



## (51) International Patent Classification:

B33Y 70/00 (2020.01) C08K 3/36 (2006.01)

C03C 1/10 (2006.01) C08K 7/20 (2006.01)

C03C 12/00 (2006.01) C09D 11/02 (2014.01)

## (21) International Application Number:

PCT/US2019/064882

## (22) International Filing Date:

06 December 2019 (06.12.2019)

## (25) Filing Language:

English

## (26) Publication Language:

English

## (30) Priority Data:

16/212,525 06 December 2018 (06.12.2018) US

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## (54) Title: ENGINEERED FEEDSTOCKS FOR ADDITIVE MANUFACTURE OF GLASS

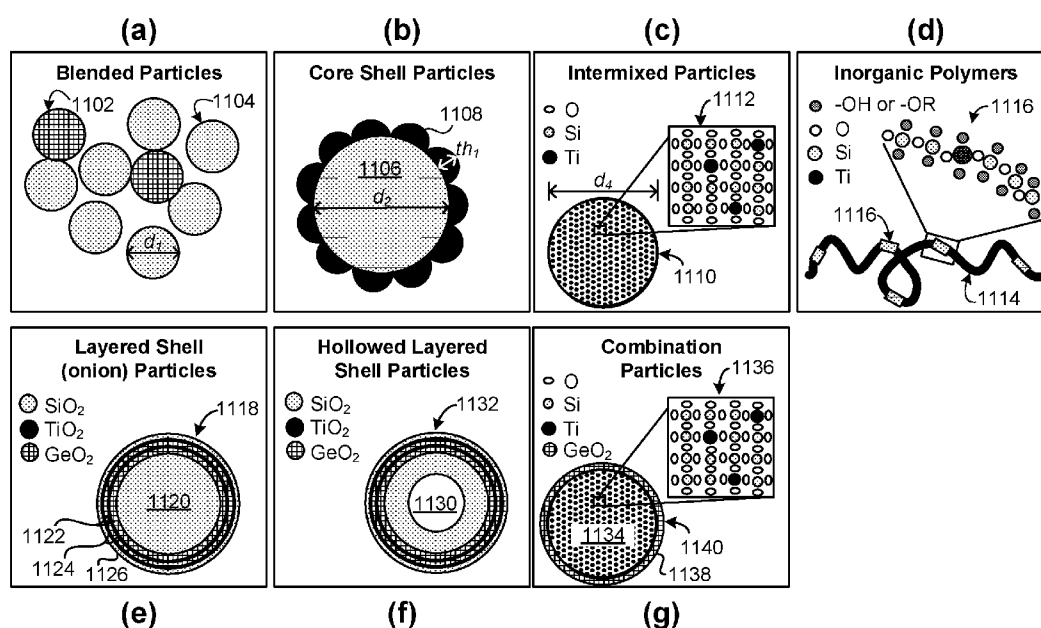


FIG. 11

(57) **Abstract:** According to one aspect of an inventive concept, a composition for an additive manufacturing process includes a glass-forming material, where the composition is configured to form a three-dimensional structure, wherein the three-dimensional structure is self-supporting. According to another aspect of an inventive concept, a composition for an additive manufacturing process includes a glass-forming material that includes blended particles, where the blended particles comprise at least two types of particles having different compositions, and a solvent. According to yet another aspect of an inventive concept, a composition for an additive manufacturing process includes a glass-forming material comprising core-shell particles and a solvent.



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(81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Published:**

— with international search report (Art. 21(3))

# ENGINEERED FEEDSTOCKS FOR ADDITIVE MANUFACTURE OF GLASS

[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] The composition of glass determines its material properties; therefore, hundreds of different commercial glass types exist to serve a multitude of needs. Most glass compositions include 2 or more different oxide species. During the conventional process of melt production of glass, various raw materials of different composition

(powders or cullet) are batched together in specific proportions. The materials are blended together first as powders, and then melted in crucibles and mixed thoroughly in a liquid phase to yield the desired final glass composition having a desired homogeneity. The raw materials may include particles of nonspecific sizes, shapes, and varying degrees of agglomeration, and even varying individual compositions. Thus, the individual raw materials may begin to melt at different temperatures (e.g., each melting temperature specific to the individual raw material of the blend), however, the materials remain confined together within the crucible, and are blended together reaching homogeneity in the final melt. Therefore, although highly pure raw materials with low levels of impurities are important for conventional melt glass processing, the characteristics of the raw material in terms of powder size, size uniformity, particle shape(s), chemical distributions, etc. do not determine the optimal processing parameters or optimal material homogeneity.

**[0004]** Moreover, using conventional processes, gradients in glass 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.

**[0005]** Some attempts have been made to create single-composition glasses via additive manufacturing (AM). 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.

[0006] In recent studies, AM processes for forming glass have relied on feedstocks such as fumed silica, glass rod stock, and glass powders or cullet produced from melt-processed glasses. Despite a large number of cataloged commercial glasses, only a limited number of glass compositions have been demonstrated using AM techniques. However, many of these glass compositions are not transparent due largely to challenging factors such as the chemical composition and the spatial distribution of the composition. Furthermore, the shape and the form factor of the feedstocks used to produce glass via AM techniques are important for processability of the feedstocks using AM techniques. In addition, the composition, shape and form of the feedstocks determine specific properties of the resulting glass formed from the feedstocks. These factors of the

feedstocks may affect yield, transparency, and homogeneity of the glass formed by AM techniques.

[0007] Feedstock characteristics become even more important in processes that include multiple feedstocks having multiple compositions that are to be patterned and processed together. Thus, engineering the size, structure, composition, format, and surface properties of the feedstocks is critical to successful glass formation by AM.

[0008] Various aspect of an inventive concepts 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.

[0009] 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

[0010] Various aspects of an inventive concept 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.

[0011] According to one aspect of an inventive concept, a composition for an additive manufacturing process includes a glass-forming material, where the composition is configured to form a three-dimensional structure, wherein the three-dimensional structure is self-supporting.

[0012] According to another aspect of an inventive concept, a composition for an additive manufacturing process includes a glass-forming material that includes blended particles, where the blended particles comprise at least two types of particles having different compositions, and a solvent. In addition, the composition is configured to form a three-dimensional structure, wherein the three-dimensional structure is self-supporting.

[0013] According to yet another aspect of an inventive concept, a composition for an additive manufacturing process includes a glass-forming material comprising core-shell particles and a solvent.

[0014] 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

[0015] FIG. 1 is a flow chart of a method to prepare glass components with custom-tailored composition profiles, according to one aspect of an inventive concept.

[0016] FIG. 2A is a schematic drawing of a method to prepare a single composition glass components, according to one aspect of an inventive concept.

[0017] FIG. 2B is a schematic drawing of a method to prepare a multiple composition glass components, according to one aspect of an inventive concept.

[0018] FIG. 3A is an image of an extrusion of glass-forming ink onto a substrate, according to one aspect of an inventive concept.

[0019] FIG. 3B is an image of a printed low density form, according to one aspect of an inventive concept.

[0020] FIG. 3C is an image of a glass form following heat treatment of a printed low density form, according to one aspect of an inventive concept.

[0021] 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 aspect of an inventive concept.

[0022] 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 aspect of an inventive concept.

[0023] FIG. 5A is an image of a low density form with a gradient in the axial direction following multiple component printing, according to one aspect of an inventive concept.

[0024] 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 aspect of an inventive concept.

[0025] FIG. 5C is an image of a low density form with a gradient in the radial direction following multiple component printing, according to one aspect of an inventive concept.

[0026] FIG. 5D 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 aspect of an inventive concept.

[0027] FIGS. 6A-6C are images of printed parts formed with a silica composition, according to one aspect of an inventive concept.

[0028] FIGS. 6D-6E are images of printed parts formed with a silica-titania composition, according to one aspect of an inventive concept.

[0029] FIG. 6F is an image after consolidation of the dried green body of FIG. 6E.

[0030] FIG. 7A is a plot of refractive index profile verses titania concentration of glass formed according to one aspect of an inventive concept.

[0031] FIG. 7B is an image of the resultant glass structures formed with different titania concentrations, according to one aspect of an inventive concept.

[0032] FIG. 8 is a plot of the thermal treatment profile of the formation of a consolidated structure according to one aspect of an inventive concept. Images of each step are included as insets on the profile plot.

[0033] FIG. 9A is an image of a gradient refractive index silica-titania glass lens prepared by direct ink writing, according to one aspect of an inventive concept.

[0034] FIG. **9B** is a surface-corrected interferogram of the glass lens of FIG. **9A**.

[0035] FIG. **9C** is an image of the 300- $\mu\text{m}$  focal spot from the lens of FIG. **9A**.

[0036] FIG. **10A** is an image of a composite glass comprised of a gold-doped silica glass core, according to one aspect of an inventive concept.

[0037] FIG. **10B** is a plot of the absorbance as a function of wavelength of light of the composite glass of FIG. **10A**.

[0038] FIG. **10C** is a plot of the absorbance at 525 nm versus position along the glass surface of the composite glass of FIG. **10A**.

[0039] FIG. **11** is a series of schematic drawings of glass-forming material, according to various aspect of an inventive concepts.

[0040] FIG. **12** is a schematic drawing of preparing glass-forming feedstocks for inks to be used for printing 3D glass structures, according to various aspects of an inventive concept.

[0041] FIG. **13A** is a plot of average diameter of particle preparations as measured by determined by dynamic light scattering (DLS) methods.

[0042] FIG. **13B** includes a lower magnification, part **(a)**, and higher magnification, part **(b)** of transmission electron microscope (TEM) images of core particle, according to one aspect of an inventive concept.

[0043] FIG. **13B** part **(c)** is a schematic drawing of a core particle, according to one aspect of an inventive concept.

[0044] FIG. **13C** includes a lower magnification, part **(a)**, and higher magnification, part **(b)** of transmission electron microscope (TEM) images of core-shell particle, according to one aspect of an inventive concept.

[0045] FIG. 13C part (c) is a schematic drawing of a core-shell particle, according to one aspect of an inventive concept.

[0046] FIG. 13D includes a lower magnification, part (a), and higher magnification, part (b) of transmission electron microscope (TEM) images of core-shell particle, according to one aspect of an inventive concept.

[0047] FIG. 13D part (c) is a schematic drawing of a core-shell particle, according to one aspect of an inventive concept.

[0048] FIG. 13E includes a lower magnification, part (a), and higher magnification, part (b) of transmission electron microscope (TEM) images of core-shell particle, according to one aspect of an inventive concept.

[0049] FIG. 14A is an image depicting the supernatant and nanoparticle pellets of two intermixed particle preparations, according to various aspects of an inventive concept.

[0050] FIG. 14B is an image of vials containing dried intermixed particle preparations, according to various aspects of an inventive concept.

[0051] FIG. 15A part (a) is a schematic drawing of molecular precursors included in an intermixed hybrid particle preparation, according to one aspect of an inventive concept.

[0052] FIG. 15A part (b) is a schematic drawing of an intermixed hybrid particle, according to one aspect of an inventive concept.

[0053] FIG. 15B is an image of a vial of an intermixed hybrid particle preparation in suspension, according to one aspect of an inventive concept.

[0054] FIG. 15C includes a lower magnification, part (a), and higher magnification, part (b) of transmission electron microscope (TEM) images of intermixed hybrid particles, according to one aspect of an inventive concept.

[0055] FIG. 16A is a schematic drawing of the general process for forming an inorganic polymer suitable for printing, according to one aspect of an inventive concept.

[0056] FIG. 16B part (a) is an image of products of inorganic polymer feedstocks, according to one aspect of an inventive concept.

[0057] FIG. 16B part (b) is an image of glass product formed from inorganic polymer feedstocks, according to one aspect of an inventive concept.

[0058] FIG. 16B part (c) is an image of a calcined product from an inorganic polymer feedstock, according to one aspect of an inventive concept.

[0059] FIG. 17A is a schematic drawing of forming a layered shell particle, according to one aspect of an inventive concept.

[0060] FIG. 17B is a series of scanning electron microscope (SEM) images of forming a layered shell particles, according to one aspect of an inventive concept. Part (a) shows core particles, part (b) shows core particles having a shell of one layer, part (c) shows core particles having a shell of at least two layers.

[0061] FIG. 18A is a schematic drawing of forming a hollow layered particle, according to one aspect of an inventive concept.

[0062] FIG. 18B is a series of transmission electron microscope (TEM) images of hollow layer particles, according to one aspect of an inventive concept. Part (a) is at lower magnification, and part (b) is at higher magnification.

[0063] FIG. 18C is a plot of an energy dispersive X-ray (EDX) spectrum of hollow layer shell particles, according to one aspect of an inventive concept.

## DETAILED DESCRIPTION

[0064] 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.

[0065] 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.

[0066] 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.

[0067] A nanoscale is defined as having a diameter or length less than 1000 nanometers (nm).

[0068] It is noted that ambient room temperature may be defined as a temperature in a range of about 20°C to about 25°C.

[0069] It is also noted that, as used in the specification and the appended claims, wt% is defined as the percentage of weight of a particular component is to the total weight/mass of the mixture. Vol% is defined as the percentage of volume of a particular compound to the total volume of the mixture or compound. Mol% is defined as the percentage of moles of a particular component to the total moles of the mixture or

compound. Atomic % (at%) is defined as a percentage of one type of atom relative to the total number of atoms of a compound.

[0070] Unless expressly defined otherwise herein, each component listed in a particular approach may be present in an effective amount. An effective amount of a component means that enough of the component is present to result in a discernable change in a target characteristic of the ink, printed structure, and/or final product in which the component is present, and preferably results in a change of the characteristic to within a desired range. One skilled in the art, now armed with the teachings herein, would be able to readily determine an effective amount of a particular component without having to resort to undue experimentation.

[0071] The present disclosure includes several descriptions of exemplary “inks” used in an additive manufacturing process to form the inventive concepts described herein. It should be understood that “inks” (and singular forms thereof) may be used interchangeably and refer to a composition of matter comprising a plurality of particles coated with/dispersed throughout a liquid phase such that the composition of matter may be “written,” extruded, printed, or otherwise deposited to form a layer that substantially retains its as-deposited geometry and shape with perhaps some, but preferably not excessive, sagging, slumping, or other deformation, even when deposited onto other layers of ink, and/or when other layers of ink are deposited onto the layer. As such, skilled artisans will understand the presently described inks to exhibit appropriate rheological properties to allow the formation of monolithic structures via deposition of multiple layers of the ink (or in some cases multiple inks with different compositions) in sequence.

[0072] The following description discloses several preferred structures formed via direct ink writing (DIW), extrusion freeform fabrication, or other equivalent techniques and therefore exhibit unique structural and compositional characteristics conveyed via the precise control allowed by such techniques. The physical characteristics a structure formed by DIW may include having lower layers of the structure are slightly flattened, slightly disfigured from original extrusion, etc. by weight of upper layers of structure, due to gravity, etc. The three-dimensional structure formed by DIW may have a single continuous filament that makes up at least two layers of the 3D structure.

[0073] The following description discloses several preferred aspect of an inventive concepts of preparing optical and non-optical glass components with custom-tailored composition profiles, and/or related systems and methods.

[0074] According to one general aspect of an inventive concept, a composition for an additive manufacturing process includes a glass-forming material, where the composition is configured to form a three-dimensional structure, wherein the three-dimensional structure is self-supporting.

[0075] According to another general aspect of an inventive concept, a composition for an additive manufacturing process includes a glass-forming material that includes blended particles, where the blended particles comprise at least two types of particles having different compositions, and a solvent. In addition, the composition is configured to form a three-dimensional structure, wherein the three-dimensional structure is self-supporting.

[0076] According to yet another general aspect of an inventive concept, a composition for an additive manufacturing process includes a glass-forming material comprising core-shell particles and a solvent.

[0077] A list of acronyms used in the description is provided below.

|       |                                         |
|-------|-----------------------------------------|
| 3D    | Three dimensional                       |
| DIW   | Direct ink write                        |
| DLS   | Dynamic Light Scattering                |
| EDX   | Energy Dispersive X-ray                 |
| 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                 |
| TEM   | Transmission electron microscopy        |
| Ti    | Titanium                                |
| TIP   | Titanium (IV) isopropoxide              |
| UV    | Ultraviolet                             |

[0078] In sharp contrast to materials used to form glass by conventional processing techniques, physical and chemical properties of the raw materials used to form glass by additive manufacturing (AM) techniques are critical to determine optimal processing

parameters and optimal material homogeneity. For example, during AM processing, raw material is deposited in small regions or layer-by-layer, rather than prepared in a bulk batch. Further, the material is mixed prior to a heating stage (e.g., the molten mixing in the crucible during conventional processes), to help ensure a high degree of chemical uniformity. Thus, the spatial distribution of the composition, the shape, and the form factor of the feedstocks used to produce glass via AM techniques are important for the ultimate processability using AM techniques. For example, the shapes and sizes of the particles, as well as the size distribution, determine the physical properties of the feedstocks, e.g., how the particles pack, flow, or spread. In addition, it is important to understand whether the physical properties of the feedstocks are affected if the material is a solid powder or distributed in a solvent or resin.

