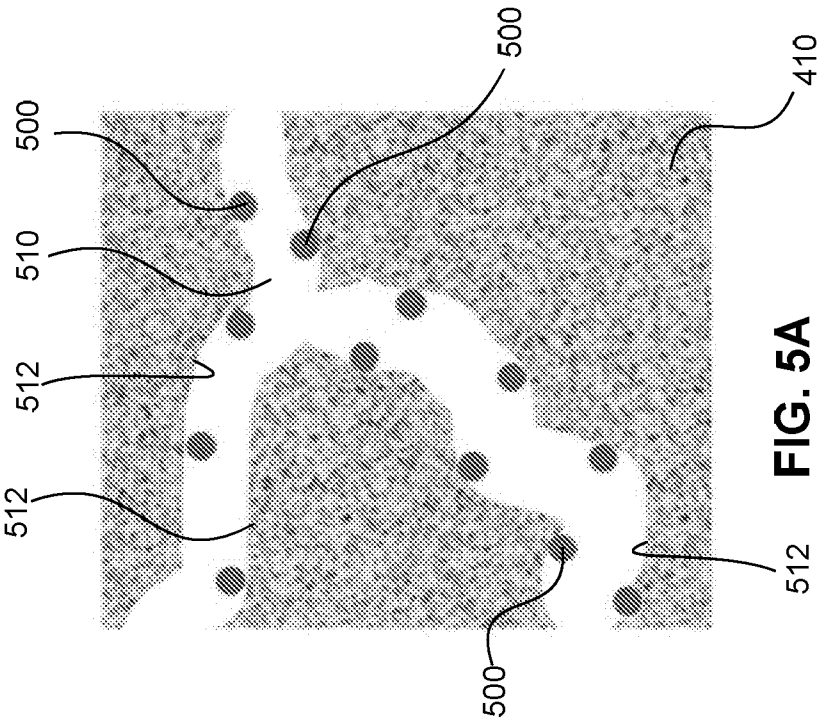
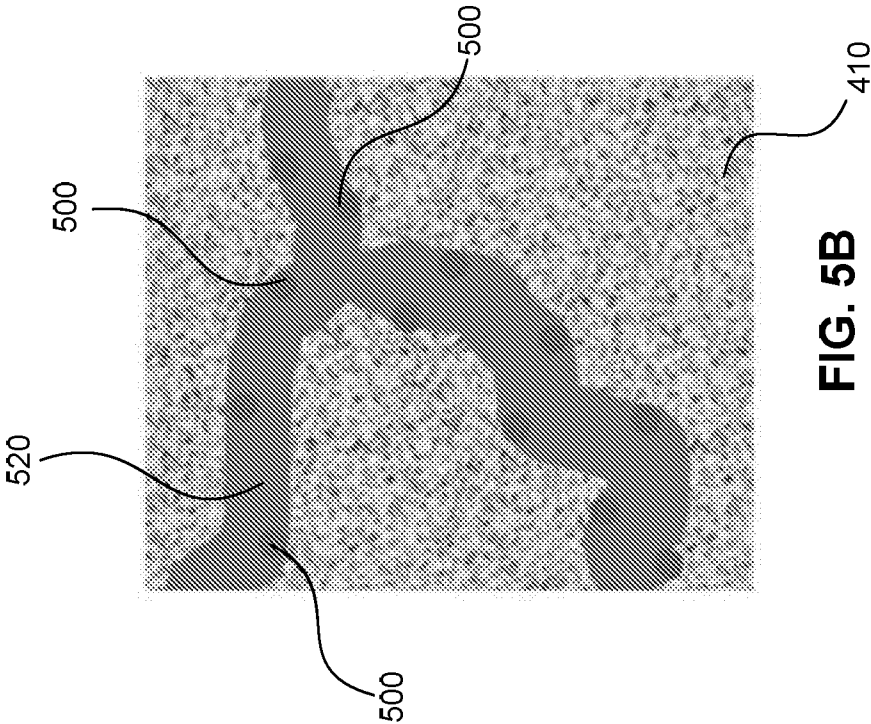


