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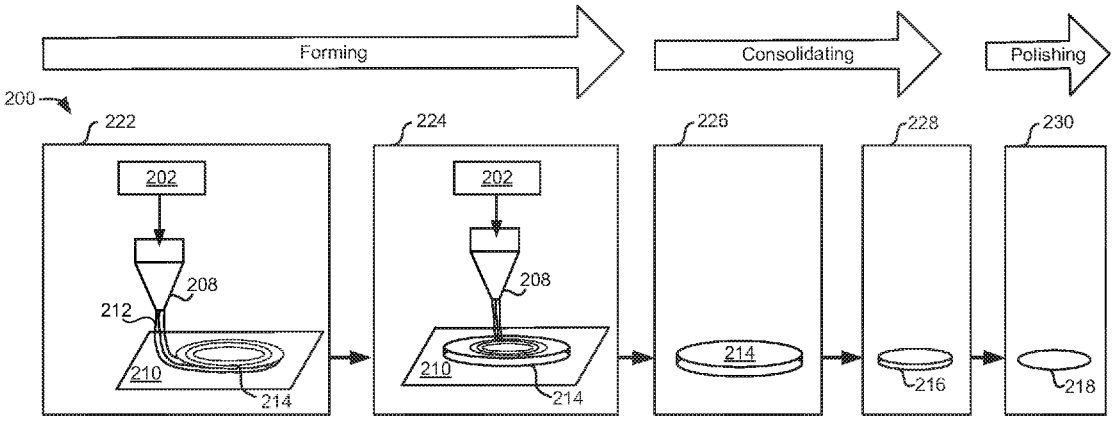

FIG. 2A

(57) Abstract: According to one embodiment, a method includes forming a structure by printing an ink, the ink including a glass-forming material, and heat treating the formed structure for converting the glass-forming material to glass.

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GLASS COMPONENTS WITH CUSTOM-TAILORED COMPOSITION PROFILES AND METHODS FOR PREPARING SAME

[0001] The United States Government has rights in this invention pursuant to Contract No. DE-AC52-07NA27344 between the United States Department of Energy and Lawrence Livermore National Security, LLC for the operation of Lawrence Livermore National Laboratory.

FIELD OF THE INVENTION

[0002] The present invention relates to glass components , and more particularly, this invention relates optical and non-optical glass components with custom-tailored composition profiles and methods for preparing same.

BACKGROUND

~~[0003]~~ Conventionally, gradients in material compositions are introduced either (1) axially, by fusing together multiple layers containing uniform composition, or (2) radially, by diffusing species (typically small, fast diffusing ions) into or out of rod-

shaped silica sol-gels or solids at elevated temperatures. Unfortunately, purely diffusion-based gradients are limited to symmetric, parabolic profiles and have maximum achievable diameters (in the case of radial gradient refractive index lenses) of ~20 mm, with most commercial versions being < 2 mm in diameter. Introduction of larger, slower diffusing species proves challenging.

[0004] Some attempts have been made to create single-composition glasses via additive manufacturing. Silica glass of a single composition has been prepared via additive manufacturing using the selective laser melting (SLM) to melt and fuse silica particles in a silica powder bed. In addition, glass of a single composition has been prepared via an additive manufacturing method (G3DP) that melts silica in a kiln-like high temperature reservoir and deposits a ribbon of molten glass through a nozzle. These methods leave the filaments or selectively melted regions vulnerable to thermally induced stresses on cooling, which can prevent the part from achieving optical quality, for example, by creating undesirable refractive index gradients across the thickness of the part. Moreover, the selective melted regions may also leave trapped porosity between segments thereby resulting in resistance in merging the segments. In addition, these methods are not amenable to tightly controlled introduction of different compositions. It would be desirable to print and completely form the structure in the absence of high temperature.

[0005] Various embodiments described herein use direct ink writing (DIW) additive manufacturing to introduce the composition gradient into an amorphous, low density form (LDF). Following complete formation, the LDF is heat treated to transparency as a whole structure, thus reducing edge effects.

[0006] Current methods to form glass of gradient composition have also proven challenging. In a slurry-based 3D printing (S-3DP) system, the dopants are added after the LDF is built from a slurry and dried. This process challenges the structural integrity within the LDF. In addition, the introduction of the dopant in low viscosity droplets over the dried body leaves the potential for the species of interest to diffuse radially and axially and to fill the pores of the dried structure beneath by capillary forces, leading to reduced control over the introduced compositional gradient. Composition gradients may also be limited to material that can incorporate readily into the LDF by diffusion (e.g. small molecules, ions). Thus, it would be desirable to develop a process that forms a glass of gradient composition in which the dopants are a component of the mixture during formation of the LDF and before drying the LDF.

SUMMARY

[0007] Various embodiments described herein enable (1) the formation of optical or non-optical glass with custom composition profiles that are not achievable by conventional glass processing techniques, (2) the introduction of species that cannot be introduced easily by diffusion methods, and (3) the creation of glass optics containing custom patterned material properties that are far larger than those achievable by diffusion methods.

[0008] Some embodiments described herein introduce a gradient via DIW additive manufacturing and use continuous in-line mixing of glass-forming species, with or without dopant, to achieve the desired composition changes. The LDF is fully formed before drying. The dopant itself can be an ion, molecule, and/or particle, and it may be premixed with the glass-forming species in a high viscosity suspension, which limits its diffusion at low temperature within the LDF.

[0009] According to one embodiment, a method includes forming a structure by printing an ink, the ink including a glass-forming material, and heat treating the formed structure for converting the glass-forming material to glass.

[0010] According to another embodiment, a product includes a monolithic glass structure having physical characteristics of formation by three dimensional printing of an ink comprising a glass-forming material. Other aspects and advantages of the present invention will become apparent from the following detailed description, which, when taken in conjunction with the drawings, illustrate by way of example the principles of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG. **1** is a flow chart of a method to prepare glass components with custom-tailored composition profiles, according to one embodiment.

[0012] FIG. **2A** is a schematic drawing of a method to prepare a single composition glass components, according to one embodiment.

[0013] FIG. **2B** is a schematic drawing of a method to prepare a multiple composition glass components, according to one embodiment.

[0014] FIG. **3A** is an image of an extrusion of glass-forming ink onto a substrate, according to one embodiment.

[0015] FIG. **3B** is an image of a printed low density form, according to one embodiment.

[0016] FIG. **3C** is an image of a glass form following heat treatment of a printed low density form, according to one embodiment.

[0017] FIG. **4A** is a schematic drawing of a low density form that includes a gradient in a material property of the low density form along an axial direction, according to one embodiment.

[0018] FIG. **4B** is a schematic drawing of a low density form that includes a gradient in a material property of the low density form along a radial direction, according to one embodiment.

[0019] FIG. **5A** is an image of a low density form with a gradient in the axial direction following multiple component printing, according to one embodiment.

[0020] FIG. **5B** is an image of a glass form with a gradient in the axial direction following heat treatment of a printed low density form, according to one embodiment.

[0021] FIG. **5C** is an image of a low density form with a gradient in the radial direction following multiple component printing, according to one embodiment.

[0022] FIG. **4B** is an image of a glass form with a gradient in the radial direction following heat treatment of a printed low density form, according to one embodiment.

[0023] FIGS. **6A-6C** are images of printed parts formed with a silica composition, according to one embodiment.

[0024] FIGS. **6D-6E** are images of printed parts formed with a silica-titania composition, according to one embodiment.

[0025] FIG. **7A** is a plot of refractive index profile verses titania concentration of glass formed according to one embodiment.

[0026] FIG. **7B** is an image of the resultant glass structures formed with different titania concentrations, according to one embodiment.

[0027] FIG. **8** is a plot of the thermal treatment profile of the formation of a consolidated structure according to one embodiment. Images of each step are included as insets on the profile plot.

[0028] FIG. **9A** is an image of a gradient refractive index silica-titania glass lens prepared by direct ink writing, according to one embodiment.

[0029] FIG. **9B** is a surface-corrected interferogram of the glass lens of FIG. **9A**.

[0030] FIG. **9C** is an image of the 300-μm focal spot from the lens of FIG. **9A**.

[0031] FIG. **10A** is an image of a composite glass comprised of a gold-doped silica glass core, according to one embodiment.

[0032] FIG. **10B** is a plot of the absorbance as a function of wavelength of light of the composite glass of FIG. **10A**.

[0033] FIG. **10C** is a plot of the absorbance at 525 nm versus position along the glass surface of the composite glass of FIG. **10A**.

DETAILED DESCRIPTION

[0034] The following description is made for the purpose of illustrating the general principles of the present invention and is not meant to limit the inventive concepts claimed herein. Further, particular features described herein can be used in combination with other described features in each of the various possible combinations and permutations.

[0035] Unless otherwise specifically defined herein, all terms are to be given their broadest possible interpretation including meanings implied from the specification as well as meanings understood by those skilled in the art and/or as defined in dictionaries, treatises, etc.

[0036] It must also be noted that, as used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless otherwise specified.

[0037] The following description discloses several preferred embodiments of preparing optical and non-optical glass components with custom-tailored composition profiles, and/or related systems and methods.

[0038] In one general embodiment, a method includes forming a structure by printing an ink, the ink including a glass-forming material, and heat treating the formed structure for converting the glass-forming material to glass.

[0039] In another general embodiment, a product includes a monolithic glass structure having physical characteristics of formation by three dimensional printing of an ink comprising a glass-forming material.

[0040] A list of acronyms used in the description is provided below.

3D	Three dimensional
DIW	Direct ink write
FDM	Fused deposition modeling
IR	Infrared
G3DP	Glass three dimensional printing
GRIN	Gradient index glass
LDF	Low density form
Si	Silicon
S-3DP	Slurry-based three dimensional printing
SLM	Selective laser melting
Ti	Titanium
UV	Ultraviolet

[0041] Various embodiments described herein provide methods for fabricating active or passive optical or non-optical glass components and/or glass sensors with custom material composition profiles in 1-, 2-, or 3-dimensions. Various embodiments described herein enable the three dimensional (3D) printing of a variety of inorganic glasses, with or without compositional changes. Depending on glass composition and processing conditions, the glasses may appear either transparent or opaque to the human eye. However, the term "optical glass" does not refer only to glasses useful in the visible portion of the spectrum, but may also be extended to UV, visible, near-IR, mid-IR, and far-IR.

[0042] FIG. **1** shows a method **100** for preparing optical glass components with custom-tailored composition profiles in accordance with one embodiment. As an option, the present method **100** may be implemented to devices such as those shown in the other FIGS. described herein. Of course, however, this method **100** and others presented herein may be used to form structures for a wide variety of devices and/or purposes which may or may not be related to the illustrative embodiments listed herein. Further, the methods presented herein may be carried out in any desired environment. Moreover, more or less operations than those shown in FIG. **1** may be included in method **100**, according to various embodiments. It should also be noted that any of the aforementioned features may be used in any of the embodiments described in accordance with the various methods.