[0079] Regularity in sizes and shapes of particles also influences the consistency and reliability of the AM process. In addition, the void sizes (space between particles) control the temperature at which material of a fixed composition can be sintered via viscous flow. Both the particle surface chemistry and the particle size influence the achievable solids loading at a given viscosity in a resin, paste, or solvent, which also affects the degree to which the components will shrink, potentially affecting yield. Further, the particle size and chemical distribution within the glass-forming species controls the diffusion distance that must be spanned. If the distance is too large, it will lead to poor homogeneity, phase separation, and/or crystallization. These feedstock characteristics become even more important if multiple glass compositions are to be patterned together and simultaneously processed. Thus, engineering the size, structure, composition, format, and surface properties of the feedstocks is critical to successful glass formation by AM.

Unfortunately, it very difficult to control many of these features when crushing or milling glass produced from the melt.

[0080] Current AM processes for forming glass rely on feedstocks such as fumed silica or glass powders or cullet produced from melt-processed glasses, sometimes also including a dopant such as a salt or other dissolved species to alter the composition. Yet, despite the hundreds of cataloged commercial glasses, only a few glass compositions (mostly silica) have been demonstrated using AM techniques and even fewer attempts have produced transparent glass. Although additional glass compositions have been demonstrated using sol gel chemistry in conjunction with casting/molding processes, these formulations were not specifically engineered or designed to meet the demands of AM processing techniques, where material is deposited (and structure is formed) layer by layer.

[0081] Various aspects of an inventive concept 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 aspects of an inventive concept 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.

[0082] FIG. 1 shows a method 100 for preparing optical glass components with custom-tailored composition profiles in accordance with one aspect of an inventive

concept. 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 aspect of an inventive concepts 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 aspects of an inventive concepts. It should also be noted that any of the aforementioned features may be used in any of the aspect of an inventive concepts described in accordance with the various methods.

**[0083]** In one aspect of an inventive concept as shown in FIG. **1**, a method **100** begins with an operation **102** that includes forming a structure by an additive manufacturing (AM) process. According to various aspects of an inventive concept, additive manufacturing techniques may include processes having a composition mixing capability. In one approach, a 3D structure may be formed from a composition that is an ink by an extrusion-based AM process, e.g., direct ink writing (DIW), fused deposition modeling, inkjet printing, inkjet powder bed printing, aerosol jet printing, etc. In another approach, a 3D structure may be formed from a composition that is a resin for a light-based AM process, e.g., stereolithography, projection microstereolithography, etc. In yet another approach, a 3D structure may be formed from a composition that is a powder for a laser-assisted melting AM process, e.g., selective laser melting, powder bed processes, etc. In another approach, a 3D structure may be formed from a composition used in a deposition-mediated AM process, e.g., electrophoretic deposition, PolyJet processing, Direct Deposition, , etc. One could imagine combining these processes as well.

[0084] In one approach, additive manufacturing techniques such as DIW, projection microstereolithography (PμSL), inkjet printing, etc. using ink compositions as described herein may be combined with UV curing during or after printing the ink to UV cure the newly forming or formed structure. In one approach, UV-assisted DIW may be used to create glass structures, as described herein.

[0085] According to various aspects of an inventive concept, the method **100** may be used to create filaments, films, and/or 3D monolithic, spanning free-forms, self-supporting structures, etc.

[0086] According to one aspect of an inventive concept, the ink includes a glass-forming material. According to another aspect of an inventive concept, 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.

[0087] In another aspect of an inventive concept, 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 aspect of an inventive concepts, the glass-forming material may be a single composition of inorganic-containing particles.

[0088] In one aspect of an inventive concept, 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).

[0089] In some aspects of an inventive concept, 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.

[0090] According to one aspect of an inventive concept, the glass-forming material may be a single composition of glass-forming material that may not be in the form of particles. In some approaches, 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.

[0091] According to some approaches, 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<sub>3</sub>)<sub>2</sub>, Li<sub>2</sub>CO<sub>3</sub>; 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.

**[0092]** According to some approaches, 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.

**[0093]** In one aspect of an inventive concept, the glass-forming material may be suspended in a solvent. In one approach, the solvent may be a suspending liquid. In one aspect of an inventive concept 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 approach in which the glass-forming material is hydrophobic, the solvent may be a non-polar solvent, for example, but not limited to, xylenes, alkanes.

**[0094]** According to one aspect of an inventive concept, 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 approaches, the second component may be a property altering dopant. In other approaches, more than one material property

may be affected by the addition of a second component. In various approaches, 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.

[0095] 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.

[0096] In some aspects of an inventive concept, 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.

[0097] In one approach, 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).

[0098] In one approach, 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.

**[0099]** In one approach, 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.

**[00100]** In one approach, 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.

**[00101]** In one approach, 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.

**[00102]** In one approach, 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.

**[00103]** In one approach, 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.

**[00104]** In one approach, 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.

[00105] In one approach, 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.

[00106] In one approach, 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.

[00107] In one approach, 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.

[00108] In one approach, the glass transition temperature of the resulting structure may be affected by the addition of sodium carbonate as the second component.

[00109] In one approach, 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.

[00110] In one approach, 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).

[00111] In one approach, the photoemission of the resulting structure may be affected by the addition of a second component. In another aspect of an inventive concept, the luminescence of the resulting structure may be affected by the addition of a second component. In yet another aspect of an inventive concept, the fluorescence of the resulting structure may be affected by the addition of a second component.

[00112] In one approach, 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.

[00113] In one approach, 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.

[00114] In one approach, 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.

[00115] In some approaches, 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.).

[00116] In some approaches, 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.

[00117] In one approach, 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).

[00118] In one approach, 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.

[00119] In one approach, the ink may include an additive (e.g. boric anhydride  $B_2O_3$ ) to inhibit crystallization. Other crystallization inhibitors include  $Al_2O_3$  and  $Ga_2O_3$ .

[00120] In one approach, the ink may include an additive (e.g. polydimethylsiloxanes) to strengthen the network.

[00121] In one approach, 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,  $NH_4OH$ ).

[00122] In one approach, 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)).

[00123] In one approach, the ink may include a UV-curable material to modify rheology. In one approach, the UV-curable material may be included in the solvent of the ink. In another approach, functional groups on a component of the feedstocks may be susceptible to UV-curing before, during, or after printing of the 3D glass structure. In

some approaches, functional groups that may be susceptible to UV curing include acrylate, vinyl, and styrene functionalities. In one approach, the UV-curable components may be included in the feedstock design.

**[00124]** For example, in one approach, an additive of UV-curable material may allow the ink to have optimal viscosity prior to extrusion, and then application of UV light may cure the ink as it is extruded from the nozzle.

**[00125]** In one approach, 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)).

**[00126]** In one approach, 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.

**[00127]** In various approaches, 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.

**[00128]** According to one aspect of an inventive concept, 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%.

**[00129] 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 diisopropoxide bis(acetylacetonate) |
| 0-6 wt%    | Ethylene glycol                              |
| 0-2 wt%    | Poly(dimethylsiloxane)                       |

**[00130] Example Formulation 2 of Ink**

|            |                                     |
|------------|-------------------------------------|
| 75-95 vol% | Silica-titania-containing polymers  |
| 10-25 vol% | Tetraethylene glycol dimethyl ether |
| 0-10 vol%  | H <sub>2</sub> O for prehydrolysis  |

**[00131] 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                                 |

**[00132]** According to one approach, 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.

**[00133]** In one approach, the temperature of the ink may be less than about 200 °C during the printing.

[00134] In one approach, 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.

[00135] According to one approach 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.

[00136] In one approach, 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.

[00137] In one approach, the heat-treated glass structure may be in the form of a fiber.

[00138] In another approach, the heat-treated glass structure may be in the form of a sheet.

[00139] In one approach, the heat-treated glass structure may be in the form of a three-dimensional monolith. In one approach, the heat-treated glass structure may be a self-supporting structure.

[00140] In another approach, the heat-treated glass structure may be in the form of a coating on a substrate such as a part, a tool, etc.

[00141] FIGS. **2A-2B** depict methods **200** and **250** for preparing an optical glass component with custom-tailored composition profiles in accordance with one aspect of an inventive concept. As an option, the present methods **200** and **250** may be implemented in conjunction with features from any other aspect of an inventive concept

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 aspect of an inventive concepts listed herein. Further, the methods **200** and **250** presented herein may be used in any desired environment.

[00142] An exemplary aspect of an inventive concept of method **200** to prepare a single component silica glass is illustrated in FIG. **2A**. According to one approach, 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.

[00143] 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.

[00144] According to one approach, 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.

**[00145]** A method **200** and **250** as shown in FIGS. **2A** and **2B**, respectively, of fabricating a glass structure is highly scalable and compatible with additive manufacturing (e.g. three-dimensional (3D) printing) methods such as direct ink writing (DIW) and projection micro-stereolithography (PμSL). In various approaches, the glass structure may have physical characteristics of formation by an additive manufacturing technique. In various approaches, physical characteristics may include filaments arranged in a geometric pattern, a patterned outer surface defined by stacking filaments, a defined porosity (e.g., ordered, controlled, non-random, etc.), a porosity having pores with measurable average diameters, etc. Thus, using these additive manufacturing techniques allows engineering of parts and production of optimal geometry for efficient mass transport and mechanical strength.

**[00146]** According to one approach, 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.

[00147] Step **224** of method **200** involves building layer upon layer of glass-forming DIW ink **202** to form an LDF **214**. FIG. **3A** shows an image of the colloidal silica ink being extruded onto the substrate.

[00148] The LDF **214** may be treated to multiple steps to consolidate and convert the LDF **214** to the heat-treated glass form **216**.

[00149] 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.

[00150] 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. In some aspect of an inventive concepts, 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.

[00151] In some approaches, 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<sub>2</sub> gas). In other approaches, the processing step **226** may include heating the LDF **214** under reducing gas atmospheres (e.g. H<sub>2</sub> 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<sub>2</sub>, Cl<sub>2</sub>). In yet other approaches, the processing step **226** may include heating the LDF **214** under vacuum.

[00152] In some approaches, 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.

[00153] FIG. **3B** shows an image of an LDF that has been dried.

[00154] According to one approach, 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.

[00155] 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.

[00156] In some approaches, 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 approaches, 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**).

[00157] In one approach, 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**.

[00158] In one approach, 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 approach, 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 approach, the polished optic **218** is a monolithic glass structure that has been polished.

[00159] 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.

[00160] According to one approach, 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 approaches, 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.).

**[00161]** 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 aspect of an inventive concepts, two, three, four, etc. inks may be combined by mixing before extrusion of the filament onto the substrate.

**[00162]** According to one approach, 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.

**[00163]** 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.

[00164] Looking back to FIG. 2B, in step 234 the glass structure is formed as an 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.

[00165] In some approaches, the processing step 236 may also include compacting the parts (i.e. reducing porosity) of the LDF 215 using uniaxial pressure or isostatic pressure thereby resulting in a compact form. In some approaches, the processing step 236 may also include compacting the parts (i.e. reducing porosity) of the LDF 215 under vacuum.

[00166] 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.

[00167] In one approach, 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.

[00168] 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.

[00169] In one aspect of an inventive concept, 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).

[00170] The prior art methods to 3D print optical glass have not been able to achieve aspects of an inventive concept 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.

[00171] 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 an 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.

[00172] 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.

[00173] In one approach, 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 **414** and the second glass **413**, having different compositions directly adjacent the interface **416**.

[00174] According to one approach, two different inks may be used to print a conformational change in an 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**.

[00175] 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.

[00176] 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 (T<sub>g</sub>) melting point, photoemission, fluorescence, chemical reactivity (e.g. etch rate), density/porosity.

[00177] As shown in FIG. **2B**, DIW printing in steps **232, 234** may involve forming the LDF **215**, according to one aspect of an inventive concept. 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.

[00178] In some approaches, formation of an 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 an 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.

[00179] In various approaches, the LDF may be formed in a complex shape, for example, but not limited to, a conical form, a corkscrew pattern, a cylinder, etc.

[00180] The LDF **215** may be treated to multiple steps to consolidate and convert the LDF **215** to the heat-treated glass form **217**.

[00181] 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**.

[00182] Referring back to FIG. **2B**, according to one approach, 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**).

[00183] In one approach, 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**.

[00184] According to one approach, 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 aspect of an inventive concept, 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 aspect of an inventive concept, the polished optic **220** is a monolithic glass structure that has been polished.

[00185] The various approaches 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.

[00186] **Engineered Feedstocks**

[00187] One aspect of an inventive concept describes a process for creating feedstocks that may enable the production of glass of different compositions and with different material properties using additive manufacturing. For example, an ink may include glass-forming material for extrusion-based AM processes, a resin may include a glass-forming material for photocurable AM processes, a powder may include a glass-forming material for selective laser melting AM processes, etc. Feedstocks can be engineered such that the size and chemical compositions (as well as chemical distributions) of the glass-forming feedstocks can be tuned to meet both the needs of the particular AM process as well as to

deliver the desired glass composition and properties. Liquid chemical precursors or mixtures of precursors, such as metal organics or silanes, can be reacted together under tuned reaction conditions to form particles or long chains of prescribed size, and in a variety of form factors, either by simultaneous reaction or by performing a series of reaction steps via sol gel chemistry.

**[00188]** FIG. 11 is a schematic drawing of various examples of approaches described herein of engineered feedstocks for additive manufacturing of glass.

**[00189]** (a) Blended particles. A blend of different particles (blended particles) in a single composition may be used. As shown in the schematic diagram of part (a) of FIG. 11, glass-forming feedstock of blended particles, according to one aspect of an inventive concept, include a separate growth of particles of different compositions. For example, the particles may be grown via base-catalyzed sol gel chemistry. In one approach, particles of different compositions may include SiO<sub>2</sub> particles 1102 and GeO<sub>2</sub> particles 1104. The size scale of the particles would determine sufficient intermixing during co-thermal processing, and subsequent mixture of these particles during preparation for the AM process. In some approaches, the average diameter  $d_l$  of the particles in the blended particle feedstock may be in a range of about 30 nm to about 50 nm, and the average diameter may be larger or smaller.

**[00190]** In one approach, a composition includes a glass-forming material that includes blended particles. The composition having blended particles may include at least two types of particles having different compositions than each other and a solvent. The composition may be configured to form a 3D structure. In one approach, the composition including blended particles may be an ink for an extrusion-based AM

process. In another approach, the composition including blended particles may be a resin for a light-based AM process. In yet another approach, the composition including blended particles may be a powder for a laser-assisted melting AM process, e.g., selective laser melting, powder bed processes, etc. In some approaches, the formed 3D structure may be self-supporting.

**[00191]** In one approach, blended particles may include oxide species. In some approaches, blended particles may include at least one of  $\text{SiO}_2$ ,  $\text{GeO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , etc. In one approach, blended particles may include  $\text{SiO}_2$  with metal nanoparticles. In some approaches, blended particles may include  $\text{SiO}_2$  with at least one of the following metal nanoparticles: gold, silver, nickel, copper, or a combination thereof. In one approach blended particles may include  $\text{SiO}_2\text{-PbO}$  (silica lead oxide).

**[00192]** In some approaches, compositions of blended particles may include more than two oxide species. For example, compositions of blended particles may include  $\text{SiO}_2\text{-NaO-TiO}_2$ ,  $\text{SiO}_2\text{-BaO-TiO}_2$ ,  $\text{SiO}_2\text{-PbO-TiO}_2$ ,  $\text{SiO}_2\text{-GeO}_2\text{-PbO}$ ,  $\text{SiO}_2\text{-GeO}_2\text{-TiO}_2$ ,  $\text{SiO}_2\text{-NaO-Al}_2\text{O}_3$ ,  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2\text{-GeO}_2\text{-ZrO}_2\text{-TiO}_2$ ,  $\text{SiO}_2\text{-ZrO}_2$ , etc. In one approach, each type of particle may have a unique oxide species relative to the other types of particles.

**[00193]** **(b)** Core-shell particles. As shown in the schematic diagram of part **(b)** of FIG. 11, a feedstock may include core-shell particles. Core-shell particles may be formed by initial growth of a core particle from molecular precursors, followed by subsequent reaction, resulting in a growth of a shell or coating over the surface of the core particles. In one approach as shown in part (b), a  $\text{SiO}_2$  core particle **1106** may have a  $\text{TiO}_2$  shell **1108** formed over the surface of the  $\text{SiO}_2$  core particle **1106**. In one approach, the shell

may be in islands dispersed around the particle. In another approach, the shell may be a fully formed continuous layer. In some approaches, the average diameter  $d_2$  of the core particle **1106** may be in a range of about 25 nm to about 200 nm, and the average diameter may be larger or smaller. In some approaches, the average thickness  $th_1$  of the shell **1108** may be in a range of about 2 nm to about 4 nm, and may be larger or smaller.

**[00194]** In one approach, core-shell particles may include SiO<sub>2</sub>, GeO<sub>2</sub>, TiO<sub>2</sub>, etc. In one approach, core-shell particles may include SiO<sub>2</sub> with metal nanoparticles. In some approaches, core-shell particles may include SiO<sub>2</sub> with at least one of the following metal nanoparticles: gold, silver, nickel, copper, or a combination thereof. In one approach core-shell particles may include SiO<sub>2</sub>-PbO (silica lead oxide).