FIG. 4C

FIG. 4B

FIG. 4A



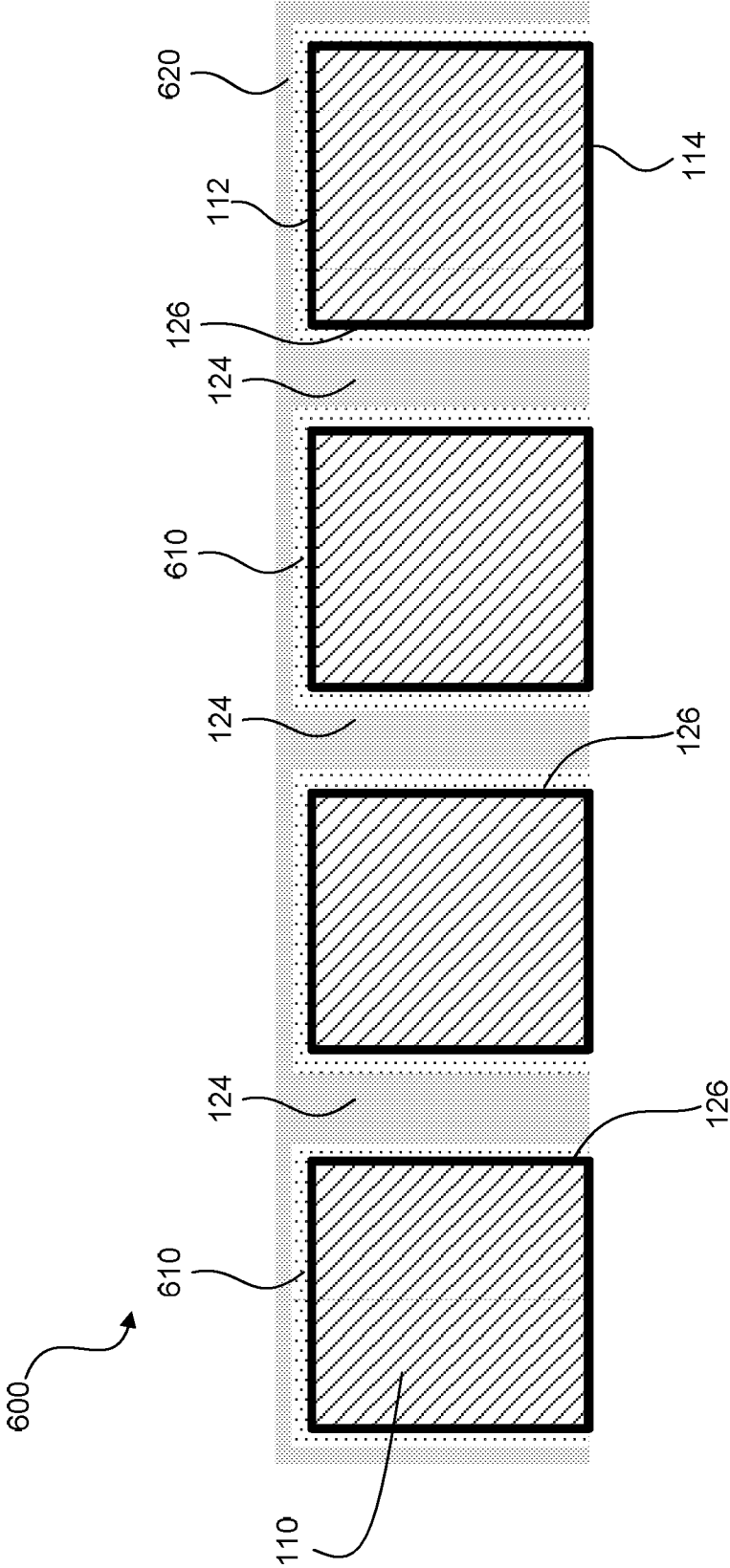


FIG. 6

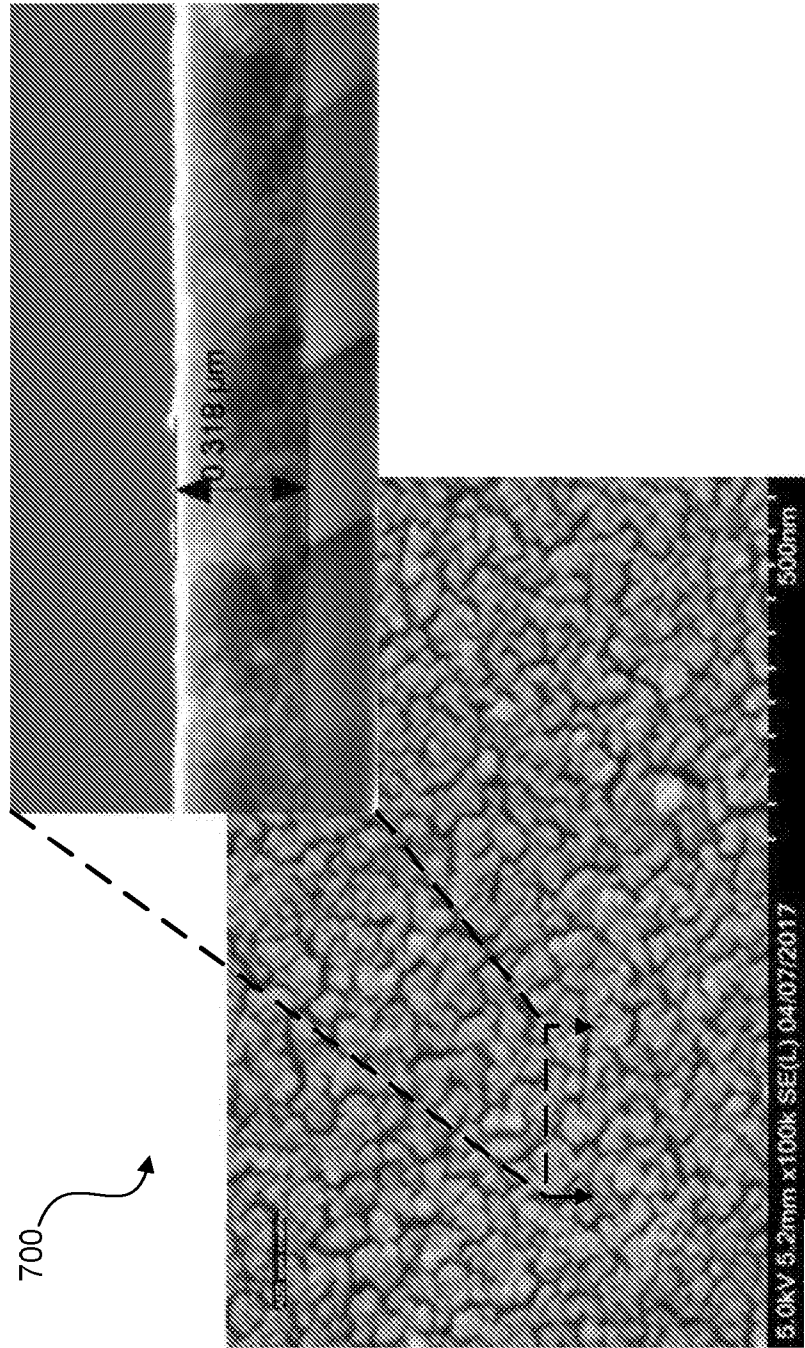


FIG. 7

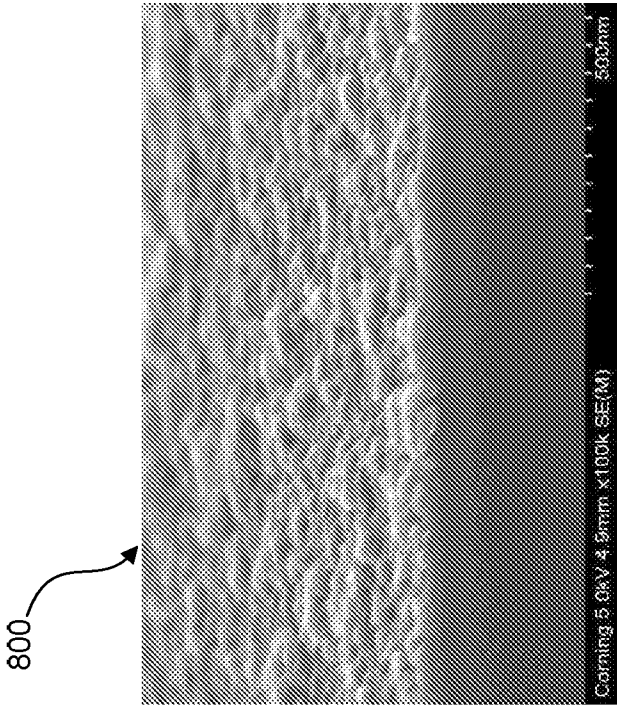