[0043] In one embodiment as shown in FIG. **1**, a method **100** begins with an operation **102** that includes forming a structure by printing an ink. According to various embodiments, printing an ink may involve one of the following additive manufacturing techniques that may have an ink mixing capability: direct ink writing (DIW), stereolithography in 3D systems, projection microstereolithography, fused deposition modeling, electrophoretic deposition, PolyJet processing, Direct Deposition, inkjet printing, inkjet powder bed printing, aerosol jet printing, etc. One could imagine combining these processes as well.

[0044] According to various embodiments, the method **100** may be used to create filaments, films, and/or 3D monolithic or spanning free-forms.

[0045] According to one embodiment, the ink includes a glass-forming material. According to another embodiment, the glass-forming material includes prepared

dispersions of particles, where the particles range in size from nanometers to microns. In some approaches, particles may be mono-dispersed. In other approaches, particles may be poly-dispersed. In another approach, particles may be agglomerated.

[0046] In another embodiment, the glass-forming material may be a single composition of inorganic particles, for example, but not limited to, fumed silica, colloidal silica, LUDOX colloidal silica dispersion, titania particles, zirconia particles, alumina particles, metal chalcogenide particles (e.g. CdS, CdSe, ZnS, PbS), etc. In yet other embodiments, the glass-forming material may be a single composition of inorganic-containing particles.

[0047] In one embodiment, the glass-forming material may be a plurality of a mixed composition particle, for example, but not limited to, a binary silica-titania particle, silica-germanium oxide particle, and/or may be a particle with an inorganic or organic chemically modified surface (i.e. titania-modified silica particles; silica-modified titania particles; 3-aminopropyltriethoxysilane modified silica particles).

[0048] In some embodiments, the glass-forming material may be a mixture of particles of different compositions, for example but not limited to, a silica particle plus titania particle mixture that when fused together forms silica-titania glass.

[0049] According to one embodiment, the glass-forming material may be a single composition of glass-forming material that may not be in the form of particles. In some embodiments, a dopant may be directly incorporated into polymers, for example but not limited to, silica, silica-titania containing polymers, silica-germanium oxide polymers, silica-aluminum oxide polymers, silica-boron trioxide polymers, etc.

According to some embodiments the glass-forming material of the ink may include large molecules and/or polymers (linear or branched) prepared from smaller metal-containing organic precursors. Examples of polymers include poly(dimethylsiloxane), silicones, diethoxysiloxane-ethyltitanate copolymer, polyhedral oligomeric silsesquioxane polymers and copolymers. Examples of large molecules include polyoxometalate clusters, oxoalkoxometalate clusters. Designer Si/Ti containing polymers may be synthesized via acid-catalyzed hydrolysis of organosilicates and organotitanates, e.g., tetraethylorthosilicate and titanium isopropoxide, with additional transesterification steps if necessary. Modifications to this process include: utilizing organometallic chemistries containing bonds other than metal-oxygen, e.g., (3-aminopropyl)triethoxysilane; doping via direct addition of salts to the polymer solution, e.g., NaF, $Cu(NO_3)_2$, Li_2CO_3; doping via inclusion of metal species into polymer chain during acid-catalyzed hydrolysis; replacement of major (for example, silicon (Si)), and minor (for example titanium (Ti)) glass components with alternatives that are able to undergo linear polymerization, e.g., Ge, Zr, V, Fe.

[0050] According to some embodiments the glass-forming material of the ink may include small metal-containing organic precursors and/or inorganic precursors, such as metalalkoxides, siloxanes, silicates, phosphates, chalcogenides, metal-hydroxides, metal salts, etc. Examples may include silicon alkoxides, boron alkoxides, titanium alkoxides, germanium alkoxides. In some approaches, the glass-forming material of the ink may include titanium isopropoxide, titanium diisopropoxide bis(acetylacetonate), tetraethyl orthosilicate, zinc chloride, titanium chloride.

[0051] In one embodiment, the glass-forming material may be suspended in a solvent. In one embodiment in which the glass-forming material is a polar and/or hydrophilic glass-forming material, the solvent is preferably a polar, aprotic solvent. In one approach, the solvent may be a pure component or mixture of the following: propylene carbonate, dimethyl ethers (e.g. tetra (ethylene glycol) dimethyl ether), and/or dimethylformamide. In another approach, the solvent may be a polar, protic solvent, for example, alcohol and/or water. In one embodiment in which the glass-forming material is hydrophobic, the solvent may be a non-polar solvent, for example, but not limited to, xylenes, alkanes.

[0052] According to one embodiment, the ink may be a combination of the glass-forming material and at least one second component that alters a property of the heat treated glass structure. In some embodiments, the second component may be a property altering dopant. In other embodiments, more than one material property may be affected by the addition of a second component. In various embodiments, the second component may affect the material property (e.g. characteristics) of the resulting structure in terms of one or more of the following: optical, mechanical, magnetic, thermal, electrical, chemical characteristics, etc.

[0053] In one approach, the second component may be in the form of ions. In another approach, the second component may be molecules. In yet another approach, the second component may be particles.

[0054] In some embodiments, the ink may contain an effective amount of one or more second components that may alter a property of the heat treated glass structure. The effective amount of a second component is an amount that alters a property of the heat

treated glass structure may be readily determined without undue experimentation following the teachings herein and varying the concentration of the additive, as would become apparent to one skilled in the art upon reading the present description.

[0055] In one embodiment, the color of the resulting structure may be affected by the addition of one or more second components selected from the following group: metal nanoparticles (gold, silver) of various sizes, sulfur, metal sulfides (cadmium sulfide), metal chlorides (gold chloride), metal oxides (copper oxides, iron oxides).

[0056] In one embodiment, the absorptivity (linear or nonlinear) of the resulting structure may be affected by the addition of a one or more second components selected from the following group: cerium oxide, iron, copper, chromium, silver, and gold.

[0057] In one embodiment, the refractive index of the resulting structure may be affected by the addition of one or more second components selected from the following group: titanium, zirconium, aluminum, lead, thorium, barium.

[0058] In one embodiment, the dispersion of the resulting structure may be affected by the addition of one or more second components selected from the following group: barium, thorium.

[0059] In one embodiment, the attenuation/optical density of the resulting structure may be affected by the addition of one or more second components selected from the following group: alkaline metals and alkaline earth metals.

[0060] In one embodiment, the photosensitivity of the resulting structure may be affected by the addition of one or more second components selected from the following group: silver, cerium, fluorine.

[0061] In one embodiment, the electrical conductivity of the resulting structure may be affected by the addition of one or more second components selected from the following group: alkali metal ions, fluorine, carbon nanotubes.

[0062] In one embodiment, the birefringence, such as having a refractive index that depends on polarization and propagation direction of light imparted by the crystalline phase formed from the second component, of the resulting structure may be affected by the addition of one or more second components selected from the following group: titanium, zirconium, zinc, niobium, strontium, lithium, in combination with silicon and oxygen.

[0063] In one embodiment, the thermal conductivity of the resulting structure may be affected by the addition of one or more second components selected from the following group: carbon nanotubes, metals.

[0064] In one embodiment, the thermal emissivity of the resulting structure may be affected by the addition of one or more second components selected from the following group: tin oxide, iron.

[0065] In one embodiment, the thermal expansion of the resulting structure may be affected by the addition of a one or more second components selected from the following group: boron oxide, titanium oxide.

[0066] In one embodiment, the glass transition temperature of the resulting structure may be affected by the addition of sodium carbonate as the second component.

[0067] In one embodiment, the melting point of the resulting structure may be affected by the addition of one or more second components selected from the following group: sodium, aluminum, lead.

[0068] In one embodiment, the gain coefficient of the resulting structure may be affected by the addition of one or more second components selected from the following group: rare earth ions (e.g. neodymium, erbium, ytterbium); transition metal ions (e.g. chromium).

[0069] In one embodiment, the photoemission of the resulting structure may be affected by the addition of a second component. In another embodiment, the luminescence of the resulting structure may be affected by the addition of a second component. In yet another embodiment, the fluorescence of the resulting structure may be affected by the addition of a second component.

[0070] In one embodiment, the chemical reactivity of the resulting structure may be affected by the addition of one or more second components selected from the following group: alkaline metals, alkaline earth metals, silver.

[0071] In one embodiment, the density of the resulting structure may be affected by the addition of one or more second components selected from the following group: titanium, zirconium, aluminum, lead, thorium, barium.

[0072] In one embodiment, the concentration of the second component in the ink may change during the printing for creating a compositional gradient in the printed structure. In some approaches, the second component in the ink may create a compositional gradient in the final heat treated structure.

[0073] In some embodiments, the concentration of the second component in the ink may create a compositional change (e.g. gradient, pattern, etc.) that may not be symmetrical about any axis, for example but not limited to, a pattern may change radially around the structure, a pattern may be formed as a complete 3D structure, etc.).

[0074] In some embodiments, the ink may contain an effective amount of one or more additional additives that may perform specific functions. For example, but not limited to, the additives may enhance dispersion, phase stability, and/or network strength; control and/or change pH; modify rheology; reduce crack formation during drying; aid in sintering; etc. The effective amount of an additive is an amount that imparts the desired function or result, and may be readily determined without undue experimentation following the teachings herein and varying the concentration of the additive, as would become apparent to one skilled in the art upon reading the present description.

[0075] In one embodiment, the ink may include one or more of the following additives to enhance dispersion: surfactants (e.g. 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MEEAA)), polyelectrolytes (e.g. polyacrylic acid), inorganic acids (e.g. citric acid, ascorbic acid).

[0076] In one embodiment, the ink may include an additive (e.g. boric anhydride (B_2O_3)) to enhance phase stabilization (i.e. to prevent phase/composition separation, which may or may not be a crystalline phase separation). Another example is ZnO, which can act as a phase stabilizer for alkali silicate.

[0077] In one embodiment, the ink may include an additive (e.g. boric anhydride B_2O_3) to inhibit crystallization. Other crystallization inhibitors include Al_2O_3 and Ga_2O_3.

[0078] In one embodiment, the ink may include an additive (e.g. polydimethylsiloxanes) to strengthen the network.

[0079] In one embodiment, the ink may include one or more of the following additives to control pH: organic acids, inorganic acids, bases (e.g. acetic acid, HCl, KOH, NH_4OH).

[0080] In one embodiment, the ink may include one or more of the following additives to modify rheology: polymers (e.g. cellulose, polyethylene glycols, poly vinyl alcohols); surfactants (e.g. MEEAA, sodium dodecyl sulfate, glycerol, ethylene glycol); metal alkoxides (e.g. titanium diisopropoxide bis(acetylacetonate)).