**[00195]** In some approaches, compositions of core-shell particles may include more than two oxide species. For example, compositions of core-shell particles may include SiO<sub>2</sub>-NaO-TiO<sub>2</sub>, SiO<sub>2</sub>-BaO-TiO<sub>2</sub>, SiO<sub>2</sub>-PbO-TiO<sub>2</sub>, SiO<sub>2</sub>-GeO<sub>2</sub>-PbO, SiO<sub>2</sub>-GeO<sub>2</sub>-TiO<sub>2</sub>, SiO<sub>2</sub>-NaO-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-GeO<sub>2</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub>, SiO<sub>2</sub>-ZrO<sub>2</sub>, etc.

**[00196]** In one approach, a composition includes a glass forming material including core-shell particles and a solvent. In one approach, the composition of core-shell particles may be configured to form a 3D structure. In one approach, the composition including core-shell particles may be an ink for an extrusion-based AM process. In another approach, the composition including core-shell particles may be a resin for a light-based AM process. In yet another approach, the composition including core-shell particles may be a powder for a laser-assisted melting AM process, e.g., selective laser melting, powder bed processes, etc. In one approach, the formed 3D structure may be self-supporting.

[00197] In one approach, a composition for an AM process includes a glass forming material where the composition may be configured to form a 3D structure. In one approach, the formed 3D structure may be self-supporting. In one approach, the composition may include a glass forming material and a solvent.

[00198] (c) Intermixed particles. As shown in part (c) of FIG. 11, a feedstock may include intermixed particles. In various approaches, intermixed particles are particles that are co-grown from a mixture of molecular precursors, with chemistry tuned to achieve an intermixture of the different chemical species within the same particles. In one approach, as illustrated in part (c), a particle 1110 may include an intermixture 1112 of O, Si, and Ti (where the intermixture 1112 is shown in a magnified view of a portion of the particle 1110). In various approaches, an average diameter  $d_A$  of the particle 1110 may be in a range of about 100 nm to about 400 nm, and the average diameter may be larger or smaller.

[00199] In one approach, a glass-forming feedstock may include an intermixture (as illustrated in the magnified view of an intermixture 1112) within formation of small clusters of particles grown together, and the clusters may not form a particle. In one approach, the intermixed feedstock may include a cluster of particles, e.g., oxo-clusters, oligomer-based clusters, small structures, agglomerate, etc. of particles containing different chemical species. In some approaches, the average diameter of the small cluster, agglomerate, oxo-cluster, etc. may be in a range of about 100 nm to about 400 nm, and may be larger or smaller.

[00200] In one approach, intermixed particles may include SiO<sub>2</sub>, GeO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, etc. In one approach, intermixed particles may include SiO<sub>2</sub> with metal nanoparticles. In

some approaches, intermixed particles may include SiO<sub>2</sub> with at least one of the following metal nanoparticles: gold, silver, nickel, copper, or a combination thereof. In one approach intermixed particles may include SiO<sub>2</sub>-PbO (silica lead oxide).

**[00201]** In some approaches, compositions of intermixed particles may include more than two oxide species. For example, compositions of intermixed particles may include SiO<sub>2</sub>-NaO-TiO<sub>2</sub>, SiO<sub>2</sub>-BaO-TiO<sub>2</sub>, SiO<sub>2</sub>-PbO-TiO<sub>2</sub>, SiO<sub>2</sub>-GeO<sub>2</sub>-PbO, SiO<sub>2</sub>-GeO<sub>2</sub>-TiO<sub>2</sub>, SiO<sub>2</sub>-NaO-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub>, SiO<sub>2</sub>-GeO<sub>2</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub>, etc.

**[00202]** In some approaches, a composition for an AM process includes a glass-forming material that includes intermixed particles. In one approach, intermixed particles may be defined as a cluster of particles that includes at least two different chemical species. In one approach, the composition includes a cluster of particles having at least one type of oxide species and at least one type of metal nanoparticle.

**[00203]** In one approach, a composition including intermixed particles may be configured to form an 3D structure. In one approach, the composition including intermixed particles may be an ink for an extrusion-based AM process. In another approach, the composition including intermixed particles may be a resin for a light-based AM process. In yet another approach, the composition including intermixed particles may be a powder for a laser-assisted melting AM process, e.g., selective laser melting, powder bed processes, etc. In one approach, the formed 3D structure may be self-supporting. In one approach, the composition may include a glass forming material and a solvent.

**[00204]** **(d)** Inorganic polymers. As shown in part **(d)** of FIG. 11, feedstocks may include inorganic polymers. In one approach, polymers may be co-grown via acid-catalyzed sol gel chemistry, from a mixture of molecular precursors, resulting in intimate

chemical species intermixture within long molecular chains rather than particles. As illustrated in part (d), the long molecular chain of polymer **1114** may have intimate chemical species intermixture **1116**. A magnified view of intermixture **1116** shows different chemical species may include Ti, Si, O, species having -OH or -OR groups, etc. The chemical species listed are by way of example only, and are not meant to be limiting in any way.

**[00205]** In one approach, a composition may include a glass-forming material having inorganic polymers. In one approach, the inorganic polymers may be linear polymers. In another approach, the inorganic polymers may be branched polymers. In yet another approach, the inorganic polymers may be combination of linear and branched polymers. In one approach, the glass-forming material may include inorganic polymers having a low molecular weight, for example, the glass-forming material may include inorganic oligomers. In approaches having oligomers, the length of the polymer chain may include a small number of repeat units whose physical properties depend on the length of the polymer chain. In one approach, the inorganic oligomers may be linear oligomers. In one approach, the inorganic oligomers may be branched oligomers. In yet another approach, the inorganic oligomers may be a combination of linear and branched oligomers.

**[00206]** In one approach, the composition including a glass forming material having inorganic polymers may be configured to form a 3D structure. In one approach, the composition including inorganic polymers is an ink for an extrusion-based AM process. For example, and not meant to be limiting, a polymeric-type glass-forming material may have an appropriate viscosity to be extruded. In another approach, the composition having glass-forming material including inorganic polymers may be a resin for a light-

based AM process. In yet another approach, the composition having glass-forming material including inorganic polymers may be a powder for a laser-assisted melting AM process. In various approaches, the 3D structure formed from a composition including inorganic polymers may be self-supporting. In one approach, the composition include a glass forming material having organic polymers may include a solvent.

**[00207]** (e) Layered shell particles. As shown in part (e) of FIG. 11, glass-forming feedstocks may include layered shell particles, e.g., layered as onion layers. In various approaches, a layered shell particle has a core particle has a shell similar to the core shell particle of part (b), but also includes repeated surface reactions performed on the core shell particle to generate additional layers of different compositions. A thickness of each layer may be tuned according to a desired specification. In some approaches, the thickness of each layer of the shell may be in a range of about 2 nm to about 10 nm, but the thickness may be higher or lower. In some approaches, a cumulative thickness of the plurality of layers of the shell being in a range of about 4 nm to about 50 nm, but the thickness may be higher or lower.

**[00208]** As illustrated in part (e), an example of layered shell particle **1118** may include a SiO<sub>2</sub> core particle **1120** may several layers of different compositions including two layers of GeO<sub>2</sub> **1122** alternated with two layers of TiO<sub>2</sub> **1124**, and a final SiO<sub>2</sub> shell layer **1126**. In one approach, a layered shell particle includes at least two shell layers above a core particle, where each of the at least two shell layers has a different composition. In some approaches, the shell layers above the core particle have alternating compositions, e.g., composition 1-composition 2-composition 1-composition 2-etc.

[00209] In one approach, layered shell particles may include  $\text{SiO}_2$ ,  $\text{GeO}_2$ ,  $\text{TiO}_2$ , etc. In one approach, layered shell particles may include  $\text{SiO}_2$  with metal nanoparticles. In some approaches, layered shell particles may include  $\text{SiO}_2$  with at least one of the following metal nanoparticles: gold, silver, nickel, copper, or a combination thereof. In one approach layered shell particles may include  $\text{SiO}_2\text{-PbO}$  (silica lead oxide).

[00210] In some approaches, compositions of layered shell particles may include more than two oxide species. For example, compositions of layered shell particles may include  $\text{SiO}_2\text{-NaO-TiO}_2$ ,  $\text{SiO}_2\text{-BaO-TiO}_2$ ,  $\text{SiO}_2\text{-PbO-TiO}_2$ ,  $\text{SiO}_2\text{-GeO}_2\text{-PbO}$ ,  $\text{SiO}_2\text{-GeO}_2\text{-TiO}_2$ ,  $\text{SiO}_2\text{-NaO-Al}_2\text{O}_3$ ,  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2\text{-GeO}_2\text{-ZrO}_2$ , etc.

[00211] In one approach, a composition having core-shell particles may include layered shell particles of which each layered shell particle includes at least two shell layers above a core particle. In one approach, the shell layers have different composition from each other.

[00212] In one approach, a composition includes a glass forming material having layered shell particles. In one approach, the composition including layered shell particles may be configured to form a 3D structure. In one approach, the composition including layered shell particles is an ink for an extrusion-based AM process. In another approach, the composition having glass-forming material including layered shell particles may be a resin for a light-based AM process. In yet another approach, the composition having glass-forming material including layered shell particles may be a powder for a laser-assisted melting AM process. In one approach, the formed 3D structure may be self-supporting. In one approach, the composition including a glass forming material having layered shell particles may include a solvent.

[00213] (f) Hollow layered shell particles. As shown in part (f) of FIG. 11, glass-forming feedstocks may include hollow layered shell particles. In one approach a layered shell particle as illustrated in part (e) may have all or part of the original core of the particle removed before subsequent layering of species via sol gel chemistry. In one approach, a hollow layered shell particle may limit the central domain size for composition, prevent phase separation, or a combination thereof.

[00214] As illustrated in part (f), in one approach a hollow layered shell particle 1132 may have a hollow core region 1130 with layers in similar format as described for the layered particle 1118 in part (e).

[00215] In one approach, a composition comprises a glass-forming material having core-shell particles that include layered shell particles having a hollow core. In one approach, the composition including layered shell particles having a hollow core may be configured to form a 3D structure. In one approach, the composition including layered shell particles having a hollow core is an ink for an extrusion-based AM process. In another approach, the composition having glass-forming material including layered shell particles having a hollow core may be a resin for a light-based AM process. In yet another approach, the composition having glass-forming material including layered shell particles having a hollow core may be a powder for a laser-assisted melting AM process. In one approach, the formed 3D structure may be self-supporting. In one approach, the composition including a glass forming material having layered shell particles with a hollow core may include a solvent.

[00216] (g) Combination or hybrid particles. In various approaches, particles of feedstocks as described in parts (a) through (f) may be combined to form hybrid and/or

combination particles. For example, as illustrated in part (g), a combination particle **1140** may be a combination of a core shell particle as illustrated in part (b) with a core particle **1134** being an intermixed particle as illustrated in part (c). As shown, the core particle **1134** may include intermixed particles **1136** as shown by the magnified view, and the core particle may have a GeO<sub>2</sub> shell **1138**. These approaches are by way of example only, and are not intended to be limiting in any way.

[00217] In various approaches, a composition may include a glass-forming material including a plurality of combination particles, and a solvent. In some approaches, the composition may be configured to form a 3D structure that is self-supporting.

[00218] In various approaches, a glass-forming feedstock may include a combination particle having at least two features as described herein: a shell, an intermixed core, a layered shell, a layered shell particle having a hollow core, and an inorganic polymer.

[00219] FIG. 12 is a schematic drawing of a process of engineering feedstocks for AM techniques leading to formation of glass structures, according to one aspect of an inventive concept. The process **1200** of growing the feedstock of SiO<sub>2</sub>-TiO<sub>2</sub> particles is illustrated in steps **1202** and **1204** thereby forming SiO<sub>2</sub> particles. In one approach, the feedstock preparation process includes a Stober sol synthesis process, as would be generally understood by one skilled in the art. Step **1206a** includes adding a TiO<sub>2</sub> shell to the SiO<sub>2</sub> particles to make the feedstock of SiO<sub>2</sub>-TiO<sub>2</sub> core-shell particles for AM processing. Image **1206b** is shows a suspension of SiO<sub>2</sub>-TiO<sub>2</sub> core-shell particles.

[00220] Process **1220** of FIG. 12 illustrates several possible steps for forming a glass structure using engineered feedstocks, according to one aspect of an inventive concept. As shown, the SiO<sub>2</sub>-TiO<sub>2</sub> core-shell particles of step **1206** may be one of several

engineered feedstocks **1212** that may be used for printing. Without meaning to be limiting in any way, two additional engineered feedstocks **1212** may be used for printing, blended particles **1208** and/or intermixed particles **1210**. A magnified view of **1210** shows the different chemical compositions that may be included in an intermixed particle.

**[00221]** In various aspects of an inventive concept, the engineered glass-forming feedstocks may be used with AM techniques to form printed glass.

**[00222]** In some approaches, the type of engineered feedstock to be used may depend on the desired length scale for printing. In one approach, a blended particle feedstock may be desirable for larger length scales of 10  $\mu\text{m}$ . In another approach, an intermixed particle feedstock may be desirable for shorter length scales of 1 nm. These approaches are presented for example only, and are not meant to be limiting in any way.

**[00223]** The properties of the feedstocks may be tailored to optimize factors critical to processing of feedstocks by AM. In some approaches, these properties include the sphericity and degree of agglomeration of the particles, which may influence the flowability of the particles as powder or the particles suspended in a solvent or resin. In some approaches, the properties include the compatibility of the feedstock material with solvents. In some approaches, the properties include the relative miscibility of the feedstock material with other feedstock materials.

**[00224]** Furthermore, the feedstocks may be tailored to optimize further processing of the green body (product of AM techniques) formed from feedstocks to form glass. In some approaches, the properties of the particle in the feedstocks may affect the sintering temperature during further processing to form glass. In some approaches, the properties

of the particles in the feedstocks include packing density and sizes of voids, which may affect the likelihood of achieving transparent, crack free glass.

[00225] In addition, particle feedstocks as described herein allows tailoring length scales to a desired specification relative to the distribution of each different species thereby allowing predefined uniformity/homogeneity of the feedstock material and reducing the propensity of species to phase separate and crystallize during thermal processing.

[00226] In various approaches, methods to prepare inks from the glass-forming feedstocks may include single pot solvent exchange, size-selective precipitation, ink filtration, etc.

[00227] In some approaches, the glasses formed by methods described herein may include rare earth dopants. In some approaches, the formed glass may include  $P_2O_5$ -based glass with dopants such as Nd, Yb, Ce, Er, Ho, Gd, Dy, Eu, Y, etc., and combinations thereof. In some approaches the glass may include  $SiO_2$ -based glass with dopants such as Nd, Yb, Ce, Er, Ho, Gd, , Dy, Eu, Y, etc., and combinations thereof.

[00228] In some approaches the glasses formed by methods described herein may include oxide species such as  $Al_2O_3$ , alumina, as an additive to improve solubility and improved phase stability.

[00229] Mixing of the inks for printing glass structures may include a mixing calibration method and printing compensation scheme to allow parts to be printed following a specification.

[00230] In some approaches, the glass structures may be printed on substrates that prevent the glass parts from cracking. Exemplary materials of substrates include silicone

rubber, silicone-treated surfaces including paper, aluminum, Teflon, porous substrates (such as porous paper), etc.

**[00231]** In some approaches, printed glass parts at the green body stage may be processed by chemical treatment. For example, chemical treatment of green bodies may include  $\text{NH}_3$ ,  $\text{CH}_3\text{COOH}$ , TEOS, triethylamine atmosphere, etc. to promote chemical bond formation, encourage solvent removal, etc.

**[00232]** In some approaches, printed glass parts at the green body stage may be processed by heat treatment atmosphere techniques. For example, heat treatment atmosphere techniques may include air, vacuum, nitrogen, helium, or mixture containing sources of chlorine or fluorine (e.g.,  $\text{Cl}_2$ ,  $\text{F}_2$ , HF, fluorinated alkoxides (e.g.,  $\text{Si}(\text{OC}_2\text{H}_5)_3\text{F}$ )), etc.

**[00233]** In some approaches, printed glass parts at the green body stage may be processed by microwave drying. In some approaches, printed glass parts at the green body stage may be processed by pressure-based methods, for example cold isostatic pressing, pressing, hot isostatic pressing, etc.

**[00234]** Engineered feedstocks may be used for producing single or multi-component glasses of a variety of compositions using different additive manufacturing techniques. This would enable glasses for which there is currently no viable feedstock to be prepared via AM processes.

**[00235]** In various aspects of an inventive concept, engineered feedstocks could be used for preparing glasses by additive manufacturing processes including direct ink writing, robocasting, computed axial lithography, projection microstereolithography (or other stereolithography printing techniques), ink jet, electrophoretic deposition, and

powder bed techniques such as selected laser melting/sintering, binder jetting, etc. In various aspects of an inventive concept, engineered feedstocks may also be used for coating processes such as dip coating, meniscus coating, spin coating, etc.