FIG. 8A

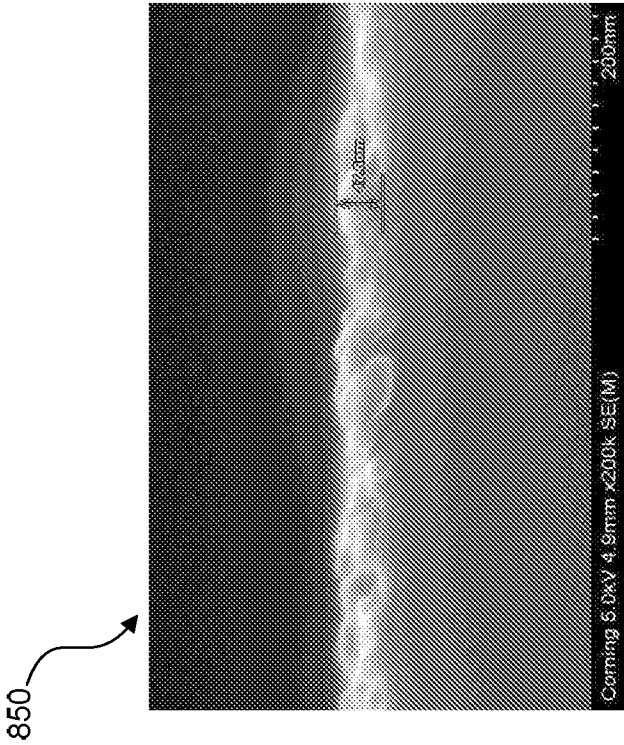


FIG. 8B



900

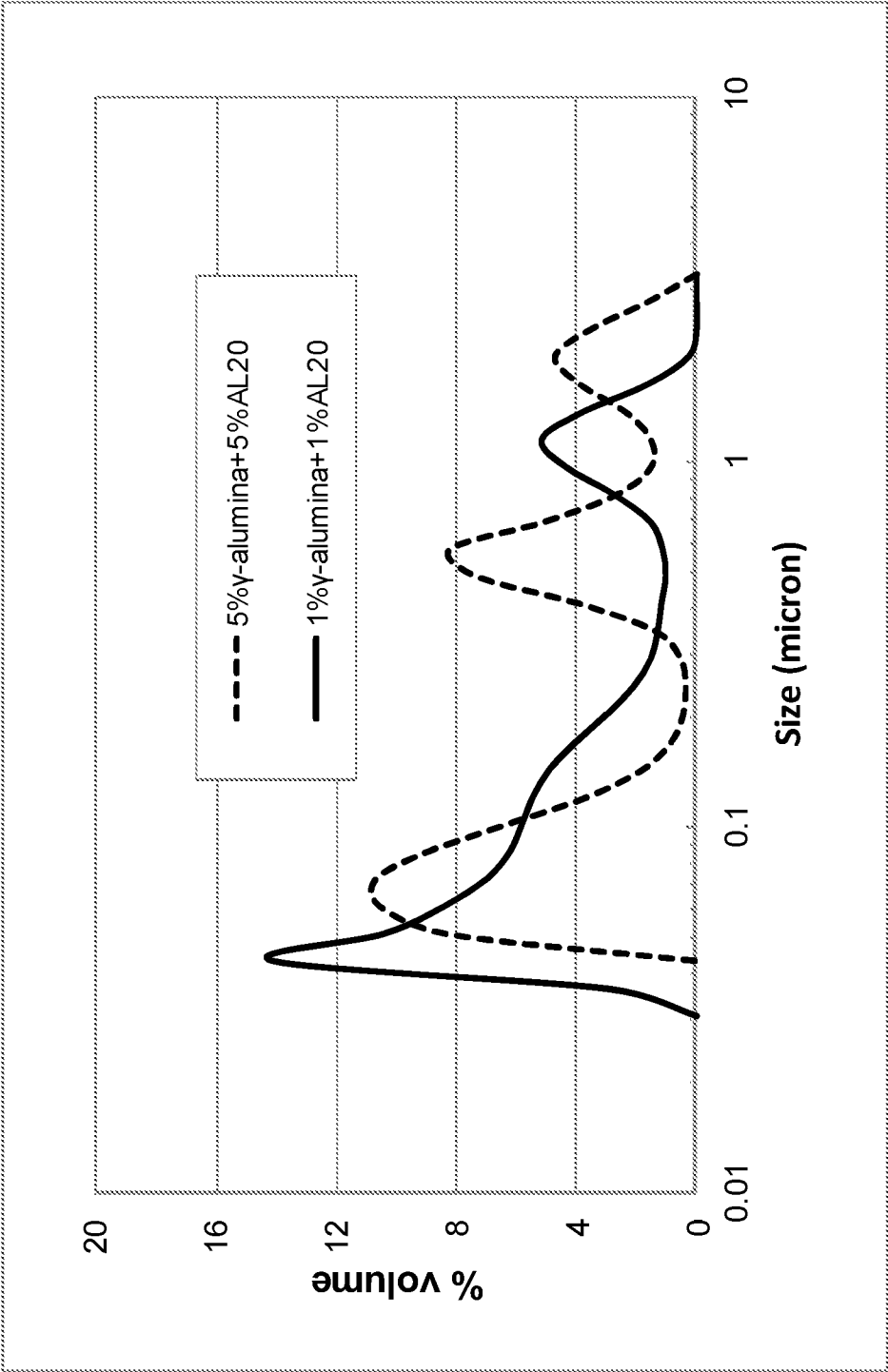


FIG. 9

10/19

1050