[0081] In one embodiment, the ink may include one or more of the following additives as a drying aid to increase resistance to cracking and/or reduce crack formation during drying: polymers (e.g. polyethylene glycol, polyacrylates), cross-linkable monomers or polymers and crosslinking reagents (e.g. polyethylene glycol diacrylate (PEGDA)).

[0082] In one embodiment, the ink may include an additive as a sintering aid. Sintering aids enhance the sintering/densification process. In the case of glass, a sintering aid may lower the viscosity of the material being sintered to glass. For example, boric anhydride (B_2O_3) may be included as a sintering aid.

[0083] In various embodiments, the formulation of glass-forming ink (i.e. glass-forming material) is optimized for the following combination of factors: printability (depending on the method of 3D printing), resistance to cracking, and sintering to transparency. In some approaches, volumetric loading of the formulation of glass-forming ink is optimized. In some approaches, the characteristics of the composition gradient of the glass-forming material may be optimized.

[0084] According to one embodiment, a formulation of glass-forming material may include: glass-forming, inorganic species in the range of about 5 vol% to about 50 vol% of total volume; solvent in the range of about 30 vol% to about 95 vol%; a second

component(s) (i.e. dopants) in the range of 0 wt% to about 20 wt%; and an additive(s) from 0 wt% to about 10 wt%.

[0085] Example Formulation 1 of Ink

5-15 vol%	Fumed Silica (Cabosil EH-5 or Cabosil OX-50)
30-95 vol%	Tetraethylene glycol dimethyl ether
0-20 wt%	Titanium diisopropixide bis(acetylacetonate)
0-6 wt%	Ethylene glycol
0-2 wt%	Poly(dimethylsiloxane)

[0086] Example Formulation 2 of Ink

75-95 vol%	Silica-titania-containing polymers
10-25 vol%	Tetraethylene glycol dimethyl ether
0-10 vol%	H_2O for prehydrolysis

[0087] Example Formulation 3 of Ink

5-20 vol%	25-nm titania-coated silica particles
25-45 vol%	Propylene carbonate
25-45 vol%	Tetraethylene glycol dimethyl ether
0-5 wt%	MEEAA

[0088] According to one embodiment, the concentration of the second component in the ink may change during the printing for creating a compositional gradient in the structure and thus, the final heat treated structure.

[0089] In one embodiment, the temperature of the ink may be less than about 200 °C during the printing.

[0090] In one embodiment, the method **100** includes drying the formed structure for removing a sacrificial material, where the drying is done prior to heat treating the formed structure. Ideally, the fully formed structure is dried in a single process.

[0091] According to one embodiment as shown in FIG. **1**, method **100** includes operation **104** that involves heat treating the formed structure for converting the glass-forming material to glass.

[0092] In one embodiment, the method includes additional processing of the heat-treated glass structure. In one approach, the method includes grinding the heat-treated glass structure. In another approach, the method includes polishing the heat-treated glass structure. In yet another approach the method includes grinding and polishing the heat-treated glass structure.

[0093] In one embodiment, the heat-treated glass structure may be in the form of a fiber.

[0094] In another embodiment, the heat-treated glass structure may be in the form of a sheet.

[0095] In one embodiment, the heat-treated glass structure may be in the form of a three-dimensional monolith.

[0096] In another embodiment, the heat-treated glass structure may be in the form of a coating on a substrate such as a part, a tool, etc.

[0097] FIGS. **2A-2B** depict methods **200** and **250** for preparing an optical glass component with custom-tailored composition profiles in accordance with one embodiment. As an option, the present methods **200** and **250** may be implemented in conjunction with features from any other embodiment listed herein, such as those

described with reference to the other FIGS. Of course, however, such methods **200** and **250** and others presented herein may be used in various applications and/or in permutations which may or may not be specifically described in the illustrative embodiments listed herein. Further, the methods **200** and **250** presented herein may be used in any desired environment.

[0098] An exemplary embodiment of method **200** to prepare a single component silica glass is illustrated in FIG. **2A**. According to one embodiment, the method to print the ink involves DIW printing as shown in steps **222** and **224**. DIW is a 3D printing process based on extrusion of viscoelastic material. Air pressure or positive displacement pushes the ink **202** through a small nozzle **208**. In some approaches, the nozzle **208** is controlled by a computer and has three degrees of freedom (x, y, and z). In other approaches the nozzle **208** may be expanded to have six axes for printing. The nozzle **208** may be positioned to extrude the ink in a controlled spatial pattern.

[0099] In steps **222** and **224**, DIW deposits filaments **212** of rheologically tuned glass-forming DIW ink **202** containing glass-forming species in a prescribed geometry to create a weakly associated, near net-shaped, porous amorphous low density form (LDF) **214**. In some approaches, there is rapid solidification of the extruded filament **212** into the LDF **214**. In some approaches, the LDF **214** may be referred to as a green body, glass-forming species, etc. The glass-forming species may be introduced as either precursors and/or as colloids/particles. In some approaches, the glass-forming DIW ink **202** may be colloidal silica ink.

[00100] According to one embodiment, the formulation of the glass-forming DIW ink is optimized for printability, drying/bakeout, and sintering. The formulation of the glass-

forming DIW ink may be optimized for printability in terms of shear thinning, ability to flow (steady flow), ability to hold shape (shape retention), low agglomeration, long print time, stable pot life (stability), etc. The formulation of the glass-forming DIW ink may be optimized for drying in terms of robustness to handling, crack resistance, low/uniform shrinkage, porosity suited to organic removal, etc. The formulation of the glass-forming DIW ink may be optimized for sintering in terms of crack resistance, low/uniform shrinkage, able to densify/become transparent, low tendency to phase separate, etc.

[00101] According to one embodiment, step **222** involves the glass-forming DIW ink **202** extruded through a nozzle **208** to deposit filaments **212** onto a substrate **210** in a single layer.

[00102] Step **224** of method **200** involves building layer upon layer of glass-forming DIW ink **202** to form a LDF **214.** FIG. **3A** shows an image of the colloidal silica ink being extruded onto the substrate.

[00103] The LDF **214** may be treated to multiple steps to consolidate and convert the LDF **214** to the heat-treated glass form **216**.

[00104] Optionally, the LDF **214**, either before or after drying, may undergo additional processing to further change the composition of the part. In some approaches, additional processing may include diffusion, leaching, etching, etc. In other approaches, additional processing may include light, sound, vibration to alter the characteristics of the printed form, or a combination thereof. In yet other approaches, a chemical treatment before closing the porosity of the LDF by heat treatment may define the optical quality of the resulting glass form.

[00105] In step **226**, the LDF may be dried, calcined (i.e. removal of residual solvents/organics at elevated temperature), etc. During drying, the liquid/solvent phase may be removed. The LDF **214** may be released from the substrate **210** on which the LDF **214** was printed. In some approaches, the drying step **226** may involve dwelling hours to weeks at temperatures below the boiling point of the solvent.

[00106] In some embodiments, a processing step **226** may involve a lower heating step (i.e. burnout) to remove organics as well as any residual and/or adsorbed water/solvent phase. In some approaches, the burnout step may involve dwelling 0.5 to 24 hours at 250-600°C.

[00107] In some embodiments, the processing step **226** may include heating the LDF **214** under alternate gas atmospheres for chemically converting the surface (e.g. conversion of free surface hydroxyls to dehydrated siloxanes). In some approaches, the processing step **226** may include heating the LDF **214** under oxidative gas atmospheres (e.g. O_2 gas). In other approaches, the processing step **226** may include heating the LDF **214** under reducing gas atmospheres (e.g. H_2 gas). In yet other approaches, the processing step **226** may include heating the LDF **214** under non-reactive gas atmospheres (e.g. Ar, He). In yet other approaches, the processing step **226** may include heating the LDF **214** under reactive gas atmospheres (e.g. N_2, Cl_2). In yet other approaches, the processing step **226** may include heating the LDF **214** under vacuum.

[00108] In some embodiments, the processing step **226** may also include compacting the parts (i.e. reducing porosity) of the LDF **214** using uniaxial pressure or isostatic pressure thereby resulting in a compact form. In some approaches, the processing step

226 may also include compacting the parts (i.e. reducing porosity) of the LDF **214** under vacuum.

[00109] FIG. **3B** shows an image of a LDF that has been dried.

[00110] According to one embodiment, the method involves heat treating the dried LDF **214**, as shown in step **228** of FIG. **2A**, to close the remaining porosity and form a consolidated, transparent glass part. In some approaches, a compact form of the LDF may be heat treated.

[00111] The heat treating step **228** may involve sintering, in which the LDF **214** (i.e. inorganic, glass-forming species) completely densifies into a solid glass consolidated form **216** at elevated temperatures. In some approaches, sintering the LDF may involve dwelling minutes to hours at 500-1600°C. The temperature for sintering depends on material composition and initial inorganic loading and porosity of the LDF. In some approaches, the sintering of the LDF may involve simultaneous use of applied pressure. In some approaches, the heat treating step **228** may occur under different atmospheric conditions. In other approaches, the heat treating step **228** may occur under vacuum.

[00112] In some embodiments, the heat treated glass form **216** may be a monolithic glass structure.FIG. **3C** shows an image of a monolithic glass structure after heat treatment of the LDF shown in FIG. **3B**. In some embodiments, the resultant glass consolidated form **216** may retain the characteristics of the ink 202 that may have been imparted during DIW printing (steps **222 224**).

[00113] In one embodiment, the glass consolidated form **216** may have a physical characteristic of the LDF **214** including spiral-shaped, arcuate and/or straight ridges along one surface of the glass form **216**.

[00114] In one embodiment, in the post-processing step **230**, the glass form **216** may be post-processed, for example to achieve the desired figure and/or surface finish of a final polished optic form **218** through techniques such as grinding and/or polishing. In one embodiment, the polished optic **218** is a polished formation by 3D printing and heat treatment, such that the properties of the LDF **214** remain and are not removed by polishing. In one embodiment, the polished optic **218** is a monolithic glass structure that has been polished.

[00115] In some approaches, the glass form **216** may be treated as bolt glass, thereby allowing removal any of the evidence of the printing process by conventional techniques known in the art. In other approaches, the glass form **216** retains features achievable only by the printing processes described herein, even after post-processing.

[00116] According to one embodiment, a schematic representation of a method **250** to form a gradient and/or a spatial pattern in a glass product is illustrated in FIG. **2B**. In other embodiments, the method may create a compositional change (e.g. gradient, pattern, etc.) that may not be symmetrical about any axis, for example but not limited to, a pattern may change radially around the structure, a pattern may be formed as a complete 3D structure, etc.).

[00117] In one approach, the method may form a gradient index (GRIN) glass. Printing a GRIN glass involves printing a monolith with no porosity in which the characteristics of the formation of the LDF result in favorable elastic modulus/viscosity as indicated by space filling, high aspect ratio, and spanning. In addition, the method may involve matching the rheology of the two DIW inks desired to create the gradient. In

some embodiments, two, three, four, etc. inks may be combined by mixing before extrusion of the filament onto the substrate.