**[00236] Example 1 of Heat Treatment**

**[00237]** 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.

**[00238] Example 2 of Heat Treatment**

**[00239]** 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.

**[00240] Experiments**

[00241] 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.

[00242] 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.

[00243] FIG. 7A is a plot of refractive index profile (y-axis) versus titania ( $\text{TiO}_2$ ) 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 ( $\blacklozenge$ , solid line) and have a variation in refractive index comparable to commercial silica ( $\blacktriangle$ ) and silica-titanate glasses ( $\circ$ ,  $\square$ ) (dotted line). FIG. 7B is an image of the resultant glass structures formed from the ink formulations represented by the diamonds ( $\blacklozenge$ ) of FIG. 7A at different concentrations of wt%  $\text{TiO}_2$  (2 wt%, 4 wt%, 5 wt%, 6 wt%, 8 wt%, 9 wt%, 10 wt%).

[00244] 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 ( $V_{\text{ink}}$ ) of the structure at each step during the heat treatment process is shown next to the image of the structure.

[00245] 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  $\text{TiO}_2$  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<sub>2</sub> 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<sub>2</sub> composition is highest, and lowest at the edges, where the TiO<sub>2</sub> 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- $\mu$ m focal spot from the lens, which has a focal length of 62 cm.

[00246] 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  $\sim$  1 mm diameter spot.

[00247] **Experiments of Feedstocks for Additive Manufacturing to Form Glass**

[00248] *Core-Shell particles*

[00249] SiO<sub>2</sub> particles were prepared by the Stöber process by mixing tetraethylorthosilicate (TEOS), water, and ammonia catalyst in an ethanol (EtOH) solvent. Particles were grown to steady state for approximately 5 days and were measured having an average diameter of  $23.6 \pm 0.7$  nm by dynamic light scattering (DLS), shown in FIG. 13A. Particle size and spherical morphology were confirmed by transmission electron microscope (TEM), as shown in part (a) and a magnified view in part (b) of FIG. 13B.

[00250] For SiO<sub>2</sub>-TiO<sub>2</sub> core-shell nanoparticles (FIGS. 13C-13E), titanium (IV) isopropoxide (TIP) was added to the aged SiO<sub>2</sub> sol and heated at 55 °C to control the reaction through evaporation of the ammonia catalyst, yielding raspberry-like particles. Resulting nanoparticles were  $25.4 \pm 0.4$  and  $34.1 \pm 4.8$  nm in diameter for 1.5 and 5 wt% TiO<sub>2</sub>-containing nanoparticles by DLS, as shown in FIG. 13A.

[00251] TEM images in part (a) and the magnified view of part (b) FIGS. 13C and 13D confirm the respective nanoparticle sizes and evolution of the raspberry-like particle morphology of 1.5 wt% and 5.0 wt% TiO<sub>2</sub>-containing nanoparticles, respectively.

[00252] A schematic of the particle is shown for each particle: SiO<sub>2</sub> in part (c) of FIG. 13B, 1.5 wt% TiO<sub>2</sub>-SiO<sub>2</sub> in part (c) of FIG. 13C, and 5.0 wt% TiO<sub>2</sub>-SiO<sub>2</sub> in part (c) of FIG. 13D. Each schematic depicts the relative extents of TiO<sub>2</sub> coatings for 1.5 and 5 wt% TiO<sub>2</sub>-SiO<sub>2</sub> nanoparticles.

[00253] FIG. 13E shows that at 8 wt% TiO<sub>2</sub> loading, the SiO<sub>2</sub>-TiO<sub>2</sub> nanoparticles did not clearly form in a raspberry morphology (part (a) and the magnified view in part (b)). However, DLS measurements show that the particles were typically  $38.8 \pm 0.5$  nm, suggestive of a larger TiO<sub>2</sub> shell as shown in FIG. 13A.

**[00254]**    *Intermixed Particles and Sub-structures*

**[00255]**    FIGS. **14A-14B** illustrate samples of intermixed particles formed by methods described herein. Two samples **1402**, **1404** of titania-silica intermixed particles are shown in FIG. **14A**, in which after centrifugation, the Supernatant of each showed no measurable particle count, and each had a pellet of nanoparticles collected at the base of the centrifuge tube.

**[00256]**    The collected titania-silica intermixed nanoparticles were filtered and dried to form the powder as shown FIG. **14B** of images of vials **1406** and vial **1408**.

**[00257]**    An example of a hybrid intermixed particle is shown in FIGS. **15A-15C**, according to one aspect of an inventive concept. As illustrated in FIG. **15A**, part (a) shows examples of molecular precursors TEOS and TIP that may be used to form a hybrid particle as drawn in part (b). The resulting hybrid particle may be in the form of small clusters, oxo-clusters, oligomer-based particles, etc. as shown rather than a distinct particle. An average diameter of the clusters forming the hybrid intermixed particle-like form may be in range of 100 nm to 400 nm.

**[00258]**    FIG. **15B** is an image of the suspended hybrid particles having estimated average diameter, as measured by DLS, of about 250 nm.

**[00259]**    FIG. **15C** are images of TEM of the hybrid particles at a lower magnification in part (a) and a higher magnification in part (b). The clusters shown in the images may be comprised of smaller structures having an average diameter of about 12 nm. Each of the structure may include the different chemical compositions as illustrated in the schematic drawing of FIG. **15A**.

**[00260]**    *Inorganic Polymers*

[00261] FIGS. **16A-16B** show an example of inorganic polymers engineered as a feedstock for using AM techniques for forming glass structures, according to one aspect of an inventive concept. FIG. **16A** demonstrates the general process for forming an inorganic polymer suitable for printing in which, sequentially, (1) a silicon alkoxide is hydrolyzed under acidic conditions using sub-stoichiometric H<sub>2</sub>O for hydrolysis, (2) a titanium alkoxide is added to introduce titanium into the partially hydrolyzed silicon oxo-polymer, (3) additional hydrolysis to promote crosslinking and viscosity tuning, (4) neutralization of the acidic species, (5) transesterification of alkoxide ligands to functionalize the polymeric strands, and (6) evaporative removal of solvents and unreacted reagents. Non-volatile alkoxide ligands inhibit shrinkage and/or cracking during ambient drying and thus, resulting in an air sensitive, oil-like ink.

[00262] The images shown in FIG. **16B** show different products of the inorganic polymer feedstocks after AM processing. Part **(a)** shows a green body using an Cr<sup>III</sup> inorganic polymer feedstock heated at 500°C and 200°C. Part **(b)** shows the glass products from the process using an Al inorganic polymer feedstock and an Al/Cr<sup>III</sup> inorganic polymer feedstock. Part **(c)** shows the product of a Ti inorganic polymer feedstock after calcination of the green body.

[00263] *Layered Shell Particles*

[00264] FIGS. **17A-17B** depict an example of a layered shell particle engineered as a feedstock for using AM techniques for forming glass structures, according to one aspect of an inventive concept. FIG. **17A** is schematic drawing of a process **1700** of forming a layered shell particle. The core particle **1702** is a SiO<sub>2</sub> nanoparticle where a shell of TiO<sub>2</sub> layer **1704** is added to form a core-shell particle **1706**. Then subsequent layers of

alternating Si layers **1708** and Ti layers **1704** are added to the core-shell particle to that an onion structure of a layered shell particle **1710** having many alternating layers.

[00265] FIG. **17B** is a series of SEM images of a suspension of layered shell particles at subsequent steps of preparation. Part **(a)** is an image of SiO<sub>2</sub> core particles **1702** (as drawn in FIG. **17A**). Part **(b)** is an image of SiO<sub>2</sub>- TiO<sub>2</sub> core-shell particles **1706**, as depicted in FIG. **17B**, having a SiO<sub>2</sub> core particle **1702** with a first shell of TiO<sub>2</sub> layer **1704**. Part **(c)** is an image of the core-shell particles **1706** having a second layer of SiO<sub>2</sub> added on the TiO<sub>2</sub> layer.

[00266] Table **1** lists the average diameter values of each step of forming the layered shell particle, as represented in the images of FIG. **17B** as determined by DLS.

Table **1**: DLS values of particles in suspension

| NP size     | SiO <sub>2</sub> core | SiO <sub>2</sub> /TiO <sub>2</sub> | SiO <sub>2</sub> /TiO <sub>2</sub> /SiO <sub>2</sub> |
|-------------|-----------------------|------------------------------------|------------------------------------------------------|
| By DLS (nm) | 62.4 ± 0.1            | 66.9 ± 0.1                         | 80.9 ± 0.1                                           |

As shown in Table **1**, the average diameter of the particles increases as each layer is added to the SiO<sub>2</sub> core particle, thereby suggesting that the particles are growing in size as an additional layer is added.

[00267] *Hollow Layered Shell Particles*

[00268] FIGS. **18A-18C** depict an example of a hollow layered shell particle engineered as a feedstock for using AM techniques for forming glass structures, according to one aspect of an inventive concept. FIG. **18A** is a schematic drawing of a process **1800** of forming a hollow layered shell particle. As described above in the

process **1700** of forming a layered shell particle, the process **1800** begins with a SiO<sub>2</sub> core particle **1802** that has a TiO<sub>2</sub> shell **1804**. An etching solution, e.g., NaOH, may be added to dissolve the SiO<sub>2</sub> core **1802** of the SiO<sub>2</sub>-TiO<sub>2</sub> core-shell particles, thereby opening a hollow space **1806** in the core location of the core-shell particle. The etching may be stopped, quenched, etc. when the core material, in this case SiO<sub>2</sub>, has dissolved and only a hollow space **1806** remains within the layered shells. In one approach, as shown in hollow layered shell particle **1810**, a TiO<sub>2</sub> shell layer **1804** remains with a hollow space **1806**. This approach is by way of example only, and not meant to be limiting in any way. The hollow layered shell particle may have a plurality of layers of different compositions.

[00269] FIG. **18B** is a series of SEM images of hollow layered shell particles at a lower magnification (part **(a)**) and a higher magnification (part **(b)**).

[00270] FIG. **18C** shows an energy dispersive X-ray (EDX) spectrum of the hollow layered shell particles that confirms the amount of Si is significantly lower than the amount of Ti and O in the particles, thereby suggesting that the core particle material has been removed from the particles.

[00271] **In Use**

[00272] Various aspect of an inventive concepts 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 (T<sub>g</sub>), melting point, photoemission, fluorescence, chemical reactivity (e.g. etch rate), or density/porosity.

[00273] Various aspect of an inventive concepts 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.

[00274] Further aspect of an inventive concepts 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.

[00275] Various aspect of an inventive concepts described herein as engineered feedstocks may be used for producing single or multi-component glasses of a variety of compositions using different additive manufacturing techniques. This would enable glasses for which there is currently no viable feedstock to be prepared via AM processes. The engineered feedstocks may be used for preparing glasses by additive manufacturing processes including direct ink writing, robocasting, computed axial lithography, projection microstereolithography, ink jet, electrophoretic deposition, and powder bed techniques such as selected laser melting/sintering or binder jetting. These AM-generated glasses may be used in a variety of applications including active and passive optics, packaging, labware, housewares, art and jewelry, glass seals, microfluidic and millifluidic devices, sensors, radiation shielding, bioglass, etc.

[00276] The inventive concepts disclosed herein have been presented by way of example to illustrate the myriad features thereof in a plurality of illustrative scenarios, aspect of an inventive concepts, 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.

[00277] While various aspects of an inventive concept 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 aspect of an inventive concept of the present invention should not be limited by any of the above-described exemplary aspect of an inventive concepts, but should be defined only in accordance with the following claims and their equivalents.

## CLAIMS

What is claimed is:

1. A composition for an additive manufacturing process, the composition comprising:  
a glass-forming material,  
wherein the composition is configured to form a three-dimensional structure,  
wherein the three-dimensional structure is self-supporting.
2. The composition of claim 1, comprising a solvent.
3. The composition of claim 2, wherein the composition is an ink for an extrusion-based additive manufacturing process.
4. The composition of claim 2, wherein the glass-forming material comprises a cluster of particles, wherein the cluster includes at least two different chemical species, wherein the cluster of particles includes intermixed particles.
5. The composition of claim 4, wherein an average diameter of the intermixed particles is in a range of about 100 nanometers to about 400 nanometers.

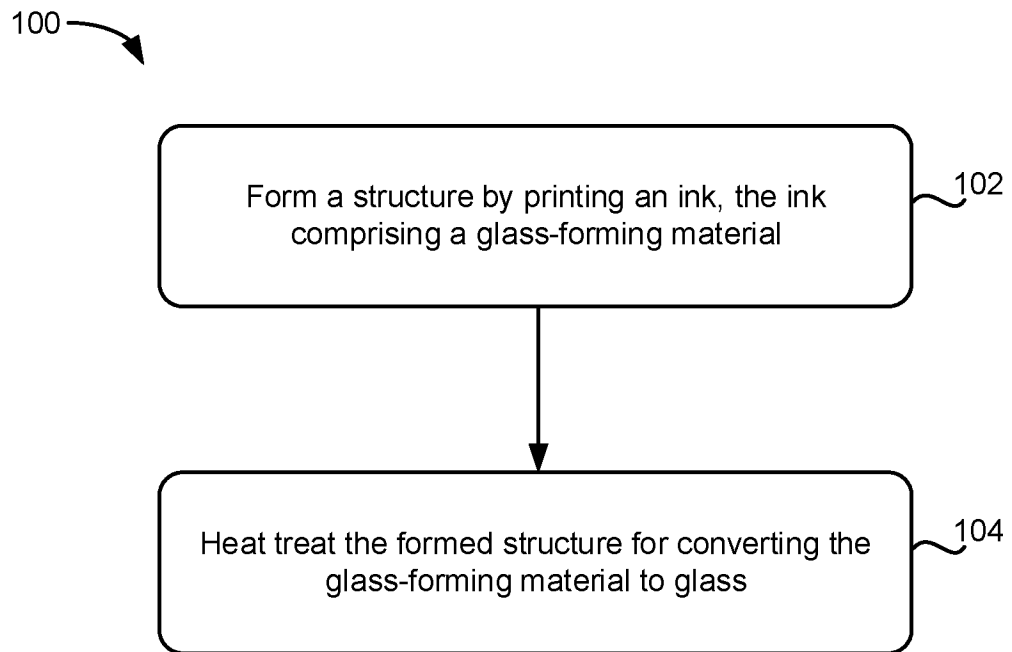
6. The composition of claim 1, wherein the glass-forming material includes greater than two oxide species selected from the group consisting of: SiO<sub>2</sub>, GeO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, and SiO<sub>2</sub>-PbO.
7. The composition of claim 1, wherein the glass-forming material includes inorganic polymers.
8. The composition of claim 1, wherein the glass-forming material includes a combination particle having at least two features selected from the group consisting of: a shell, an intermixed core, a layered shell, a layered shell particle having a hollow core, and an inorganic polymer.
9. The composition of claim 1, wherein the composition is a resin for a light-based additive manufacturing process.
10. The composition of claim 1, wherein the composition is a powder for a laser-assisted melting additive manufacturing process.
11. A composition for an additive manufacturing process, comprising:  
a glass-forming material comprising blended particles, wherein the blended particles comprise at least two types of particles having different compositions; and  
a solvent,

wherein the composition is configured to form a three-dimensional structure,  
wherein the three-dimensional structure is self-supporting.

12. The composition of claim 11, wherein the blended particles include at least one oxide species selected from the group consisting of:  $\text{SiO}_2$ ,  $\text{GeO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{SiO}_2\text{-PbO}$ .
13. The composition of claim 11, wherein each type of particle has a unique oxide species.
14. The composition of claim 11, further comprising an effective amount of a second component for altering a property of a glass structure created using the composition.
15. The composition of claim 14, wherein the property is selected from the group consisting of: an optical characteristic, a mechanical characteristic, a magnetic characteristic, a thermal characteristic, an electrical characteristic, and a chemical characteristic.
16. The composition of claim 11, wherein the composition is an ink for an extrusion-based additive manufacturing process.

17. The composition of claim 11, wherein the composition is a resin for a light-based additive manufacturing process.
18. The composition of claim 11, wherein the composition is a powder for a laser-assisted melting additive manufacturing process.
19. A composition for an additive manufacturing process, comprising:  
a glass-forming material comprising core-shell particles; and  
a solvent.
20. The composition of claim 19, wherein the composition is configured to form a three-dimensional structure, wherein the three-dimensional structure is self-supporting.
21. The composition of claim 19, wherein an average diameter of a core particle of the core-shell particles is in a range of about 25 nanometers to about 200 nanometers.
22. The composition of claim 19, wherein an average thickness of a shell of the core-shell particles is in a range of about 2 nanometers to about 4 nanometers.