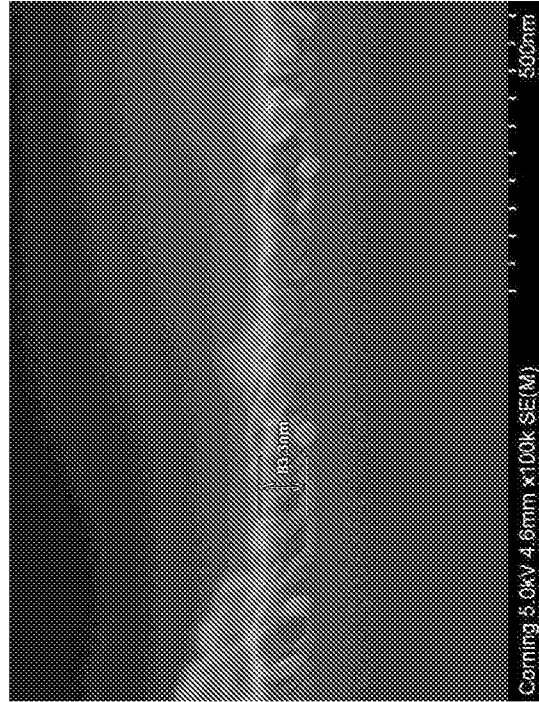


FIG. 10B

1000

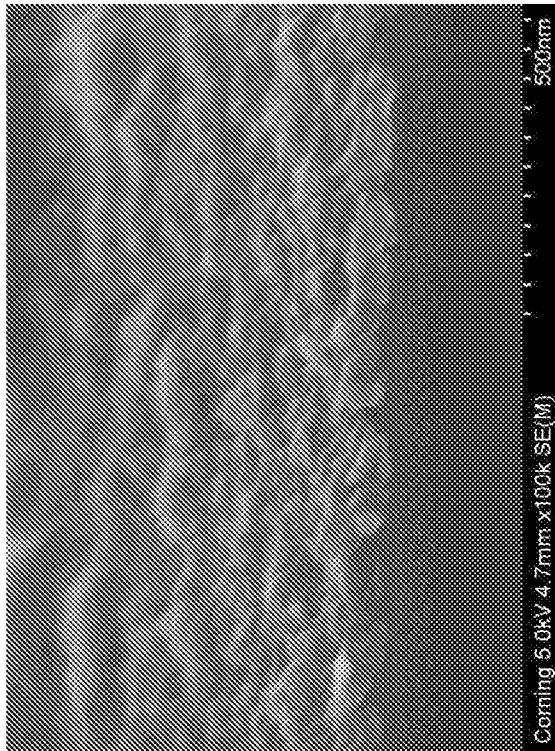


FIG. 10A

11/19

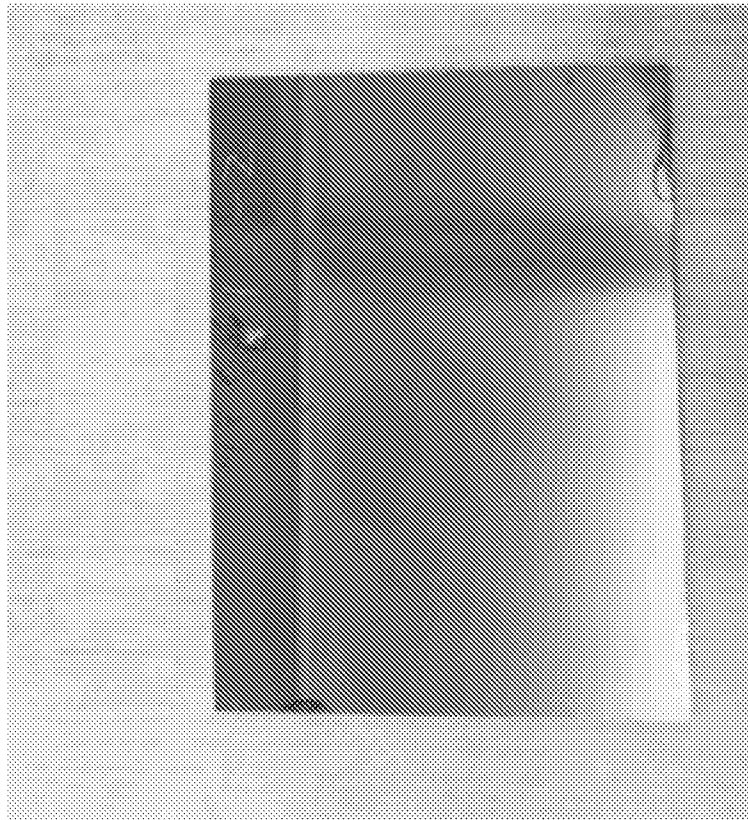



FIG. 11

1100