[00118] According to one embodiment, during DIW printing, steps **232**, **234**, the filament composition **213** may be tuned during printing by adjusting the flow rates of separate streams to introduce desired composition changes within the LDF **214** at the desired locations.

[00119] In some approaches, different inks **203**, **204** may be introduced separately to create the LDF **215**. As shown illustrated in a schematic representation of a side view in FIG. **4A**, in one approach, a monolithic glass structure **400** with the physical characteristics of formation by 3D printing (LDF **215** of FIG. **2B**) may include a gradient in a refractory index of the monolithic glass structure **400** along an axial direction of the monolithic glass structure **400**. The axial **408** direction is perpendicular to the plane **410** of deposition.

[00120] Looking back to FIG. **2B**, the glass structure is formed as a LDF (LDF **215** in FIG. **2B**) in which a first glass-forming ink **203** may be extruded followed by extrusion of a second glass-forming ink **204**. The resulting glass structure **400** in FIG. **4A** has a first glass **403** and a second glass **404**, from the first glass-forming ink **203** and second glass-forming ink **204**, respectively.

[00121] Moreover, the resulting glass structure **400** of FIG. **4A** may include an interface **406** between first glass **403** formed from the glass-forming material and second glass **404** formed from a second glass-forming material having a different composition than the glass-forming material. In some approaches, there may be no intermixing of the first glass **403** in the second glass **404** because there may no migration of the second

glass-forming material into the first glass-forming material across the interface, or vice versa.

[00122] In one embodiment, the interface **406** may be oriented substantially along a plane **410** of deposition of the monolithic glass structure **400** thereby bifurcating the monolithic glass structure into two portions, the first glass **403** and the second glass **404**, having different compositions directly adjacent the interface.

[00123] As shown in FIGS. **5A-5D**, two different inks, silica and silica with 20 nm gold nanoparticles were used to form a compositional change leading to a change in material property in the final heat-treated structure. FIGS **5A-5B** show the formation of an axial step in absorption in a final heat-treated structure. As shown in FIG. **5A**, the LDF was formed with a conformational change in which the first ink silica was used to form a portion of the LDF (bottom of LDF in FIG. **5A**), and then the ink was switched to the second ink, silica/gold nanoparticle ink (top of LDF in FIG. **5A**). The LDF was then consolidated to glass by sintering in the heat treatment (step **238** of FIG. **2B**). A resultant monolithic glass structure with a gradient in absorbance along an axial direction is shown in FIG. **5B** in which the silica/gold nanoparticle portion of the glass is up in FIG. **5B**.

[00124] In one embodiment a physical characterization of the monolithic glass structure **217** includes a gradient comprising two or more glass-forming materials such that the interface between a first glass-forming material and a second glass-forming material that is uniform. As illustrated in FIG. **5A**, there is an interface between the upper glass-forming material (silica/gold nanoparticles) and the lower material (silica). Moreover, there is no migration of the first glass-forming material (silica) into the second glass-forming material (silica/gold nanoparticles), and vice versa, there is no migration of

the second glass-forming material (silica/gold nanoparticles) into the first glass-forming material (silica).

[00125] The prior art methods to 3D print optical glass have not been able to achieve embodiments described herein because the prior art methods have difficulty controlling thermal gradients during 3D printing, have a non-uniform interface between filaments, and/or lack the capability to incorporate multiple materials within the green body or LDF.

[00126] In other approaches, a smooth composition change may be created by blending inline the ink streams from the different inks **203**, **204** via active mixing with a mixing paddle **206** near the tip of the nozzle **208**. As illustrated in a schematic representation of a top view in FIG. **4B**, in one approach, a monolithic glass structure **420** with physical characteristics of formation by 3D printing (LDF **215** of FIG. **2B**) may include a gradient in the refractive index, or another material property such as absorbance, along a radial direction of the monolithic glass structure **420**. A radial **412** direction is along the plane **410** of deposition in any direction. Looking back to FIG. **2B**, the glass structure is formed as a LDF (LDF **215** in FIG. **2B**) in which a radial step in refractive index in which the two inks **203**, **204** in FIG. **2B** were blended inline the ink streams. The resulting glass structure **420** in FIG. **4B** has a first glass **414** and a second glass **413**, from the first glass-forming ink **203** and second glass-forming ink **204**, respectively.

[00127] Moreover, the resulting glass structure **420** of FIG. **4B** includes an interface **416** between first glass **414** formed from the glass-forming material and second glass **413** formed from a second glass-forming material having a different composition than the glass-forming material. In some approaches, there may be no intermixing of the first

glass **414** in the second glass **413** because there may no migration of the second glass-forming material into the first glass-forming material across the interface, or vice versa.

[00128] In one embodiment, the interface **416** may be oriented substantially perpendicular to a plane **410** of deposition of the monolithic glass structure **420** thereby bifurcating the monolithic glass structure **420** into two portions, the first glass **413** and the second glass **414**, having different compositions directly adjacent the interface **416**.

[00129] According to one embodiment, two different inks may be used to print a conformational change in a LDF that leads to a material property of a radial step in absorbance in the final heat-treated structure. As shown in FIGS. **5C-5D** , a first ink of silica and a second ink of silica/gold nanoparticles were used to print a radial step in absorbance in which the two inks were blended inline the ink streams. FIG. **5C** shows the LDF form with the silica/gold nanoparticle ink in the center of the LDF and the silica ink on the outer portions of the LDF. A resultant monolithic glass structure with a gradient in the absorbance along a radial direction is shown in FIG. **5D**.

[00130] The compositional changes may not be limited to axial and/or radial gradients (such as those that can be achieved by diffusion techniques) but rather can be made to create arbitrary profiles in the LDF.

[00131] Compositional changes in the LDF **215** may lead to varying material properties within the formed glass **217**. Examples of material properties that may be affected by compositional changes in the LDF **215** are detailed more fully above, and may include, but may not be limited to: absorptivity, transmission, refractive index, dispersion, scatter, electrical conductivity, thermal conductivity, thermal expansion, gain

coefficient, glass transition temperature (Tg) melting point, photoemission, fluorescence, chemical reactivity (e.g. etch rate), density/porosity.

[00132] As shown in FIG. **2B**, DIW printing in steps **232**, **234** may involve forming the LDF **215**, according to one embodiment. The LDF begins in the first step **232** of DIW printing as a single layer on a substrate **210**. As the DIW printing continues in step **234**, the LDF **215** may be formed layer by layer until the desired LDF **215** (i.e. green body) is formed.

[00133] In some embodiments, formation of a LDF with single composition (method **200**) or a multiple composition (for example, a gradient) (method **250**) may involve fused deposition modeling (FDM). FDM uses thermoplastic filament, that may be a composite mixture of several materials combined with a mixing paddle similar to the ink mixture of DIW (see steps **232-234** of FIG. **2B**). The resulting filament may be extruded through a heated nozzle to form a LDF on a substrate as shown in steps **222-224** or steps **232-234** in FIGS. **2A** and **2B**, respectively. The heated nozzle, at temperatures in the range of about 150°C to 200°C, partially heats the filament for extrusion. In some approaches, a sacrificial support material may be extruded by a second nozzle to provide a support for the glass-forming material extruded by the mixing nozzle. In some approaches, the polymer of the extruded filament and/or support material may be removed after formation of the LDF.

[00134] In various embodiments, the LDF may be formed in a complex shape, for example, but not limited to, a conical form, a corkscrew pattern, a cylinder, etc.

[00135] The LDF **215** may be treated to multiple steps to consolidate and convert the LDF **215** to the heat-treated glass form **217**.

[00136] Once formed, the LDF **215** may be dried and/or receive additional processing as described above for step **226** in method **200** in FIG. **2A**.

[00137] Referring back to FIG. **2B**, according to one embodiment, step **238** of method **250** includes heat treating the dried LDF **215** to close the remaining porosity and form a consolidated, transparent glass part. The resultant glass consolidated form **217** may retain the compositional variation that may have been imparted during DIW printing (steps **232**, **234**).

[00138] In one embodiment, the glass consolidated form **217** may have a physical characteristic of the LDF **215** including spiral-shaped, arcuate and/or straight ridges along one surface of the glass form **217**.

[00139] According to one embodiment, in a post-processing step **240**, the glass form **217** may be further processed, for example to achieve the desired figure and/or surface finish of a final polished optic **220** through techniques such as grinding and/or polishing. In one embodiment, the polished optic **220** is a polished formation by 3D printing and heat treatment, such that the properties of the LDF **215** remain and are not removed by polishing. In one embodiment, the polished optic **220** is a monolithic glass structure that has been polished.

[00140] The various embodiments described herein may be extended to a variety of (predominantly) amorphous, inorganic glass materials in addition to silica-based glasses, including phosphate-based glasses, borate glasses, germanium oxide glasses, fluoride glasses, aluminosilicate glasses, and chalcogenide glasses.

[00141] **Example 1 of Heat Treatment**

[00142] Printed monolithic silica or silica-titania green-bodies (25 mm diameter, 5 mm thick) are placed onto a hot-plate at 100 °C. After 3 hours, the printed green bodies are released from the substrate. The green bodies are then dried in a box furnace at 100 °C for 110 hours. Next, the liquid-free green bodies are heated to 600 °C at a ramp rate of 10 °C/min and left to dwell for 1 hour to burn out remaining organic components. The green bodies are then ramped at 100 °C/hr to 1000 °C and held for 1 hr under vacuum. Last, the part is sintered in a preheated furnace at 1500 °C for 3-10 minutes. The parts are then removed and rapidly cooled to room temperature. All non-vacuum processing steps are performed in air.

[00143] **Example 2 of Heat Treatment**

[00144] Printed monolithic silica green-bodies composed of 25-nm diameter silica or silica-titania particles (25 mm diameter, 5 mm thick) ramped in a box furnace to 75 °C at a rate of 3 °C/h. Once the oven reaches 75 °C, the printed green bodies are released from the substrate. The green bodies are then dried in a drying oven at 75 °C for 120 hours. Next, the liquid-free green bodies are heated to 600 °C at a ramp rate of 1 °C/min and left to dwell for 1 hour to burn out remaining organic components. Last, the part is sintered in a preheated furnace at 1150 °C for 1 hour. The parts are then removed and rapidly cooled to room temperature. All non-vacuum processing steps are performed in air.

[00145] **Experiments**

[00146] FIGS. **6A-6F** are images of printed parts made with Formulation 3 of Ink (as described above). FIGS. **6A-6C** are images of printed parts formed with a silica-only composition. FIG. **6A** is an images of the green body formed after printing. FIG. **6B** is an

image after drying of the green body of FIG. **6A**. FIG. **6C** is an image after consolidation of the dried green body of FIG. **6B**.