23. The composition of claim 19, wherein the core-shell particles include at least one oxide species selected from the group consisting of: SiO<sub>2</sub>, GeO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, and SiO<sub>2</sub>-PbO.
24. The composition of claim 19, wherein the core-shell particles include greater than two oxide species.
25. The composition of claim 19, wherein the core-shell particles comprises a layered shell particle, wherein each layered shell particle includes at least two shell layers above a core particle, wherein the shell layers have different compositions.
26. The composition of claim 25, wherein the layered shell particle has a hollow core.
27. The composition of claim 19, wherein the composition is an ink for an extrusion-based additive manufacturing process.
28. The composition of claim 19, wherein the composition is a resin for a light-based additive manufacturing process.
29. The composition of claim 19, wherein the composition is a powder for a laser-assisted melting additive manufacturing process.

**FIG. 1**

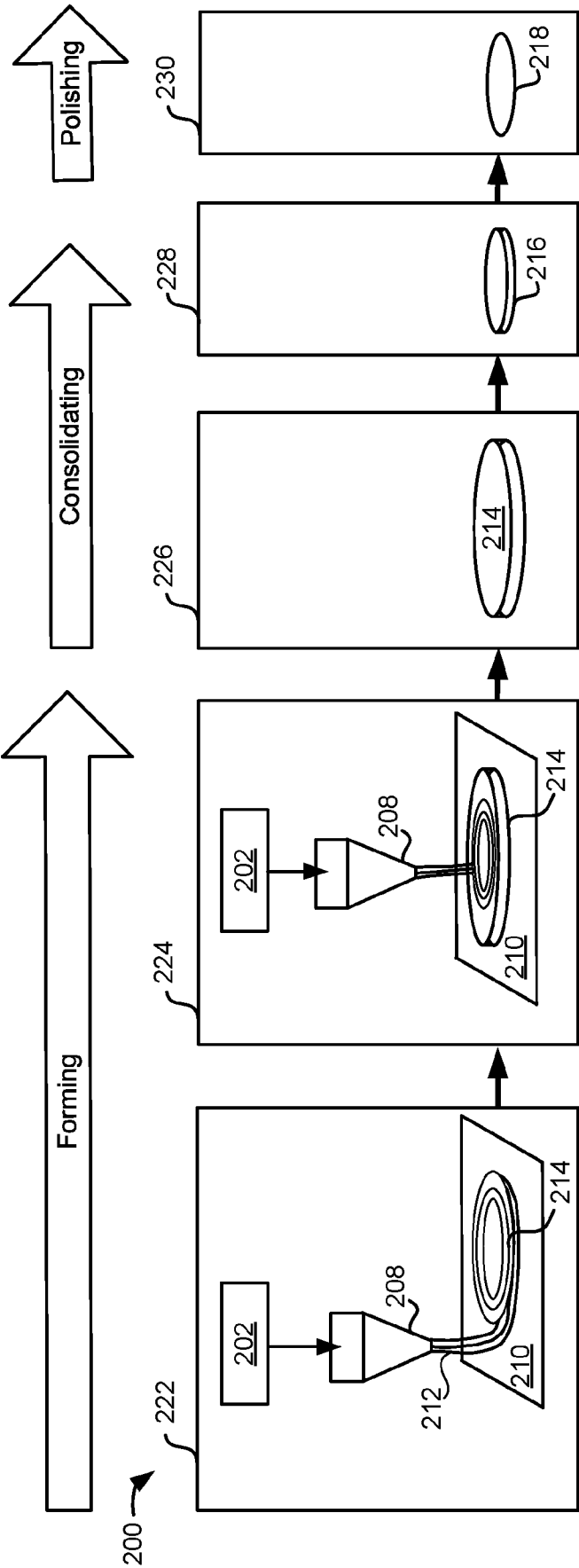


FIG. 2A

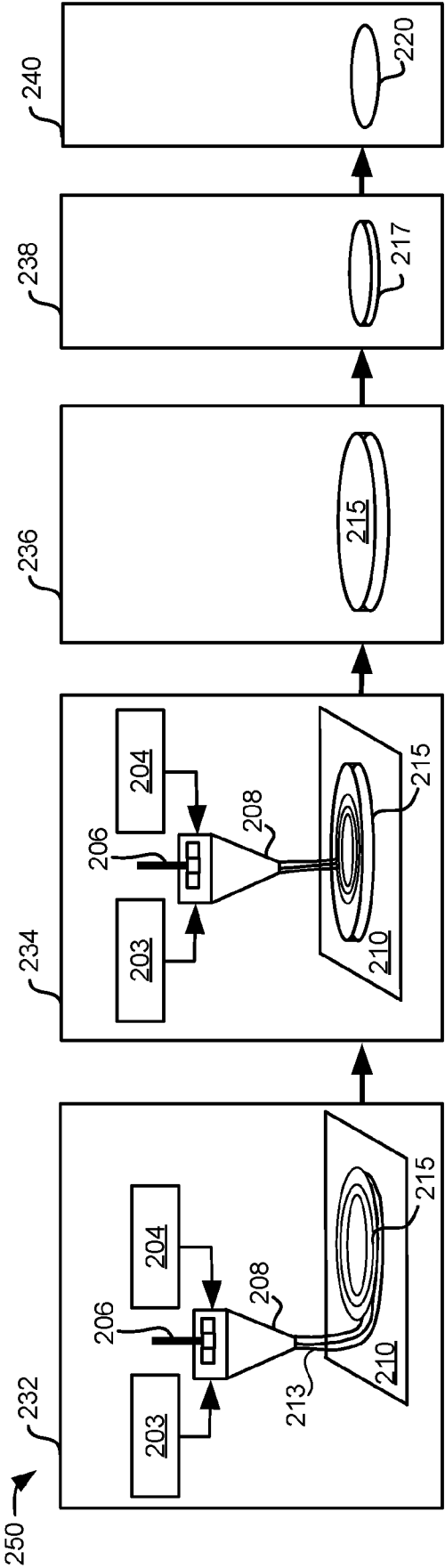


FIG. 2B

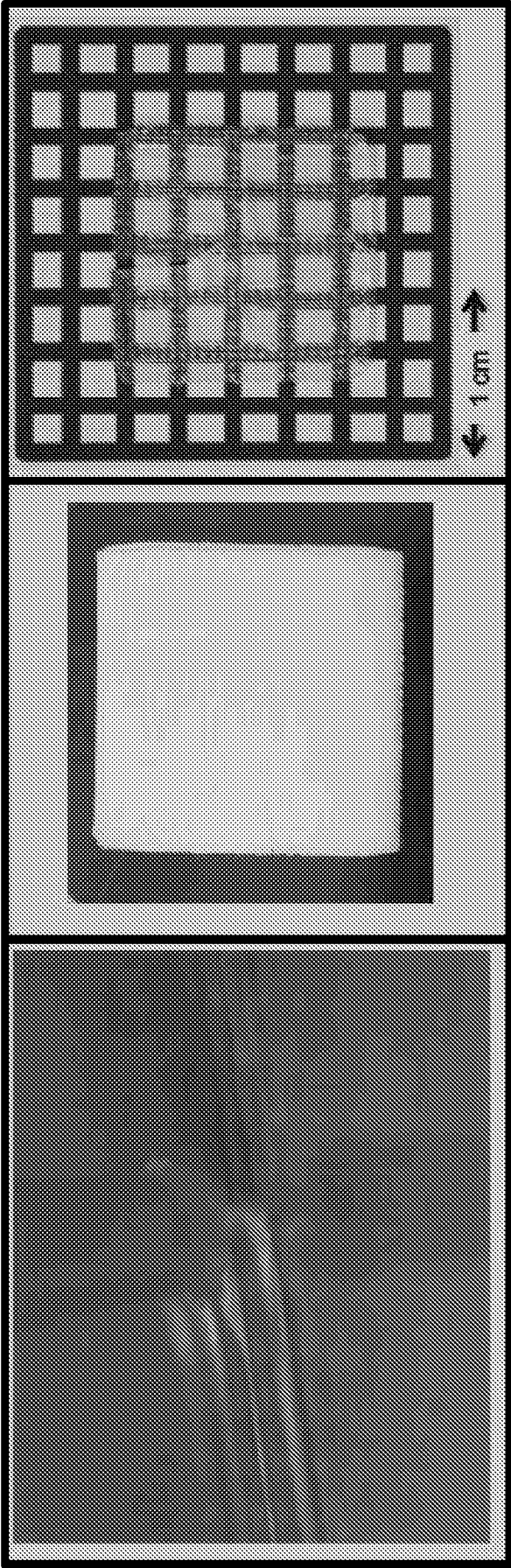


FIG. 3A

FIG. 3B

FIG. 3C

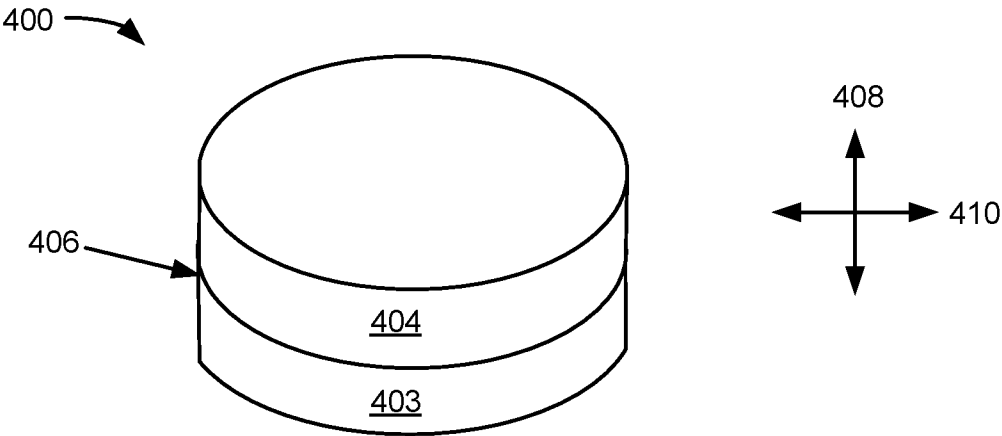


FIG. 4A

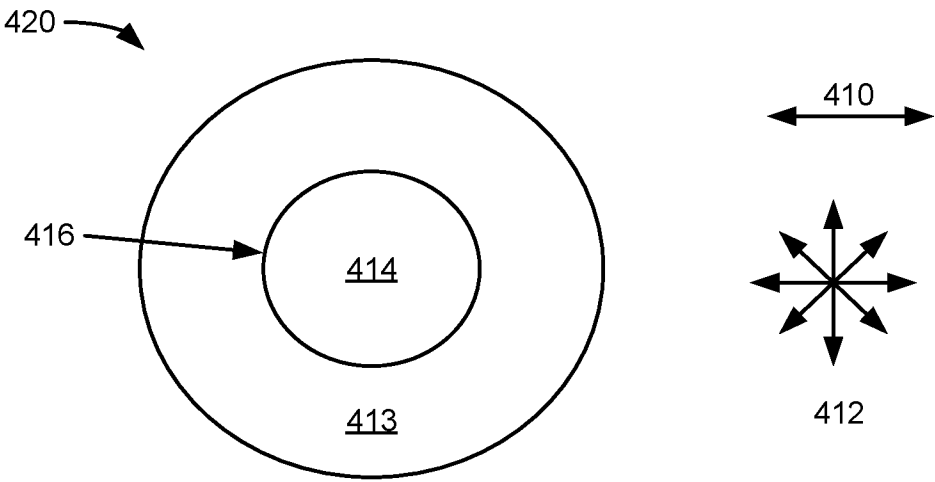


FIG. 4B

FIG. 5B

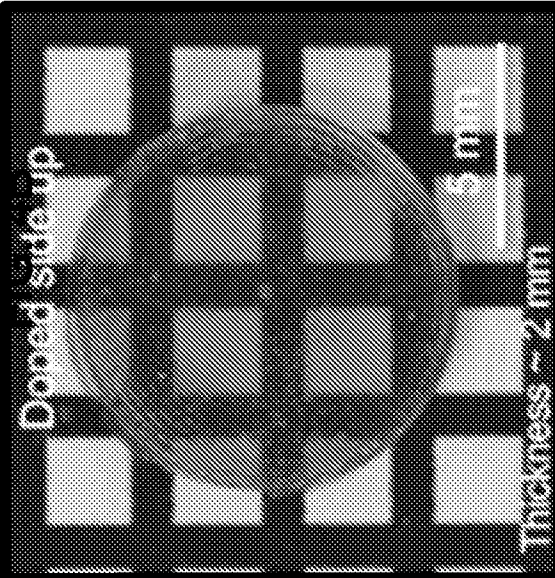
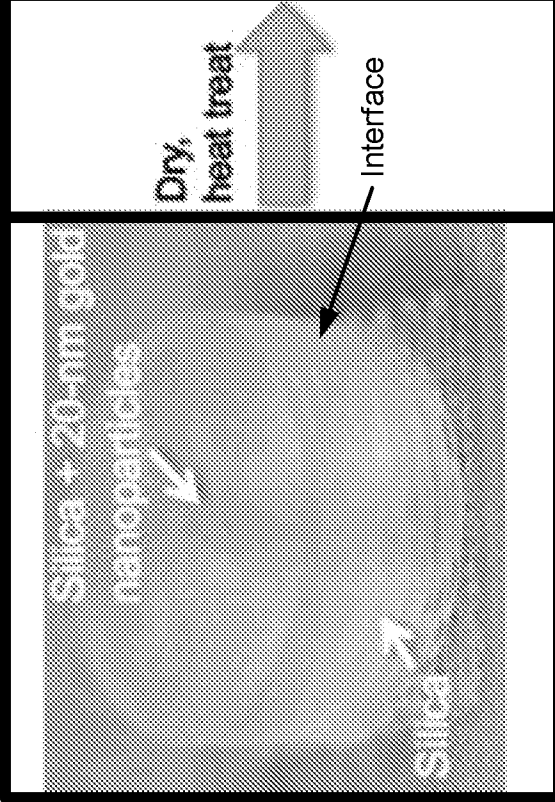