1200

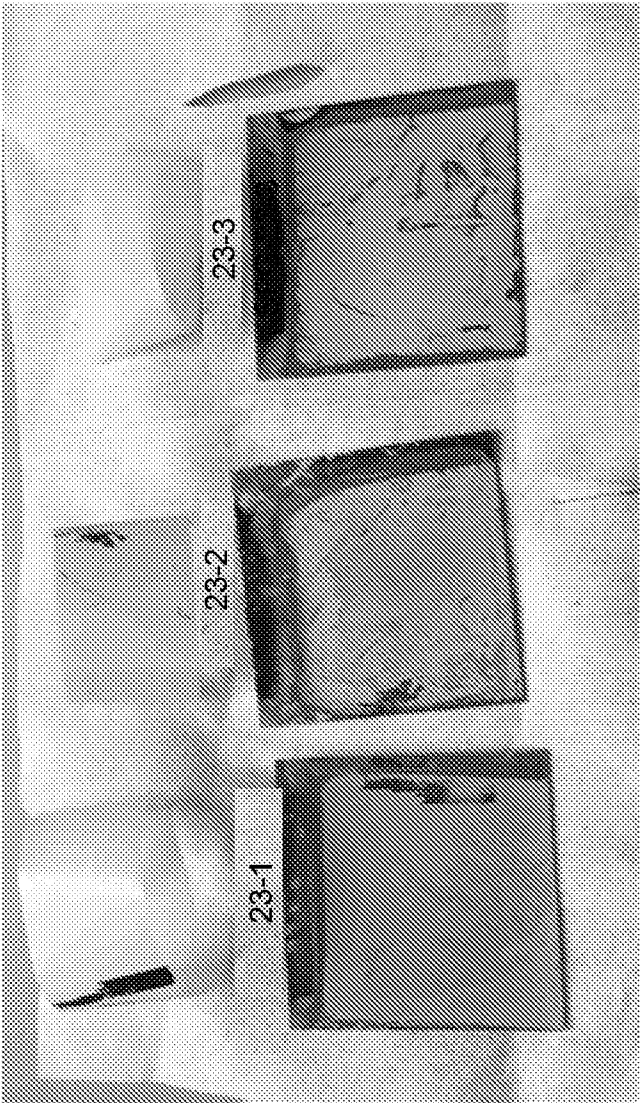


FIG. 12

1300

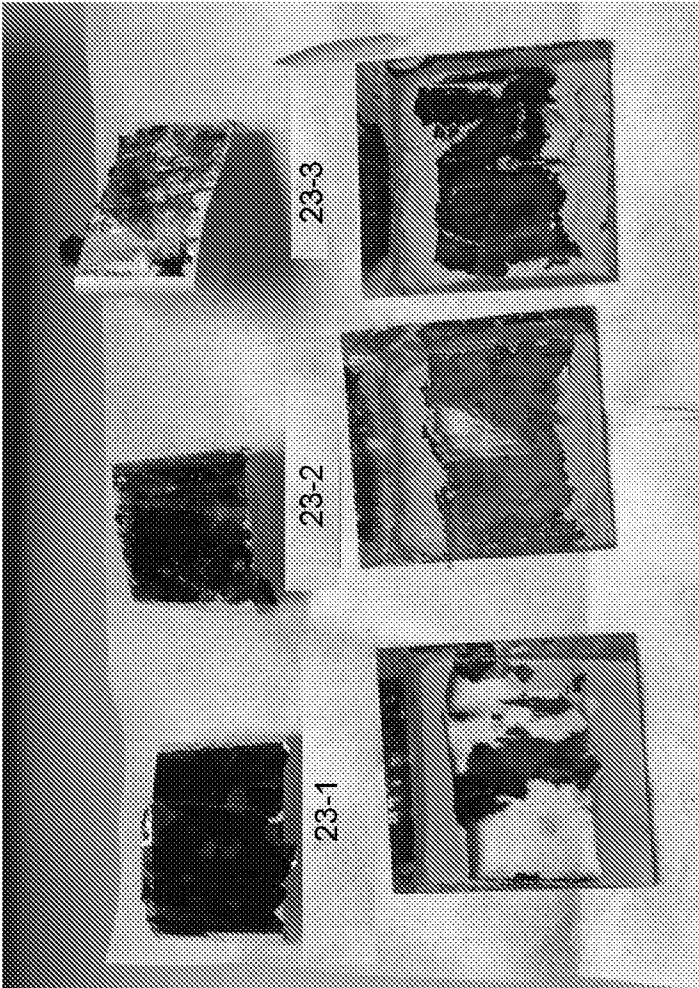


FIG. 13

1450

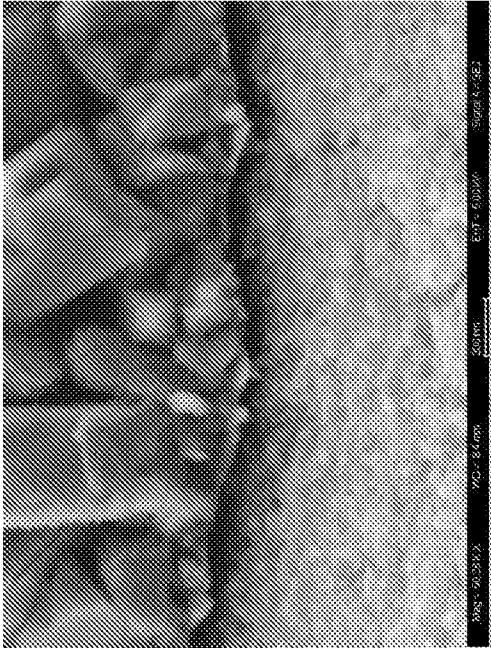