[00147] FIGS. **6D-6F** are images of printed parts formed with a silica-titania composition. FIG. **6D** is an image of the green body formed after printing. FIG. **6E** is an image after drying of the green body of FIG. **6D**. FIG. **6F** is an image after consolidation of the dried green body of FIG. **6E**.

[00148] FIG. **7A** is a plot of refractive index profile (y-axis) versus titania (TiO_2) concentration (wt%, x-axis) in a resultant glass. Glasses made from the inks of Formulation 1 (as described above) are represented on the plot as diamonds (♦, solid line) and have a variation in refractive index comparable to commercial silica (▲) and silica-titanate glasses (○, □) (dotted line). FIG. **7B** is an image of the resultant glass structures formed from the ink formulations represented by the diamonds (♦) of FIG. **7A** at different concentrations of wt% TiO_2 (2 wt%, 4 wt%, 5 wt%, 6 wt%, 8 wt%, 9 wt%, 10 wt%).

[00149] FIG. **8** is a plot of the thermal treatment profile of the formation process of a consolidated printed parts using Formulation 1 Ink (as described above). The volumetric shrinkage (V_{ink}) of the structure at each step during the heat treatment process is shown next to the image of the structure.

[00150] FIG. **9A** is an optical image of a gradient refractive index silica-titania glass lens prepared by direct ink writing the LDF while blending two inks inline at the printhead in the required ratio to deposit a radial gradient in TiO_2 concentration. Two inks were used from the Formulation 1 Ink (described above), Ink A contained 0% titanium alkoxide and Ink B contained enough titanium alkoxide to result in 1.6 wt% TiO_2 in the final consolidated glass. The glass was consolidated using the heat treatment

profile shown in FIG. **8** and then polished using ceria pad polishing. FIG. **9B** is a surface-corrected interferogram, which shows how the refractive index changes within the bulk of the material shown in the image of FIG. **9A**. The refractive index is highest at the center, where the TiO_2 composition is highest, and lowest at the edges, where the TiO_2 concentration is lowest. A lineout across the center shows that the refractive index change across the center is parabolic, as shown by the inset plot of FIG. **9B** ($\delta n/(n_0-1)$ on y-axis, Distance (mm) on x-axis), which suggests the part can function as a lens. FIG. **9C** is an image of the 300-μm focal spot from the lens, which has a focal length of 62 cm.

[00151] FIG. **10A** is an optical image of a composite glass comprised of a gold-doped silica glass core with an undoped silica glass cladding, which was prepared by direct ink writing the composition change into the LDF. Two silica inks were used, with one ink containing gold nanoparticles. FIG. **10B** is a plot of the absorbance as a function of wavelength of light, with each spectrum corresponding to the indicated positions across the glass. The peaks at 525 nm were attributed to absorbance from the gold nanoparticles. FIG. **10C** is a plot of the absorbance at 525 nm (y-axis) versus position along the glass surface (x-axis, with the position 0 being the center of the glass). The plot of FIG. **10C** represents that the absorbance at 525 nm was tuned within this glass. The spot size measured was an average over a ~ 1mm diameter spot.

[00152] **In Use**

[00153] Various embodiments described herein may be used to make active or passive optical glass components (e.g. lenses, corrector plates, windows, screens, collectors, waveguides, mirror blanks, sensors, etc.) with specialized compositions and material properties for both commercial or government applications. These methods may be used

to introduce ions, molecules, or particles in arbitrary (i.e. custom) locations within the glass components (monoliths, films, or free-forms) to achieve spatially varying material properties within the glass, including: absorptivity, transmission, refractive index, dispersion, scatter, electrical conductivity, thermal conductivity, thermal expansion, gain coefficient, glass transition temperature (Tg), melting point, photoemission, fluorescence, chemical reactivity (e.g. etch rate), or density/porosity.

[00154] Various embodiments described herein provide methods for preparing intricate 3D and controlled color glass art, jewelry, etc. The control of the dopants of silver and gold nanoparticles allows control of the reflective and transmissivity properties of the art piece.

[00155] Further embodiments include active or passive optical glass components useful for lenses, corrector plates, windows, screens, collectors, waveguides, mirror blanks, sensors, etc., as well as non-optical glass components useful in conventional applications.

[00156] The inventive concepts disclosed herein have been presented by way of example to illustrate the myriad features thereof in a plurality of illustrative scenarios, embodiments, and/or implementations. It should be appreciated that the concepts generally disclosed are to be considered as modular, and may be implemented in any combination, permutation, or synthesis thereof. In addition, any modification, alteration, or equivalent of the presently disclosed features, functions, and concepts that would be appreciated by a person having ordinary skill in the art upon reading the instant descriptions should also be considered within the scope of this disclosure.

[00157] While various embodiments have been described above, it should be understood that they have been presented by way of example only, and not limitation. Thus, the breadth and scope of an embodiment of the present invention should not be limited by any of the above-described exemplary embodiments, but should be defined only in accordance with the following claims and their equivalents.

CLAIMS

What is claimed is:

1. A method, comprising:

forming a structure by printing an ink, the ink comprising a glass-forming material; and

heat treating the formed structure for converting the glass-forming material to glass.

2. The method as recited in claim 1, comprising drying the formed structure for removing a sacrificial material, wherein the drying is done prior to heat treating the formed structure.

3. The method as recited in claim 1, wherein the ink is a combination of the glass-forming material and a second component that alters a property to the heat treated structure.

4. The method as recited in claim 3, wherein a concentration of the second component in the ink changes during the printing for creating a compositional gradient in the structure.

5. The method as recited in claim 1, wherein a temperature of the ink is less than about 200 °C during the printing.

6. The method as recited in claim 1, wherein the glass-forming material is selected from a group of materials consisting of: silica, fumed silica, colloidal silica, LUDOX colloidal silica dispersion, titania particles, zirconia particles, alumina particles, and metal chalcogenide particles.

7. The method as recited in claim 1, wherein the glass-forming material is suspended in a solvent during forming.

8. The method as recited in claim 1, comprising at least one of grinding and polishing the heat-treated structure.

9. The method as recited in claim 1, wherein the heat-treated structure is in the form of a fiber.

10. The method as recited in claim 1, wherein the heat-treated structure is in the form of a sheet.

11. The method as recited in claim 1, wherein the heat-treated structure is in the form of a three-dimensional monolith.

12. The method as recited in claim 1, wherein the heat-treated structure is in the form of a coating on a substrate.

13. The method as recited in claim 1, wherein the ink comprises an effective amount of an additive that imparts at least one of the following characteristics: enhance dispersion, enhance phase stability, enhance network strength, control pH, change pH, modify rheology, reduce crack formation during drying, and aid in sintering.

14. A product, comprising:

a monolithic glass structure having physical characteristics of formation by three dimensional printing of an ink comprising a glass-forming material.

15. The product as recited in claim 14, wherein the physical characteristics of formation by three dimensional printing include ridges along one surface of the monolithic glass structure.

16. The product as recited in claim 14, wherein the monolithic glass structure comprises an additive selected from a group of additives consisting of: 2-[2-(2-methoxyethoxy)ethoxy]acetic acid, polyelectrolytes, polyacrylic acid, inorganic acids, citric acid, ascorbic acid, boric anhydride, polydimethylsiloxanes, organic acids, bases, acetic acid, HCl, KOH, NH_4OH, cellulose, polyethylene glycols, poly vinylalcohols, sodium dodecyl sulfate, glycerol, ethyleneglycol, metal

alkoxides, titanium diisopropoxide bis(acetylacetonate, polymers, polyethylene glycol, polyacrylates, crosslinkable monomersor polymers, and polyethylene glycol diacrylate.

17. The product as recited in claim 14, wherein the physical characteristics of formation by three dimensional printing include a gradient in a refractive index of the monolithic glass structure along an axial direction of the monolithic glass structure.

18. The product as recited in claim 14, wherein the physical characteristics of formation by three dimensional printing include a gradient in the refractive index along a radial direction of the monolithic glass structure.

19. The product as recited in claim 14, wherein the physical characteristics of formation by three dimensional printing include an interface between first glass formed from the glass-forming material and second glass formed from a second glass-forming material having a different composition than the glass-forming material, wherein there is no intermixing of the first glass in the second glass.

20. The product as recited in claim 19, wherein the interface is oriented substantially along a plane of deposition of the monolithic glass structure thereby bifurcating the monolithic glass structure into two portions having different compositions directly adjacent the interface.

21. The product as recited in claim 19, wherein the interface is oriented substantially perpendicular to a plane of deposition of the monolithic glass structure thereby bifurcating the monolithic glass structure into two portions having different compositions directly adjacent the interface.

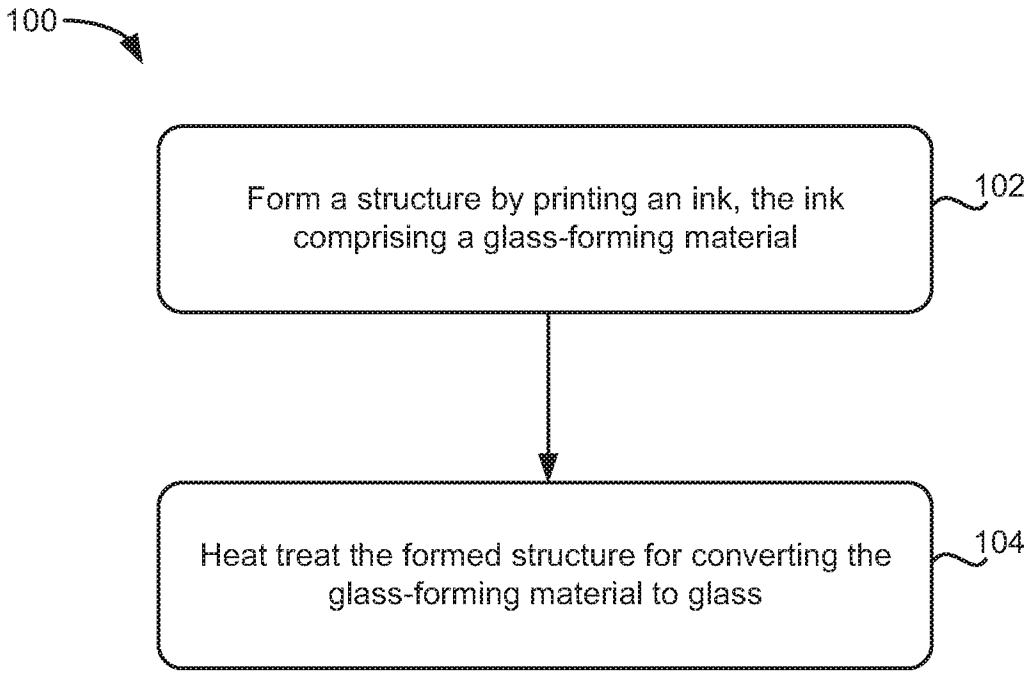

100
Form a structure by printing an ink, the ink comprising a glass-forming material
102
Heat treat the formed structure for converting the glass-forming material to glass
104