FIG. 5A



Interface

FIG. 5D

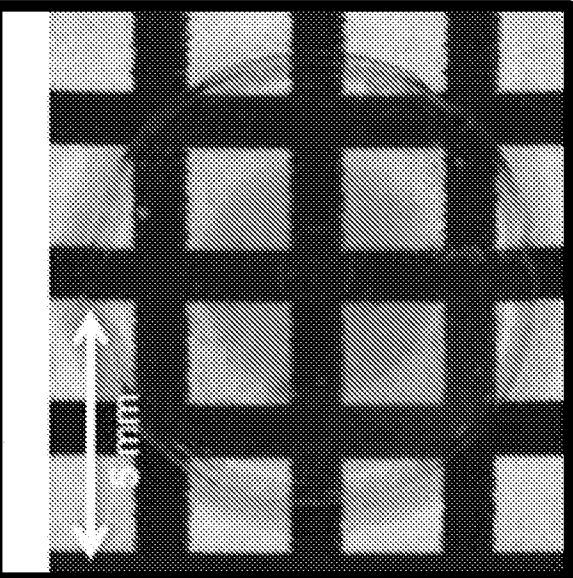


FIG. 5C

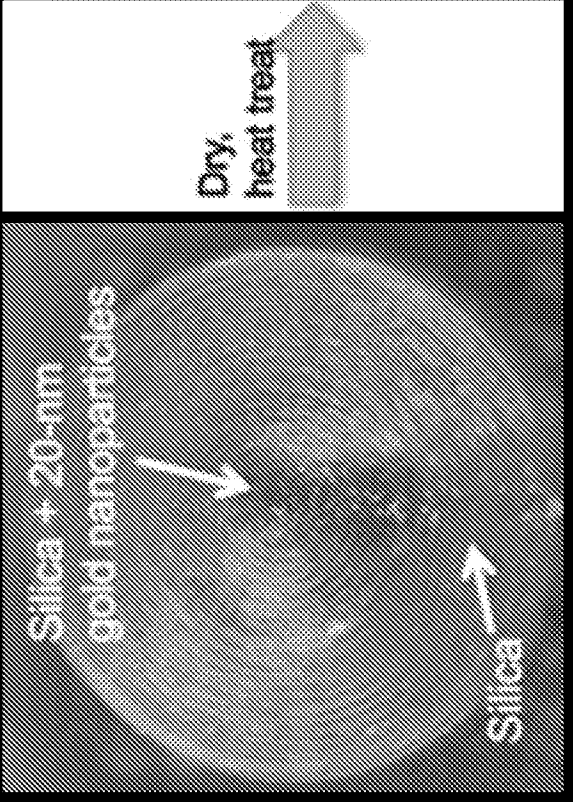


FIG. 6C

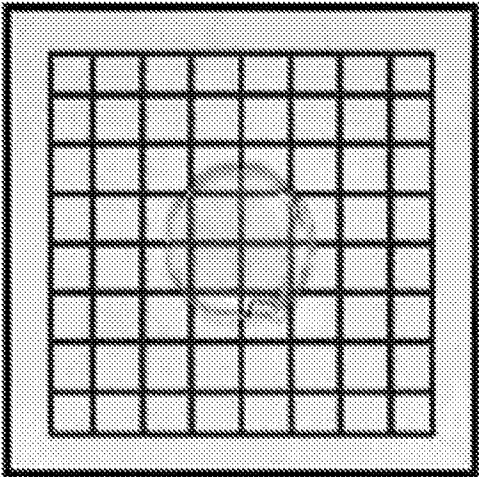


FIG. 6B

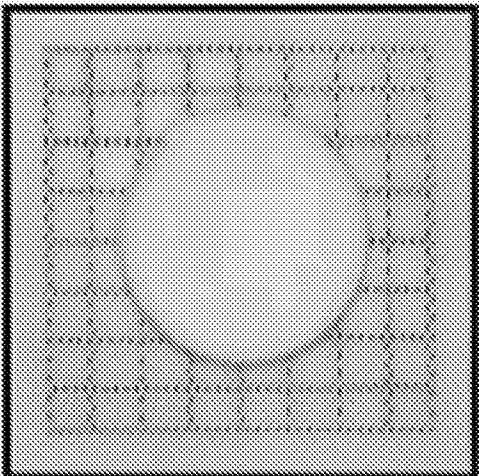


FIG. 6A

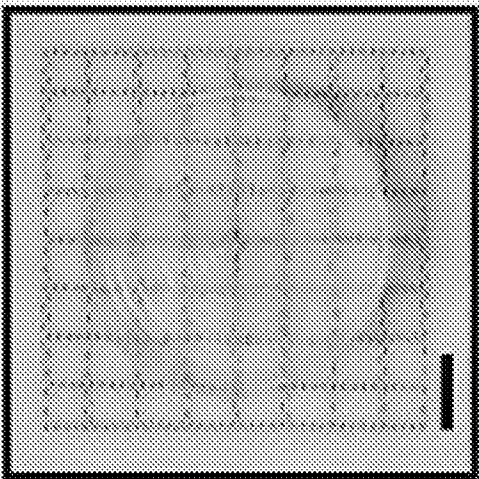


FIG. 6F

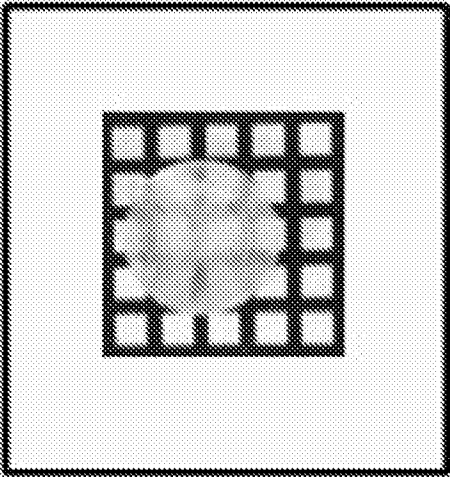


FIG. 6E

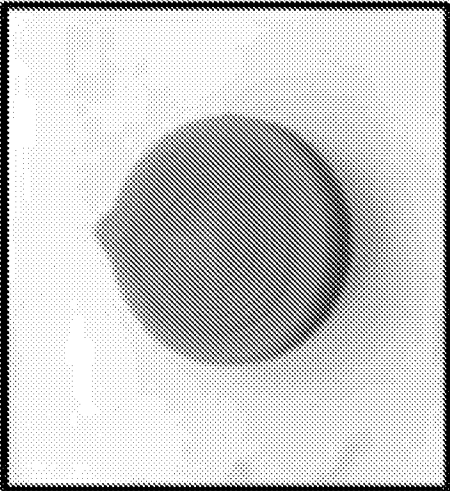


FIG. 6D

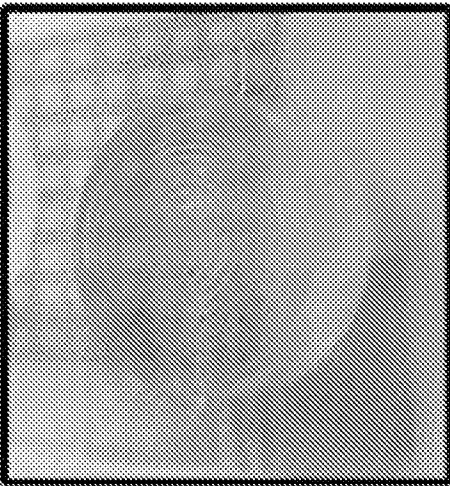
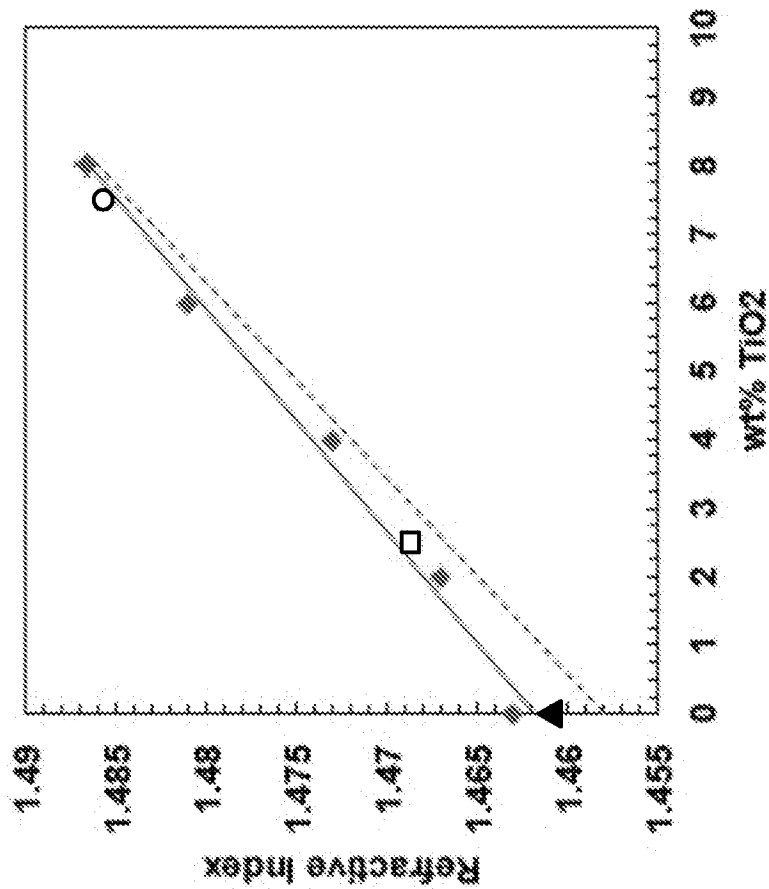


FIG. 7A



TiO<sub>2</sub>:SiO<sub>2</sub> glasses from inks

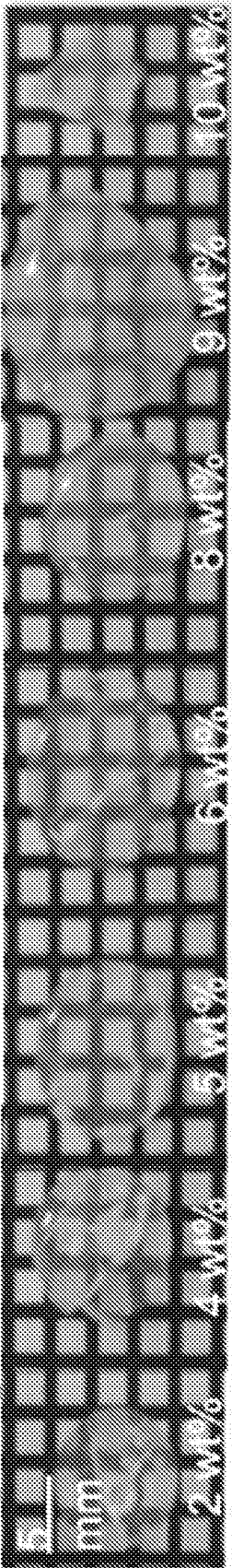


FIG. 7B

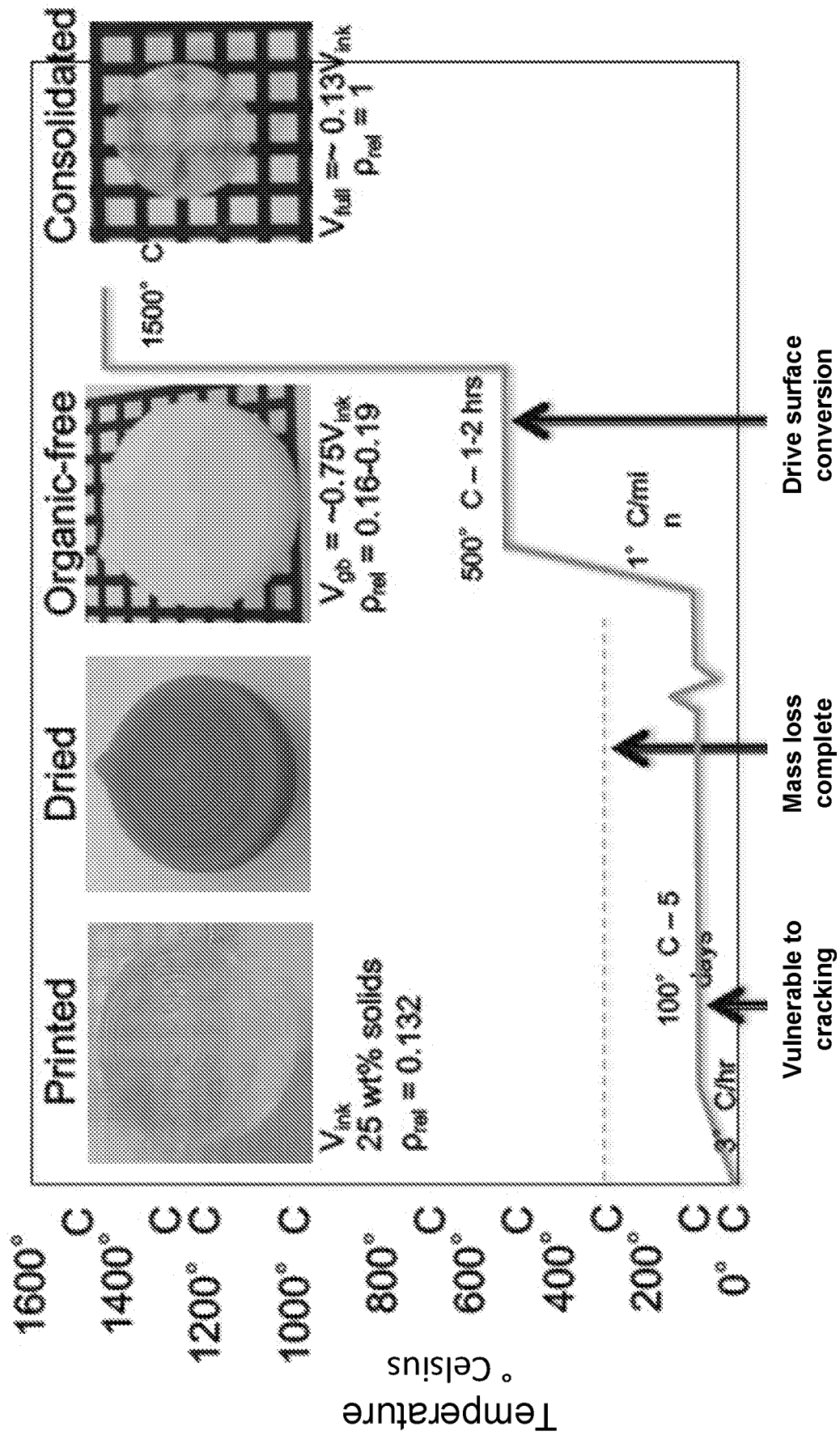


FIG. 8

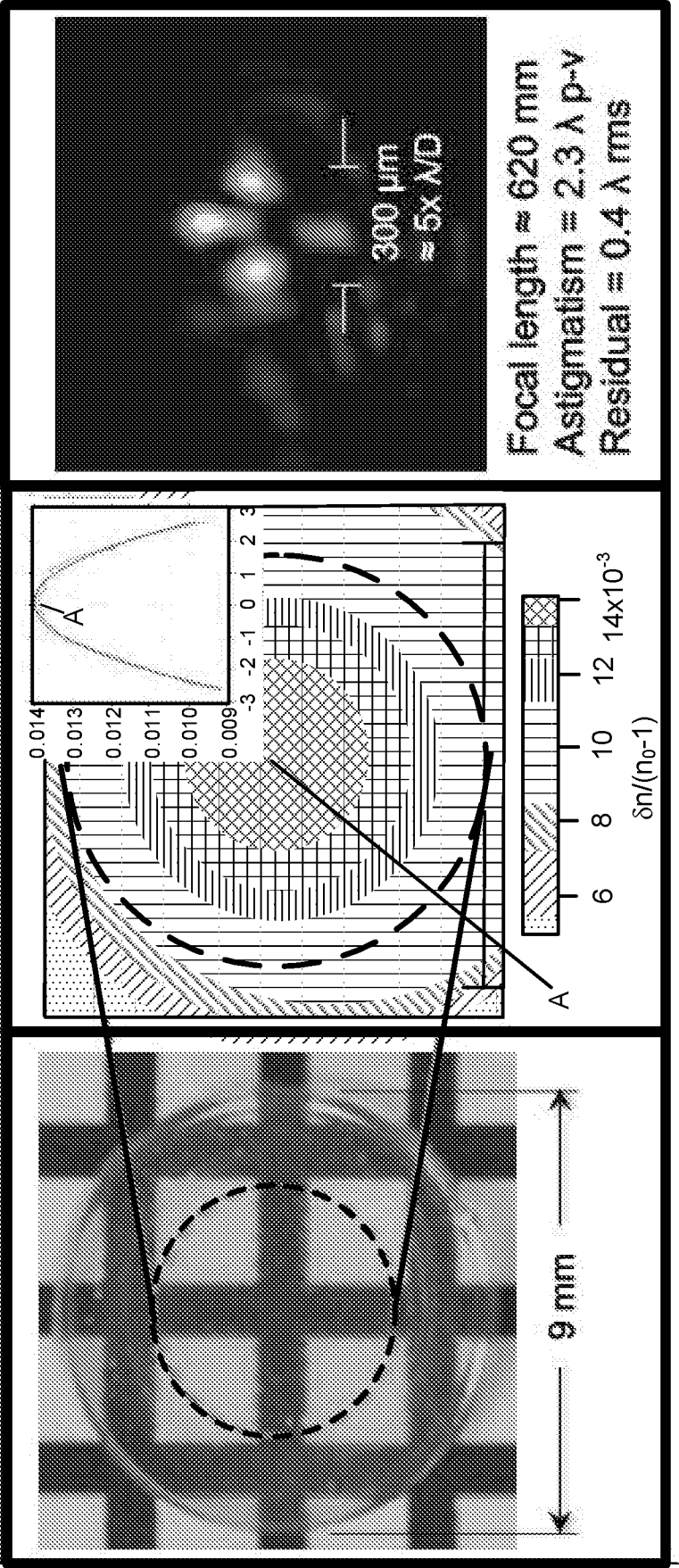


FIG. 9A

FIG. 9B

FIG. 9C

FIG. 10A

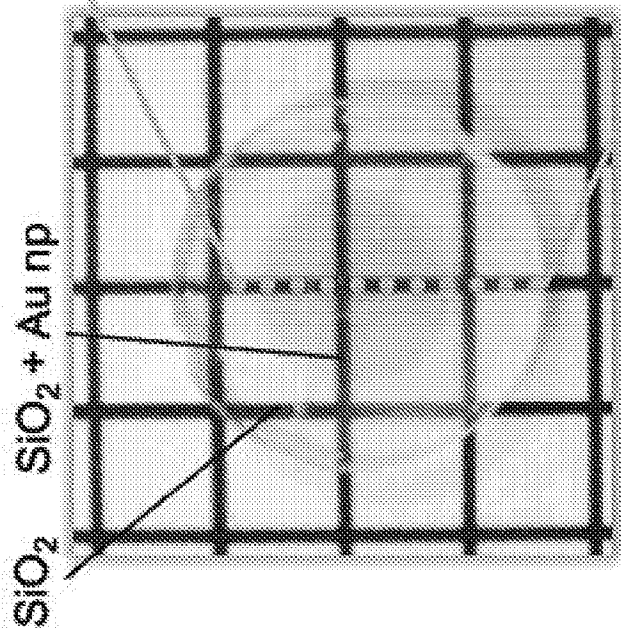


FIG. 10B

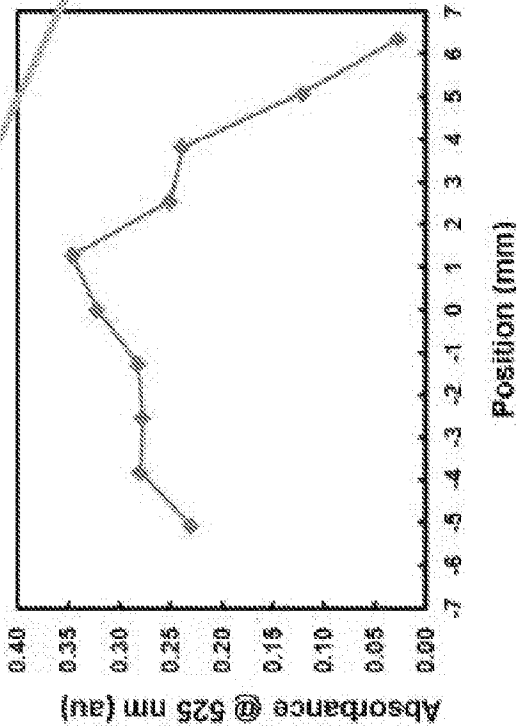
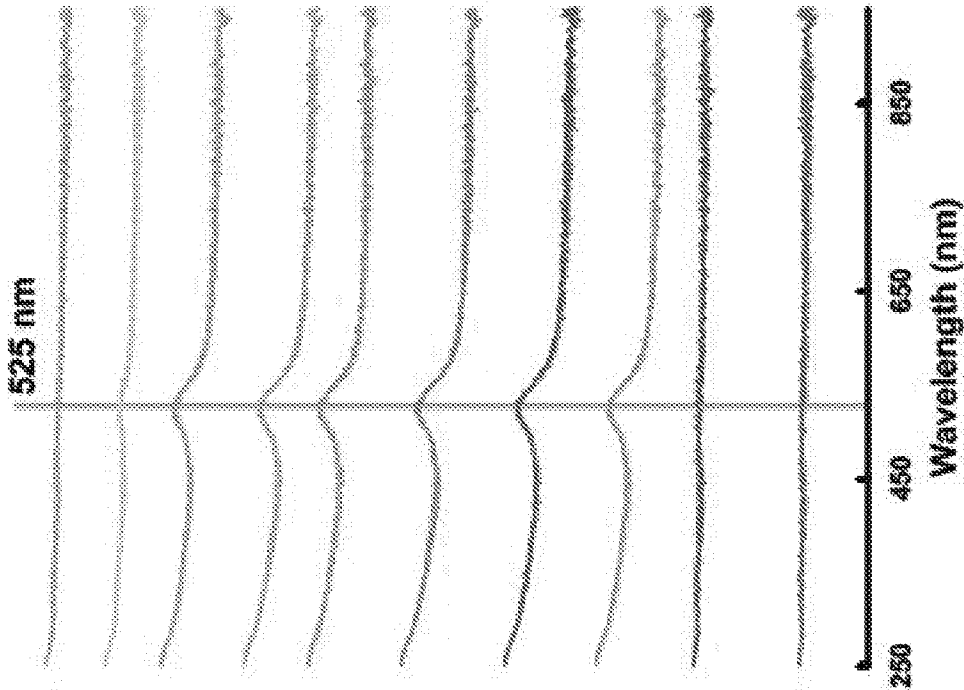