FIG. 14B

1400

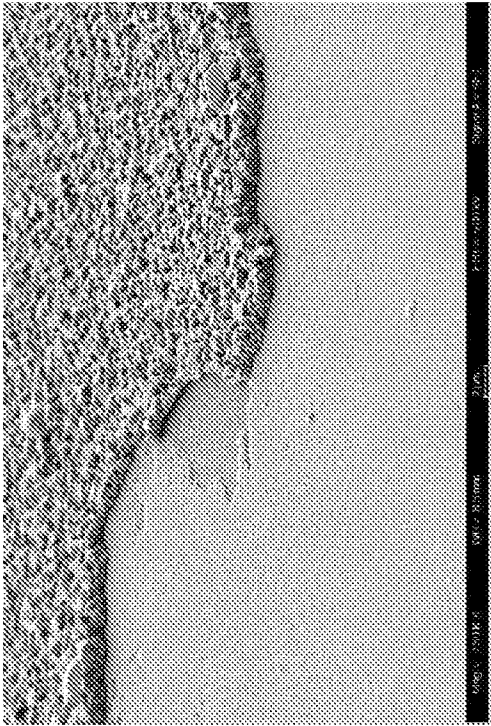


FIG. 14A

1500

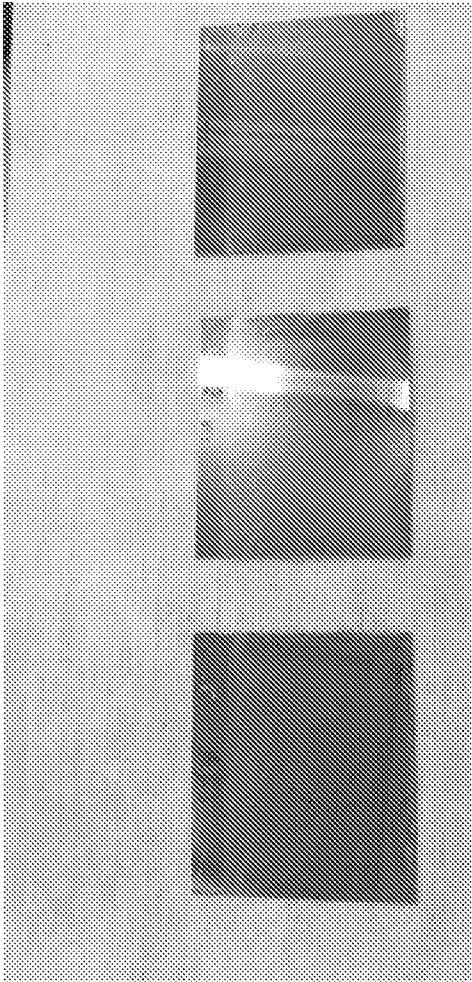


FIG. 15

1600

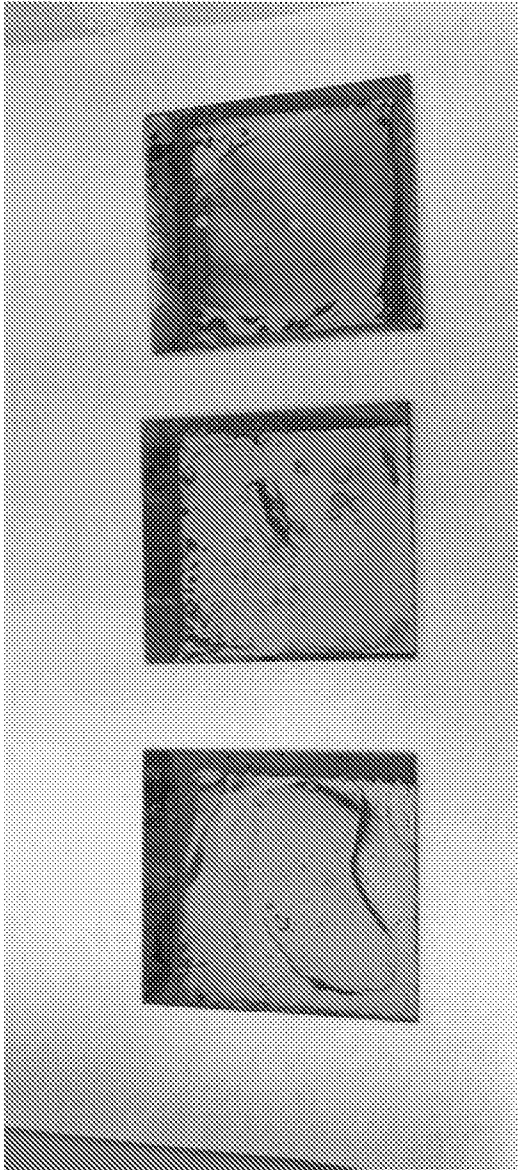