FIG. 1

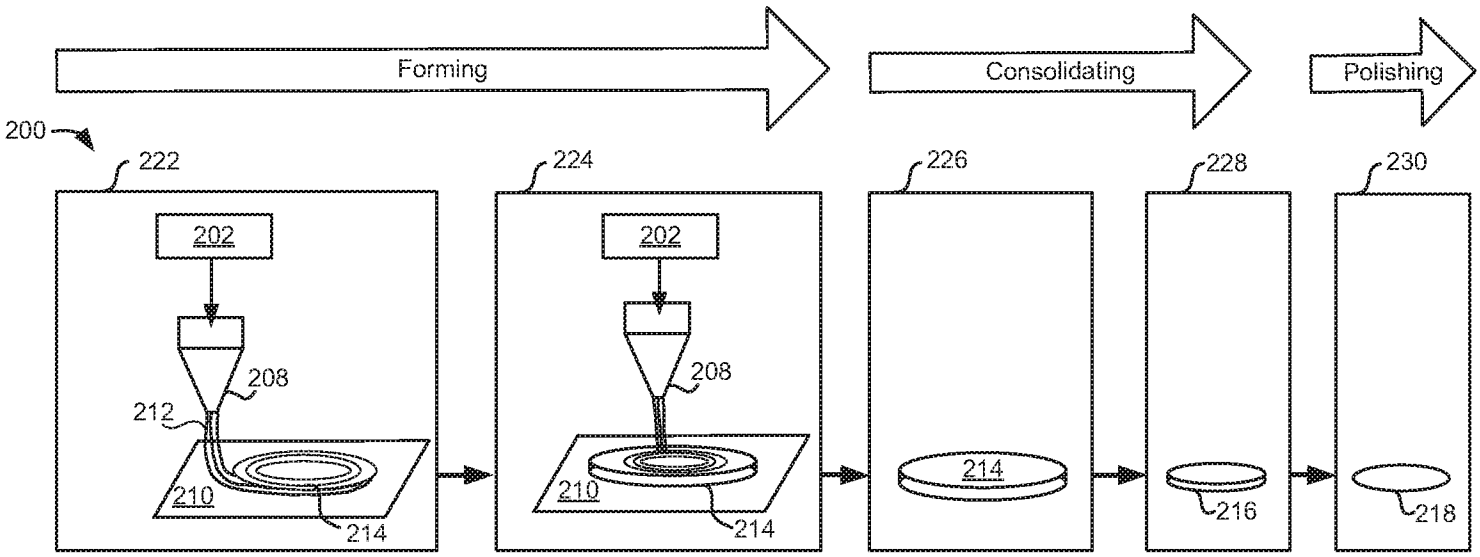

Forming
Consolidating
Polishing
200
222
224
226
228
230
202
208
212
210
214
216
218