FIG. 10C

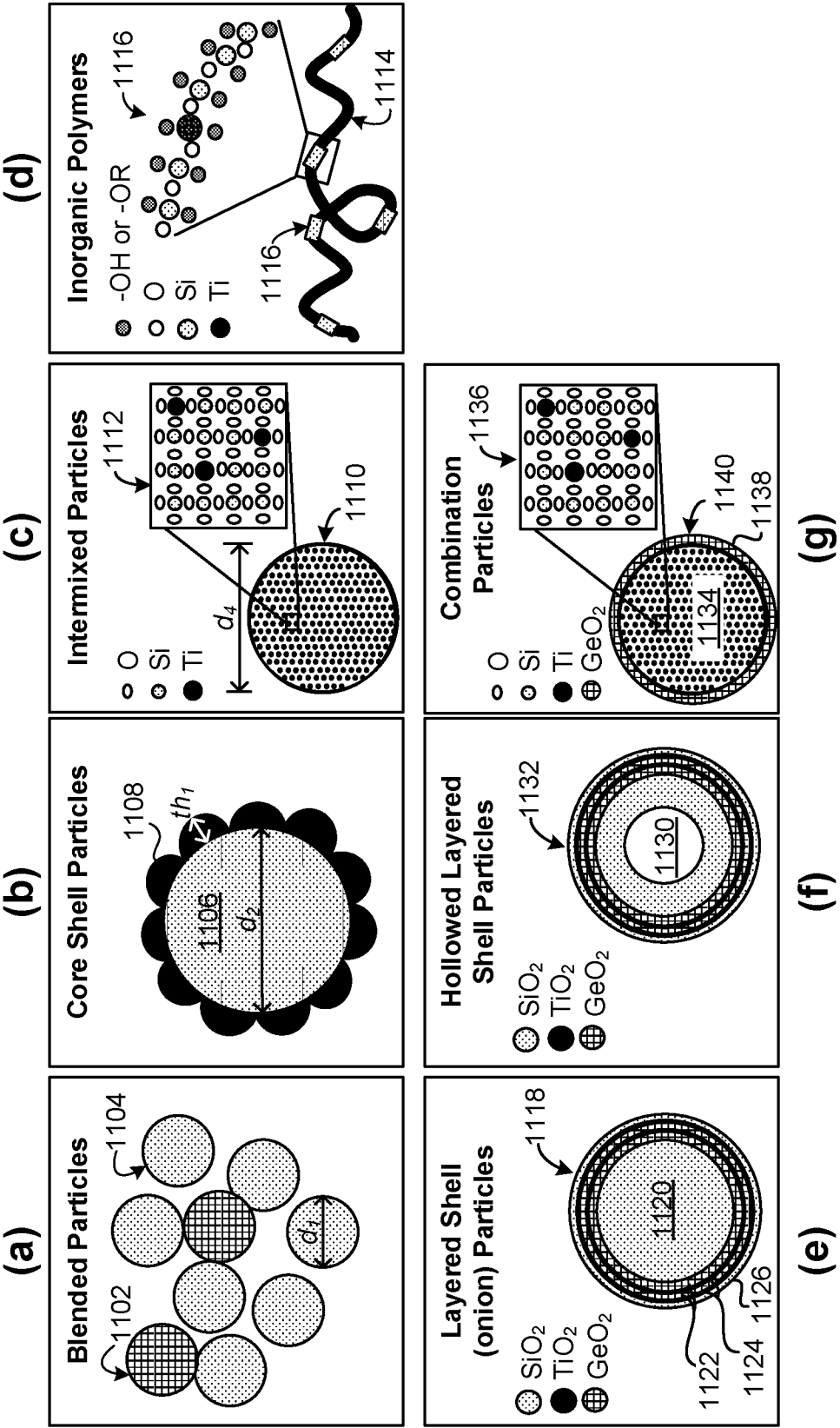


FIG. 11

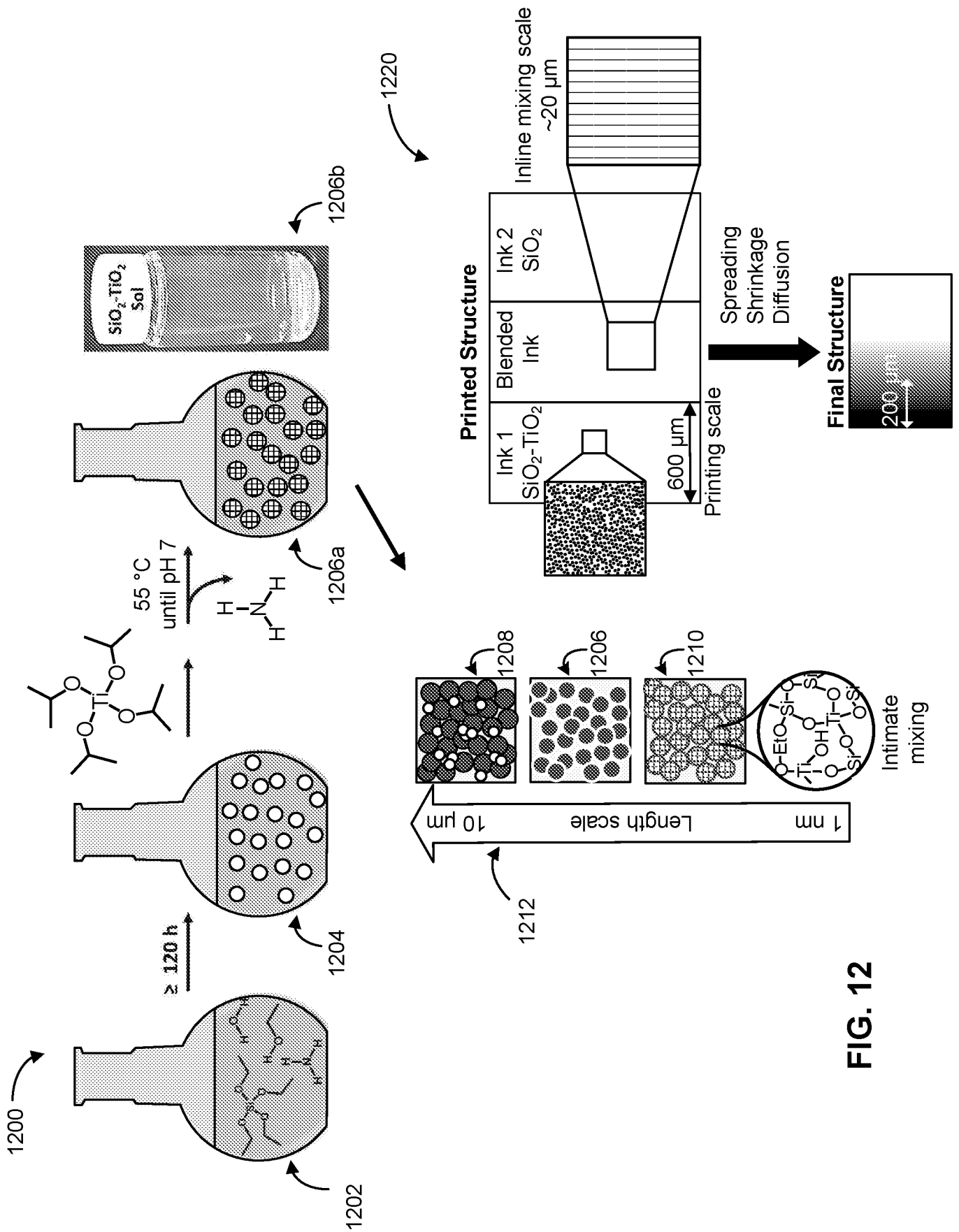
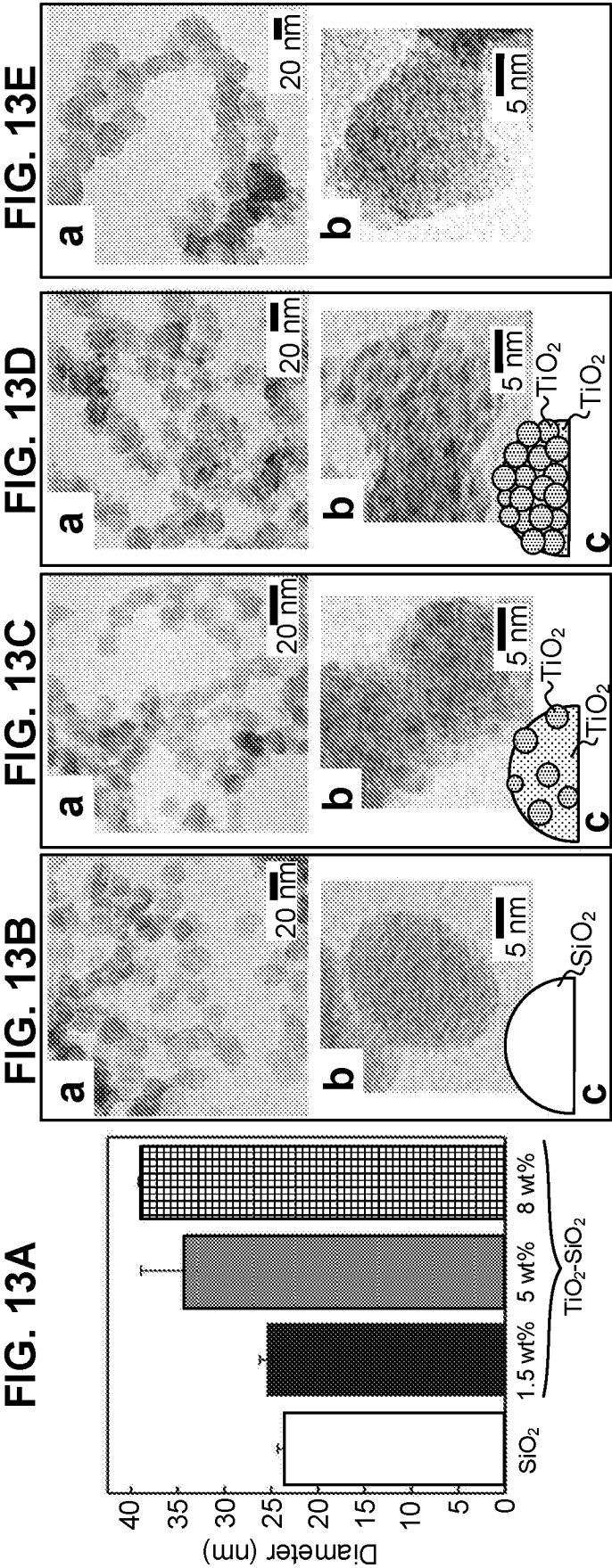