FIG. 16



1700

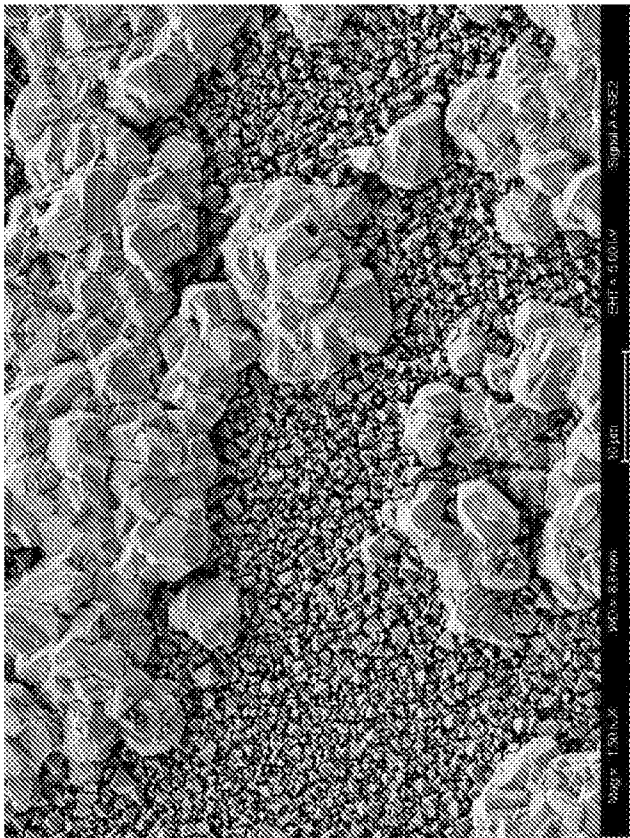
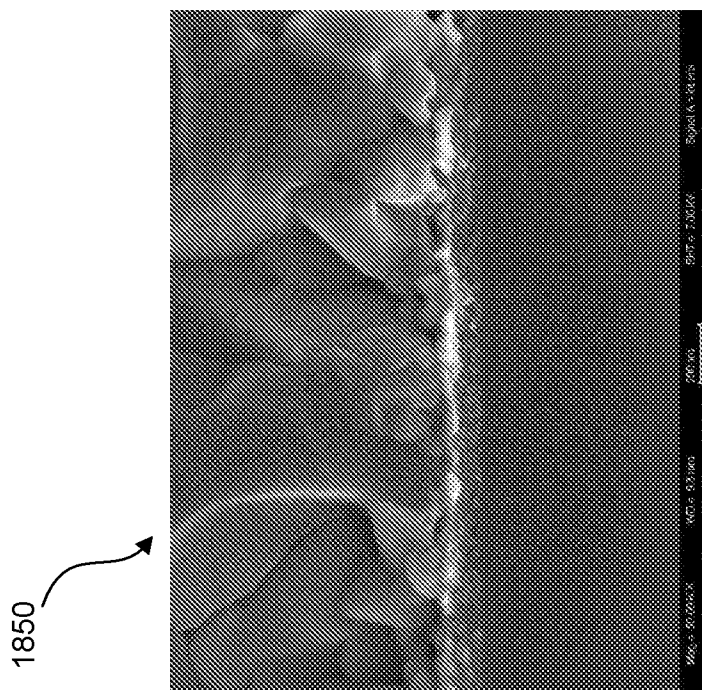
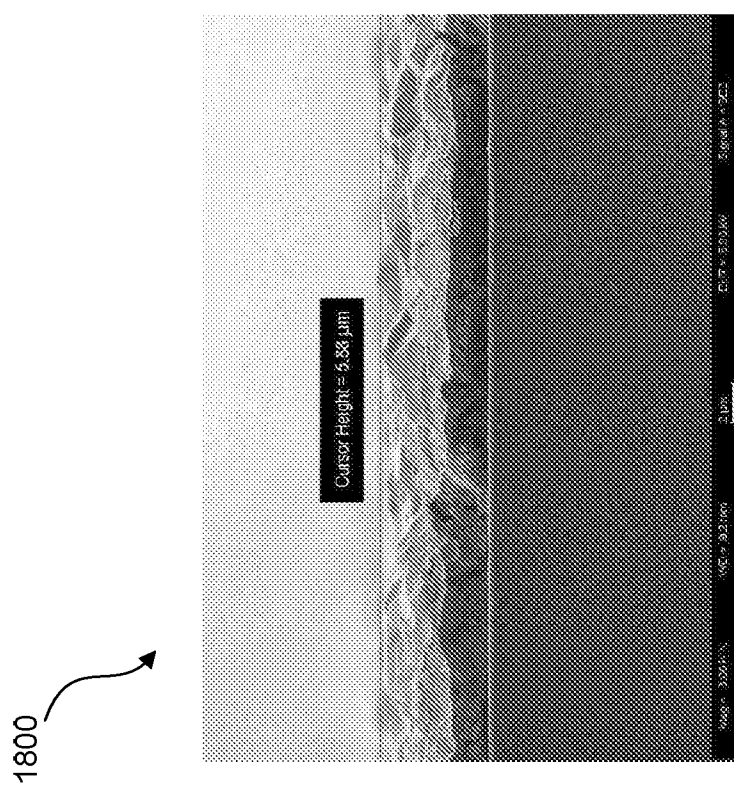