FIG. 2A

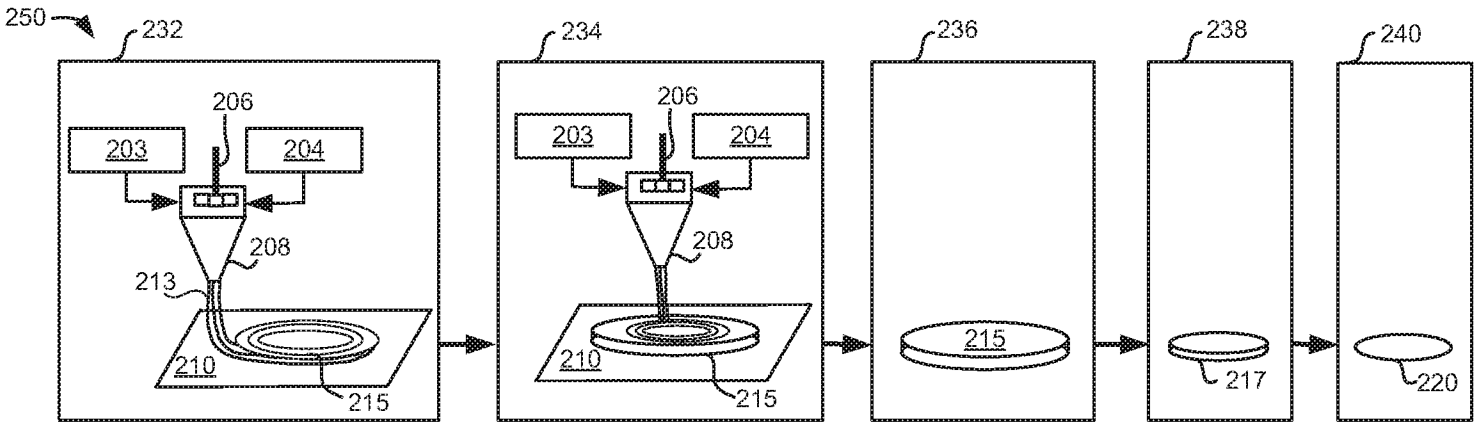

250
232
234
236
238
240
206
203
204
208
213
210
215
217
220

FIG. 2B

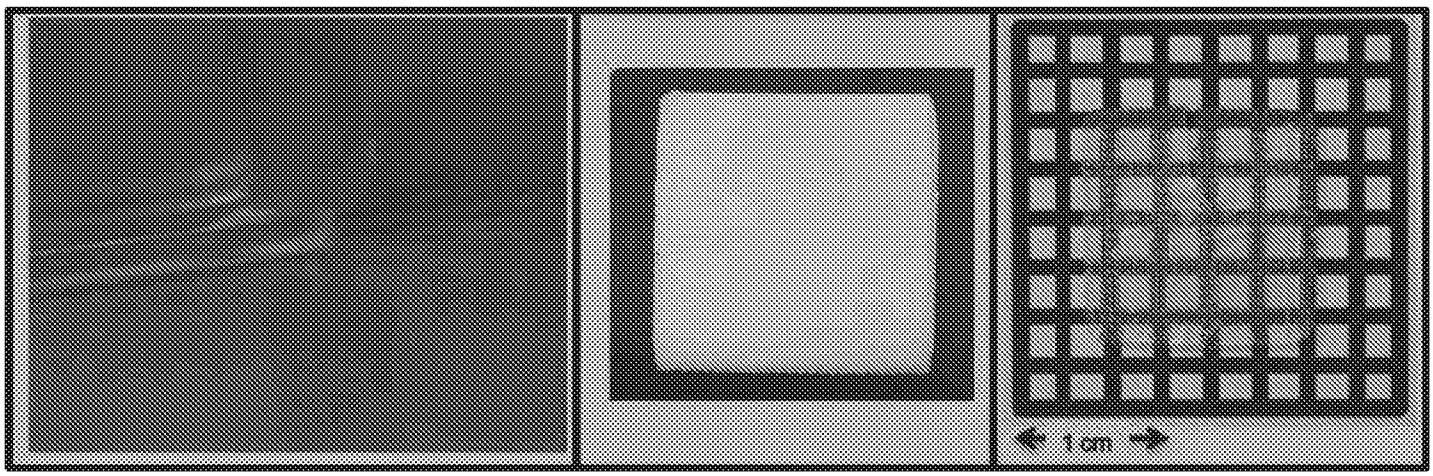


FIG. 3A FIG. 3B FIG. 3C

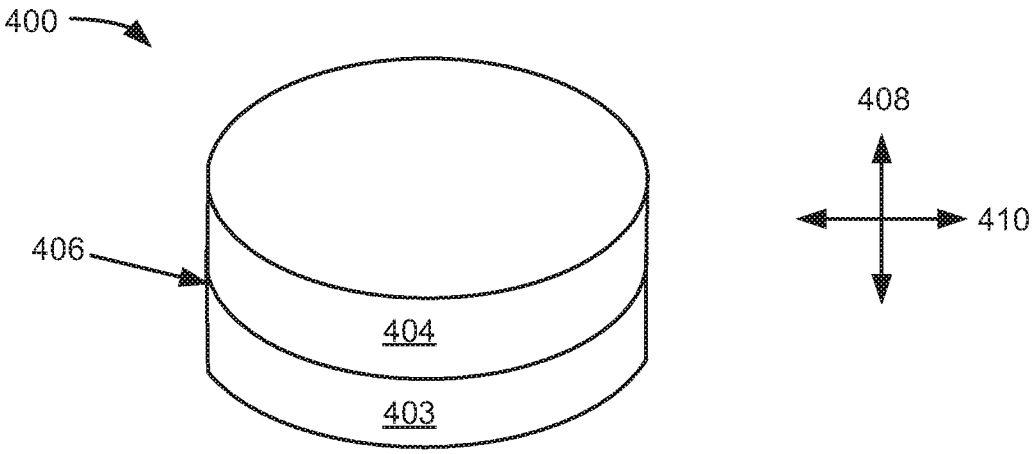


FIG. 4A

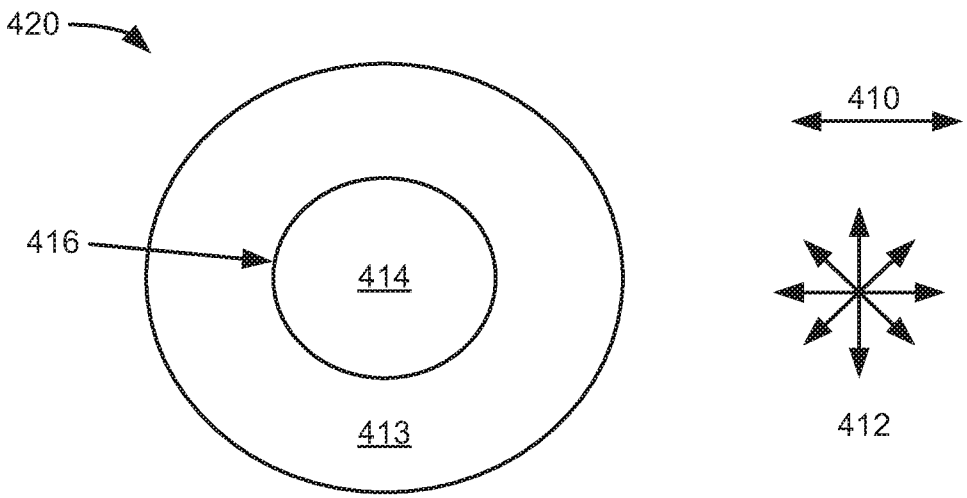


FIG. 4B

FIG. 5A

FIG. 5B

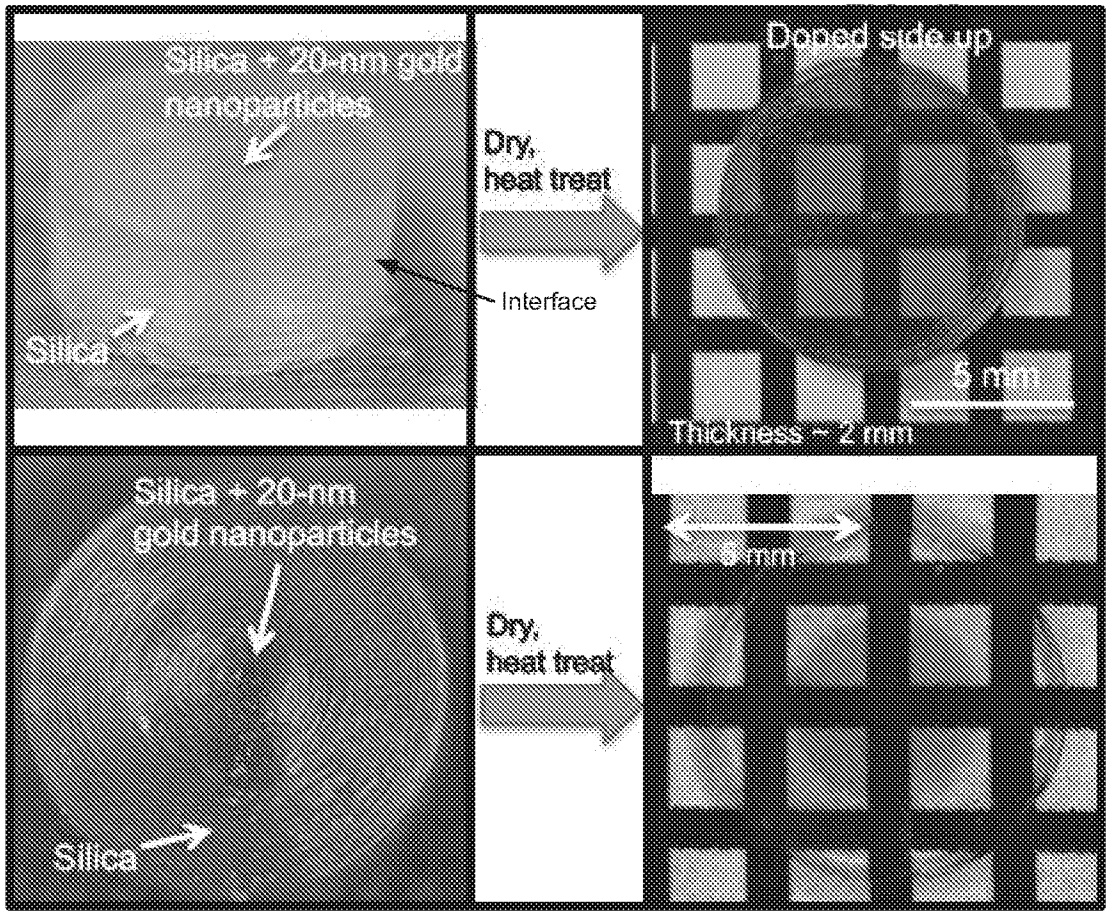


FIG. 5C

FIG. 5D

FIG. 6A

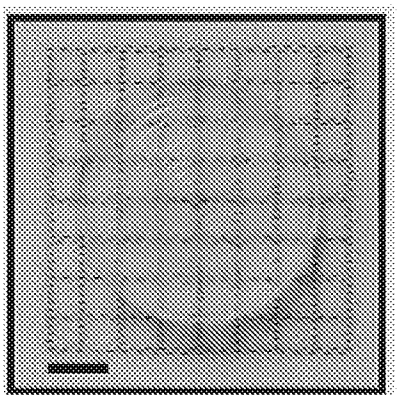


FIG. 6B

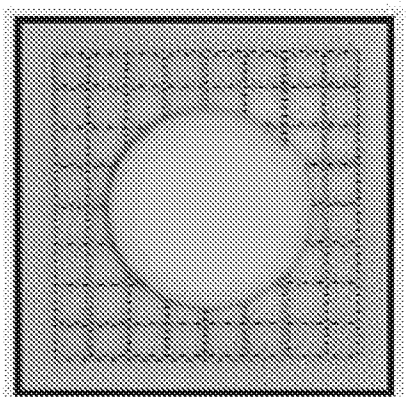
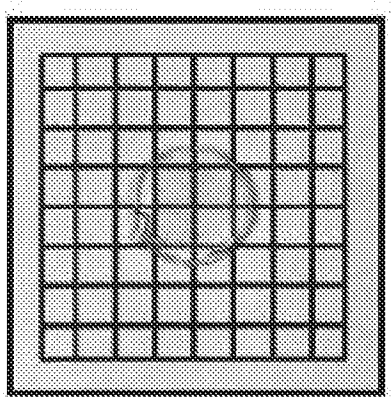


FIG. 6C



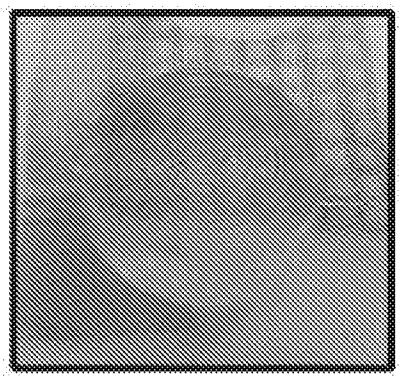


FIG. 6D

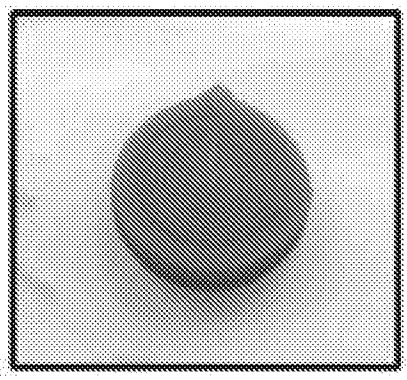


FIG. 6E

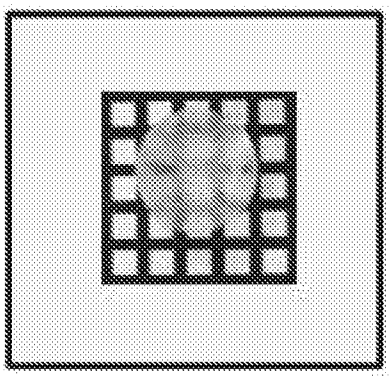
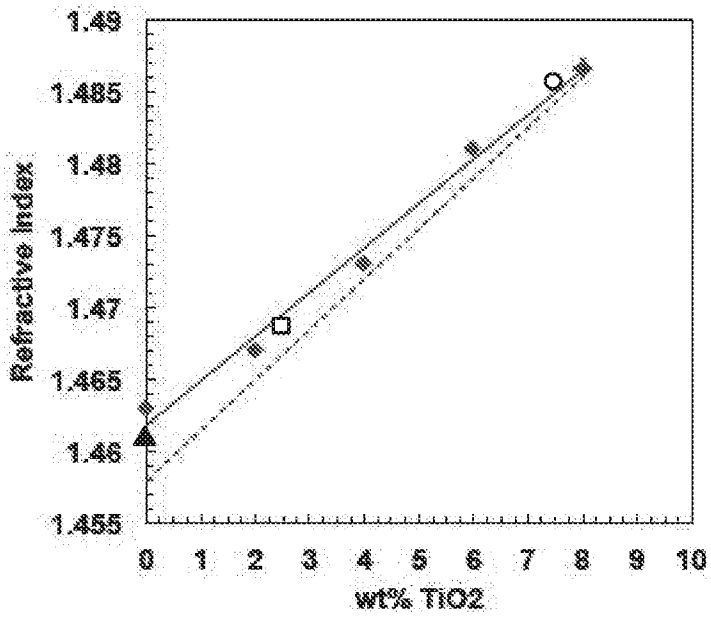


FIG. 6F

FIG. 7A


1.49
1.485
1.48
1.475
1.47
1.465
1.46
1.455
Refractive Index
0 1 2 3 4 5 6 7 8 9 10
wt% TiO2