FIG. 17



**FIG. 18B**



**FIG. 18A**

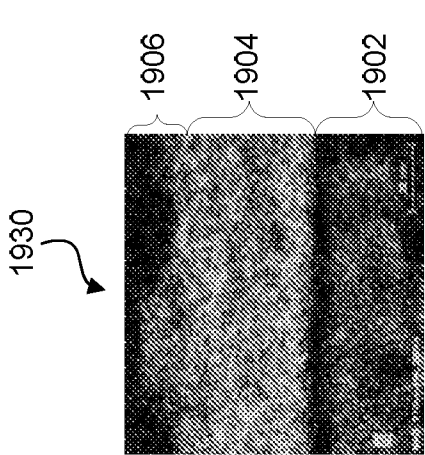


FIG. 19D

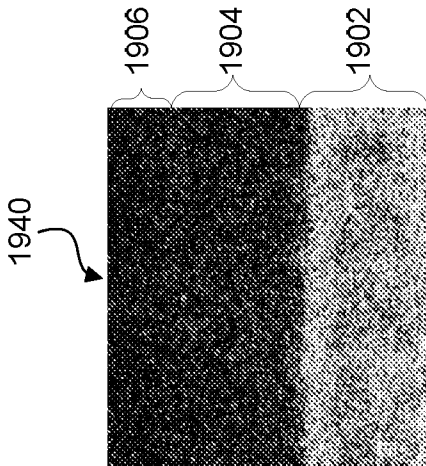


FIG. 19E

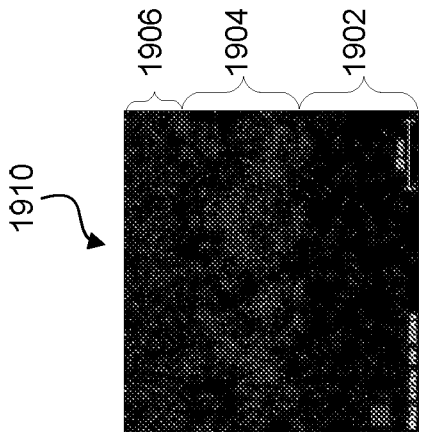


FIG. 19B

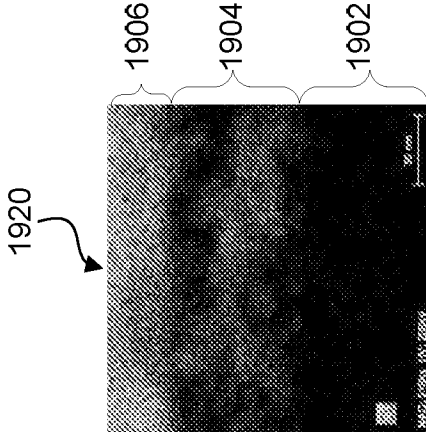


FIG. 19C

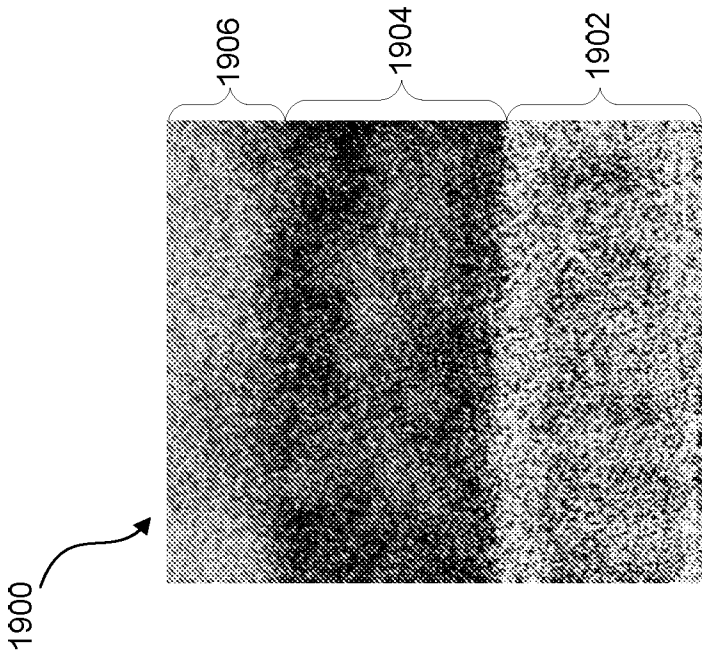


FIG. 19A

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2019/050731

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C18/12 C23C18/18 C23C18/16 C25D5/54 C03C17/25  
C03C17/27 C03C17/34 C03C17/36 C25D7/12

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)

C23C C25D C03C

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	US 2016/208387 A1 (LIU ZHIMING [US] ET AL) 21 July 2016 (2016-07-21)	29,31-37
Y	paragraph [0019] - paragraph [0027]; claims 1, 2; example 3 paragraph [0037] - paragraph [0038] paragraph [0042] paragraph [0052] paragraph [0058] - paragraph [0059] paragraph [0081] paragraph [0083] - paragraph [0084] paragraph [0088] paragraph [0124] - paragraph [0129] paragraph [0156] - paragraph [0158] paragraph [0064] - paragraph [0065] paragraph [0094] paragraph [0097] - paragraph [0103] paragraph [0118] ----- -/-	1-28,30



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2019/050731

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