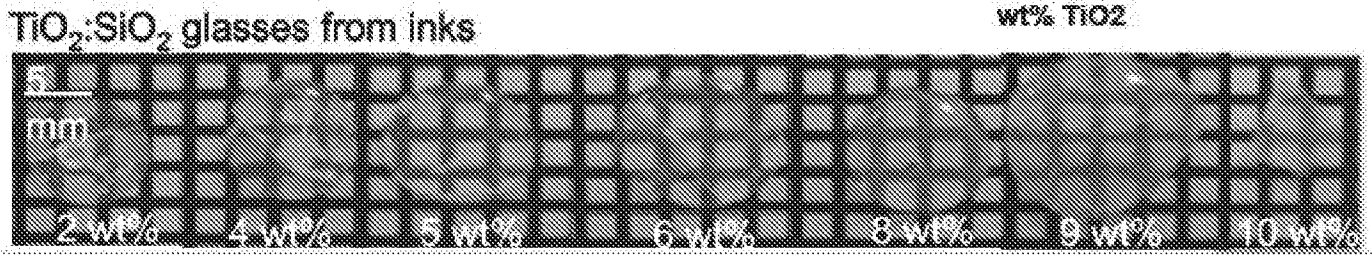

TiO2:SiO2 glasses from inks
5 mm
2 wt%
4 wt%
5 wt%
6 wt%
8 wt%
9 wt%
10 wt%

FIG. 7B

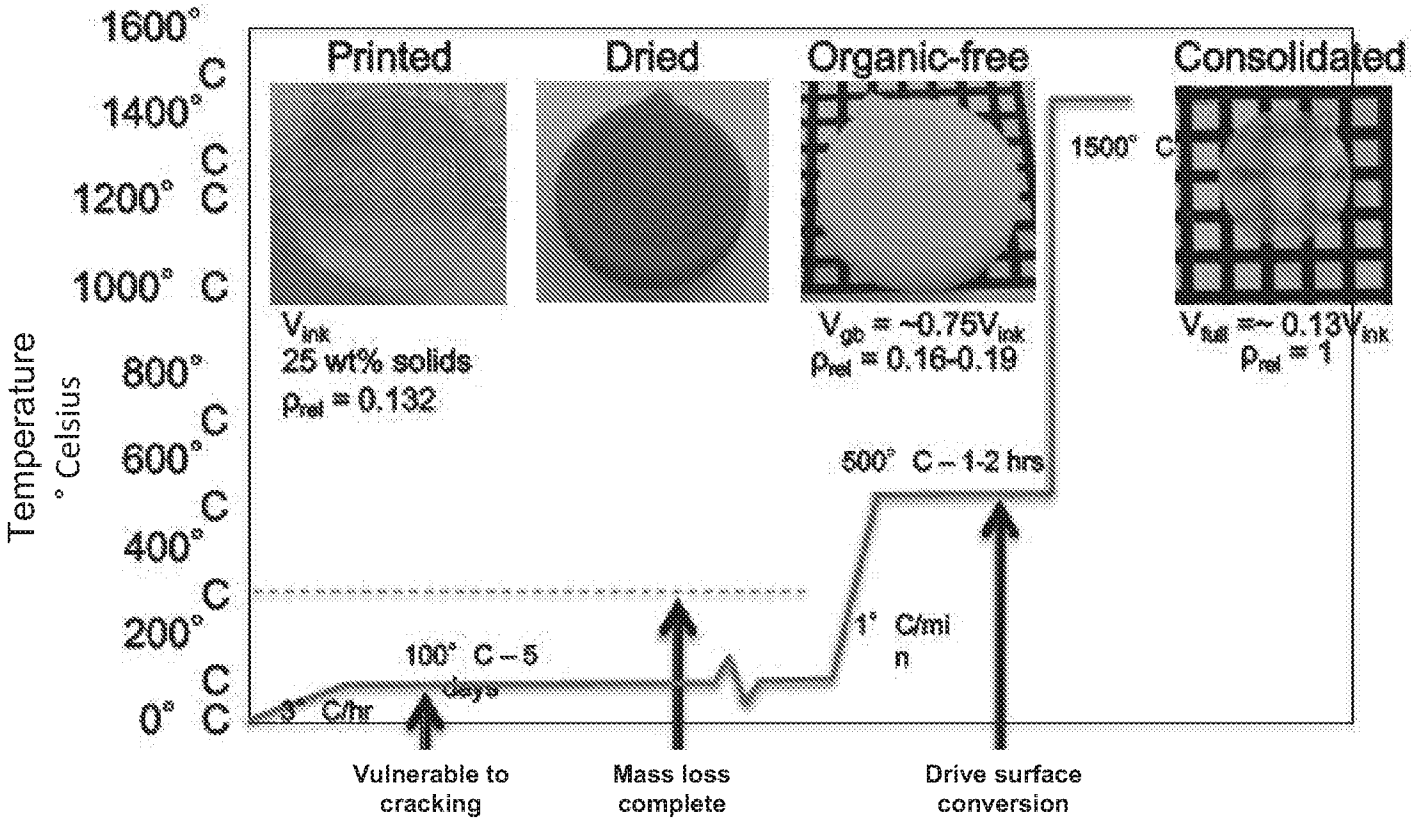

Temperature
° Celsius
1600° C
1400° C
1200° C
1000° C
800° C
600° C
400° C
200° C
0° C
Printed
Dried
Organic-free
Consolidated
V_{ink}
25 wt% solids
ρ_{rel} ≈ 0.132
V_{gb} ≈ ~0.75V_{ink}
ρ_{rel} ≈ 0.16-0.19
V_{full} ≈~ 0.13V_{ink}
ρ_{rel} ≈ 1
1500° C
500° C – 1-2 hrs
1° C/min
100° C – 5 days
3° C/hr
Vulnerable to cracking
Mass loss complete
Drive surface conversion

FIG. 8

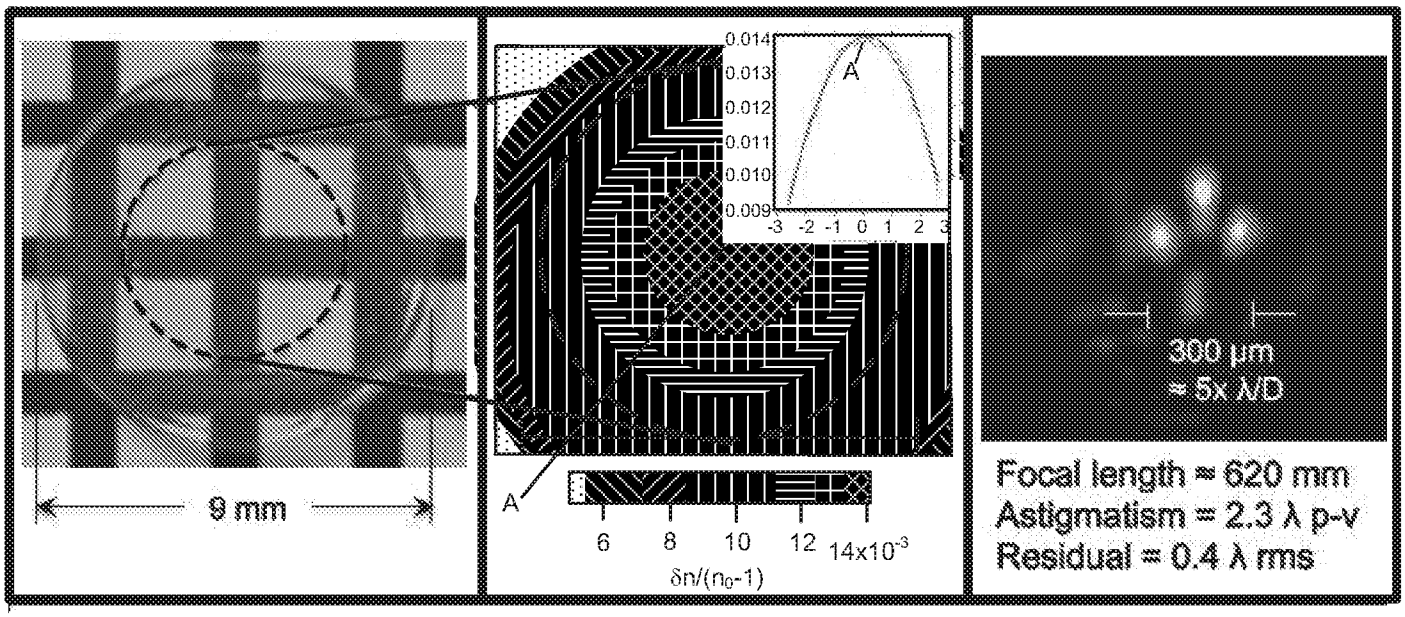


FIG. 9A FIG. 9B FIG. 9C

FIG. 10A

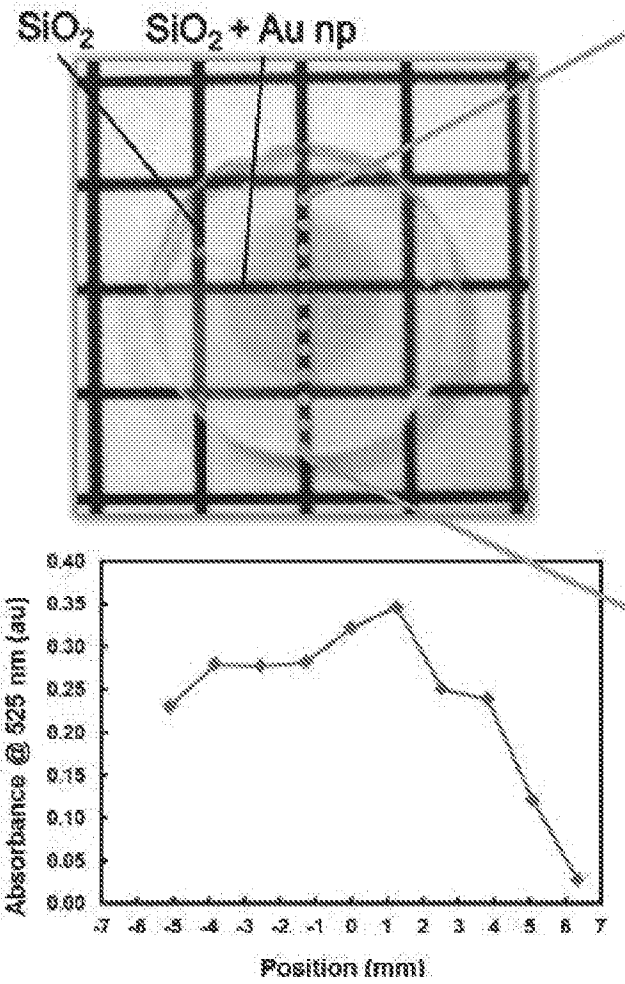
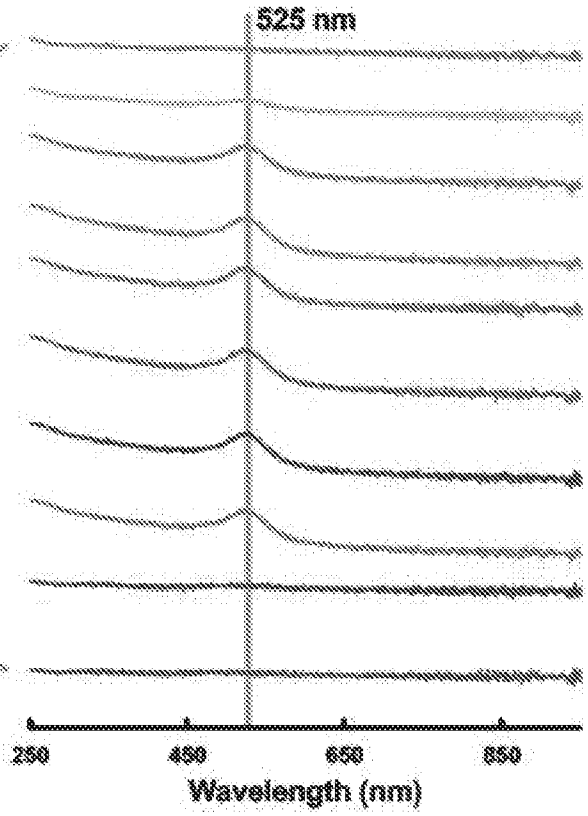


FIG. 10C

FIG. 10B



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/036197

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B33Y 10/00; B33Y 30/00; B33Y 70/00 (2017.01)
CPC - B29C 67/0055; B33Y 10/00; B33Y 30/00; C04B 2235/32 (2017.05)

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)
See Search History document

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)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	WO 2015/120429 A1 (PRESIDENT AND FELLOWS OF HARVARD COLLEGE) 13 August 2015 (13.08.2015) entire document	1, 5-9, 12, 13 ---------- 2-4, 10, 11
X --- Y	US 8,991,211 B1 (ARLOTTI et al) 31 March 2015 (31.03.2015) entire document	14-16 ---------- 11, 17, 18
Y	US 2015/0099102 A1 (SULLIVAN et al) 09 April 2015 (09.04.2015) entire document	2
Y	US 2016/0009029 A1 (SOUTHERN METHODIST UNIVERSITY) 14 January 2016 (14.01.2016) entire document	3, 4
Y	US 2014/0035423 A1 (VERONESI et al) 06 February 2014 (06.02.2014) entire document	10
Y	US 2006/0254316 A1 (LEU) 16 November 2006 (16.11.2006) entire document	17, 18

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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 July 2017	11 AUG 2017
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