FIG. 12



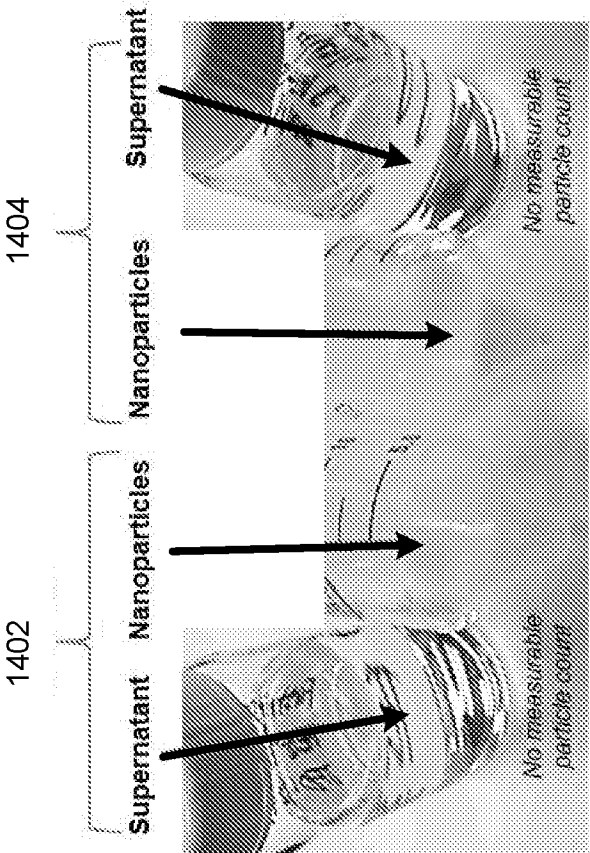


FIG. 14A

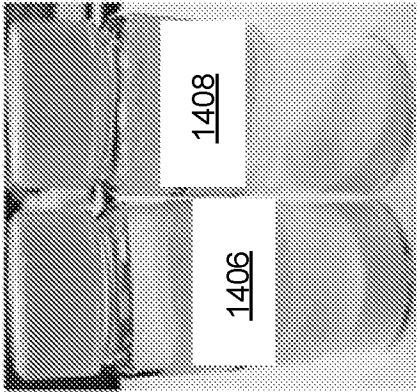


FIG. 14B

FIG. 15A

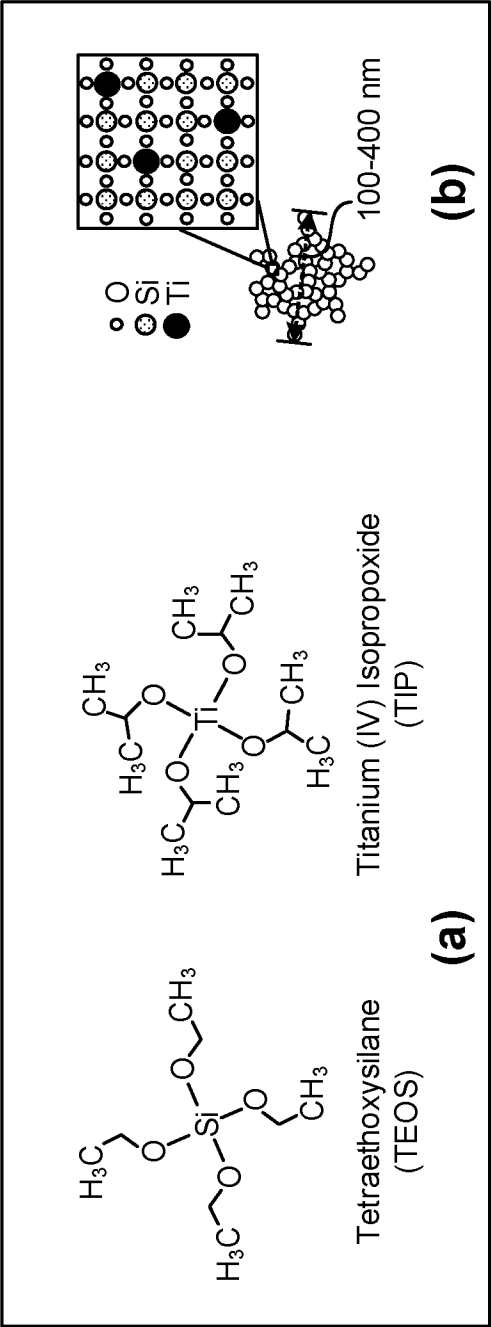


FIG. 15B

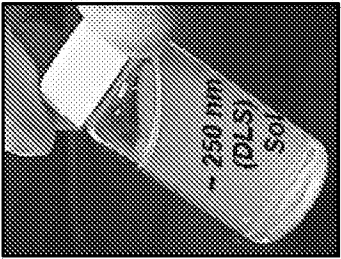
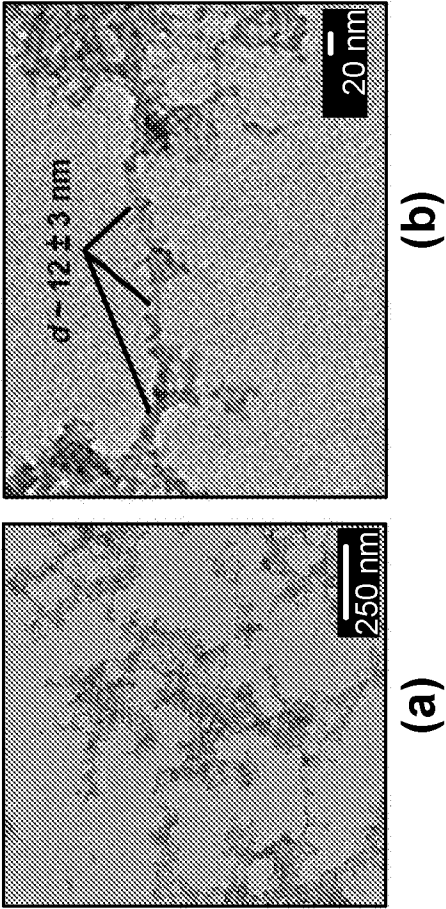
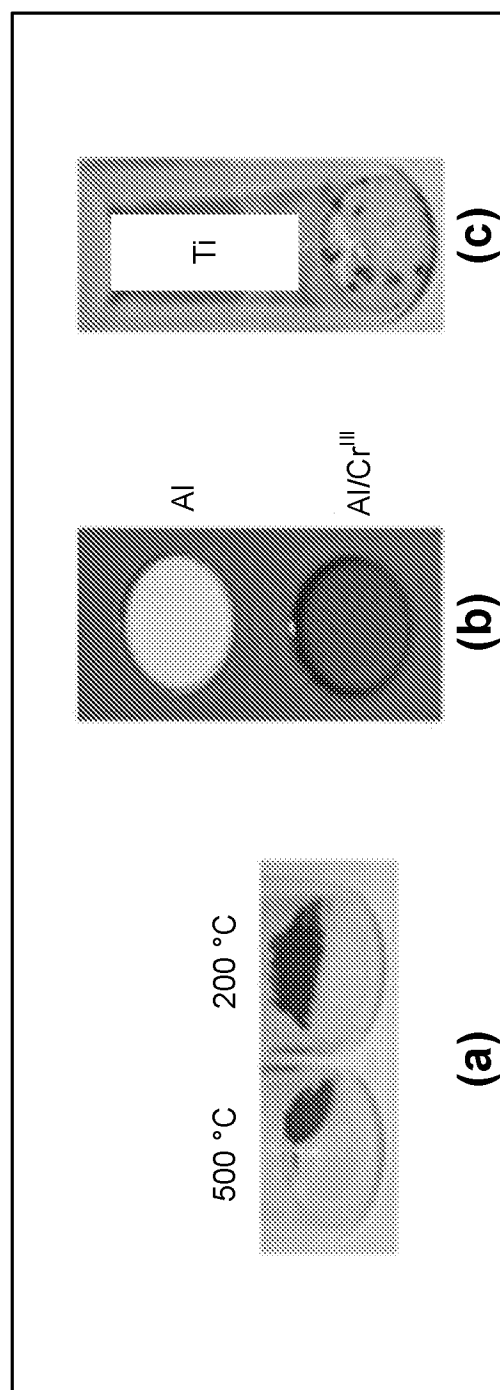
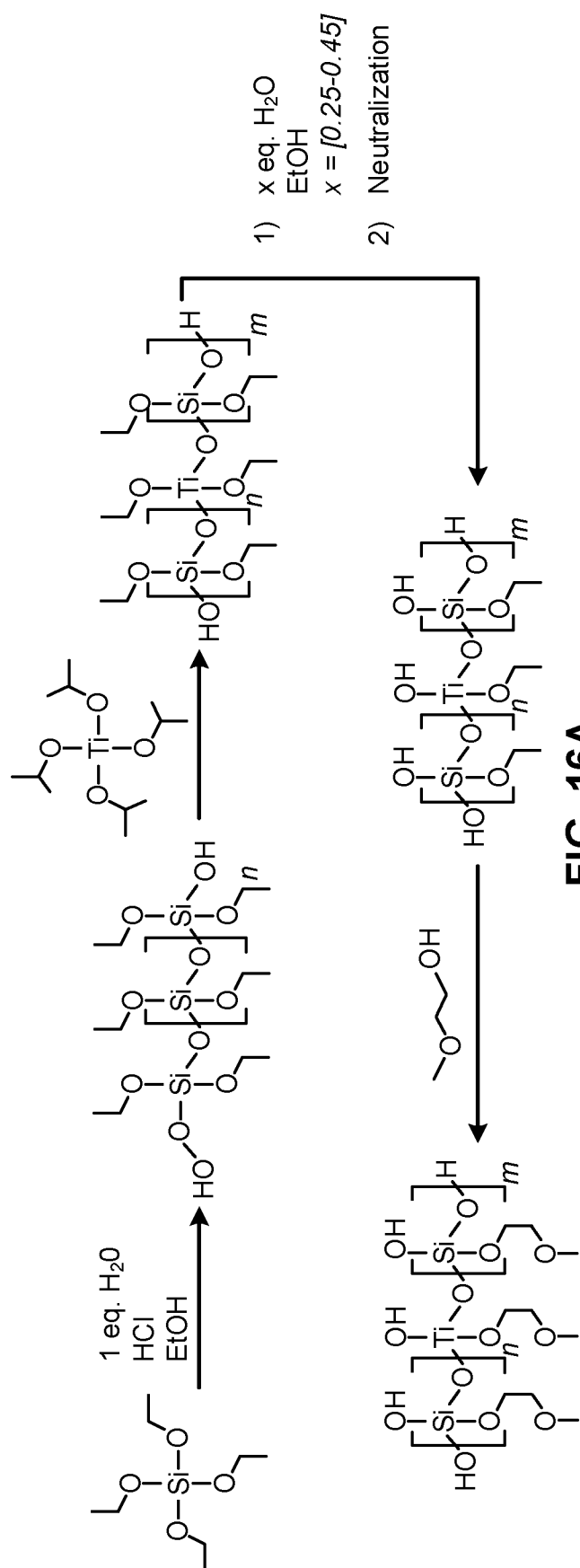


FIG. 15C





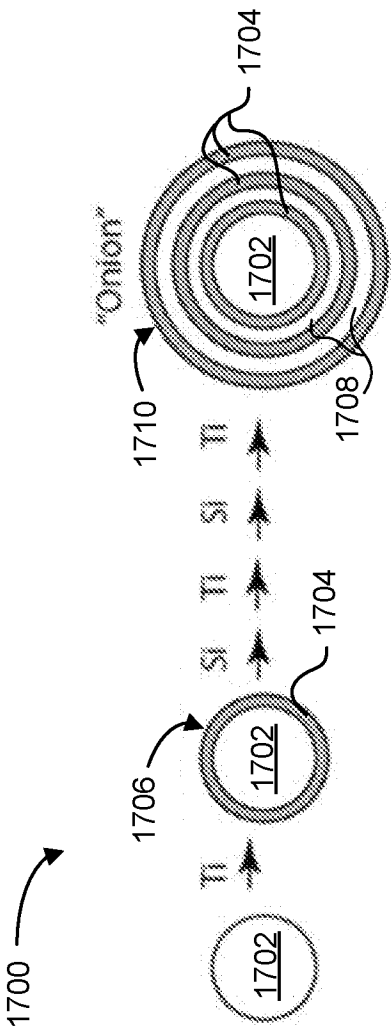


FIG. 17A

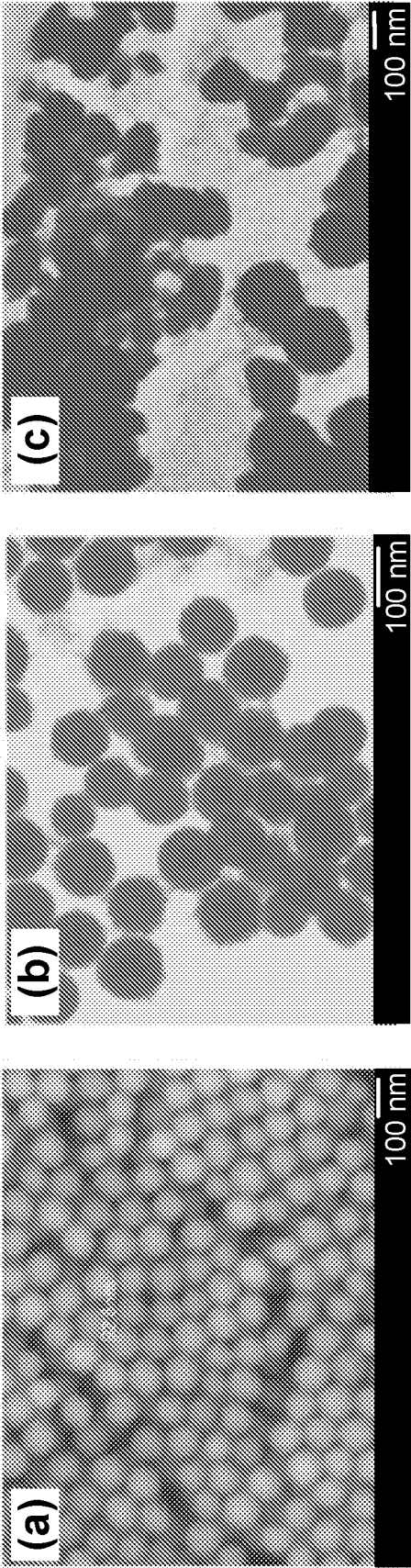


FIG. 17B

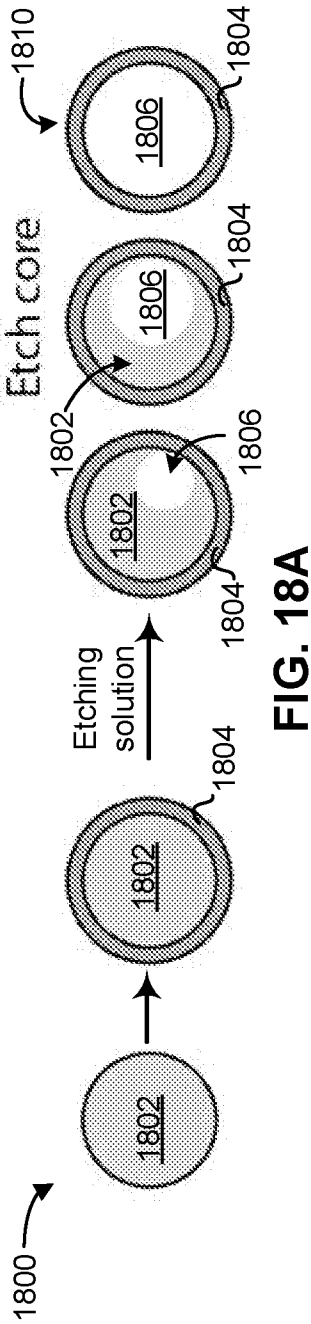


FIG. 18A

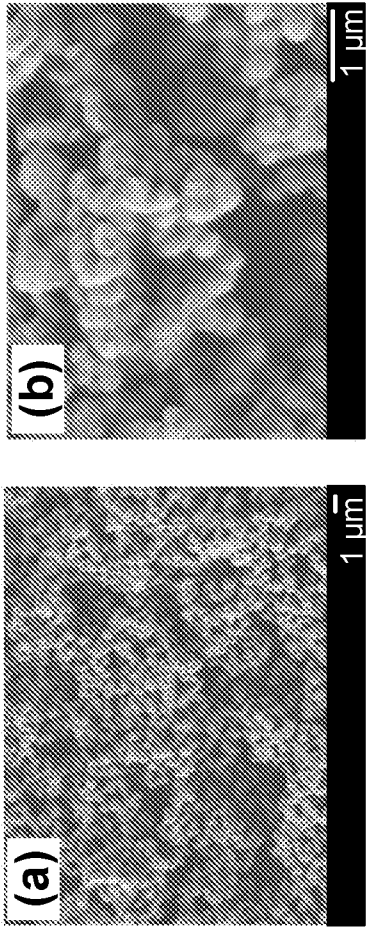


FIG. 18B

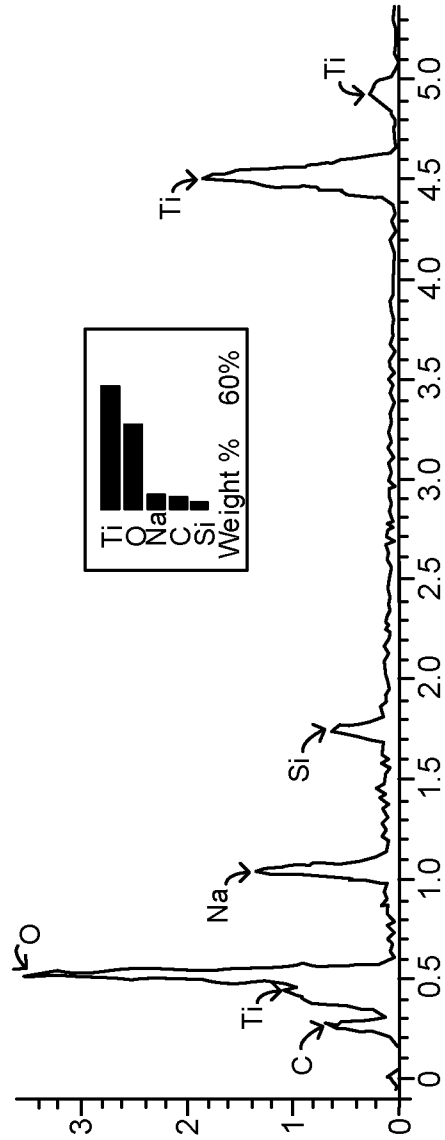


FIG. 18C

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/64882

## A. CLASSIFICATION OF SUBJECT MATTER

IPC - B33Y 70/00; C03C 1/10; C03C 12/00; C08K 3/36; C08K 7/20; C09D 11/02 (2020.01)

CPC - B33Y 70/00; C03C 1/10; C03C 12/00; C08K 3/36; C08K 7/20; C09D 11/02

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

See Search History document

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<br>---<br>Y<br>---<br>A | WO 2017/214179 A1 (Lawrence Livermore National Security, LLC) 14 December 2017 (14.12.2017); entire document, but especially: para [0010], para [0043], para [0045], para [0047], para [0048], para [0049], para [0052], para [0084], para [00151] | 1-6, 9, 11-17, 19-25, 27-28<br>-----<br>29<br>-----<br>7-8, 26 |
| X<br>---<br>Y<br>---<br>A | US 2016/0368806 A1 (Yamaguchi et al.) 22 December 2016 (22.12.2016); entire document, but especially: para [0008], para [0018], para [0065], para [0091], para [0156]                                                                              | 1-2, 6, 10-15, 18<br>-----<br>29<br>-----<br>7-8, 26           |
| X<br>---<br>A             | Nguyen et al. "3D-Printed Transparent Glass" Advanced Materials, Vol 29 Issue 26 (28 April 2017); pages 1-5; abstract, page 2 col 1 para 1 to col 2 para 1                                                                                         | 1-3<br>-----<br>7-8, 26                                        |
| X, E                      | US 2020/0024465 A1 (Lawrence Livermore National Security, LLC) 23 January 2020 (23.01.2020); entire document                                                                                                                                       | 1-29                                                           |



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

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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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

03 February 2020

Date of mailing of the international search report

02 MAR 2020

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/64882

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

| Category*     | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                   | Relevant to claim No. |
|---------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X, E          | Sasan et al. "Additive Manufacturing of Optical Quality Germania-Silica Glasses" ACS Applied Materials & Interfaces (14 January 2020); pages 1-6; entire document                    | 1-6, 11-13, 16        |
| X<br>---<br>A | Cooperstein et al. "Additive Manufacturing of Transparent Silica Glass from Solutions" ACS Applied Materials & Interfaces, Vol 10 Issue 22 (09 May 2018); pages 1-7; entire document | 1-2<br>-----<br>3-29  |
| A             | US 2018/0127297 A1 (Goodrich Corporation) 10 May 2018 (10.05.2018); entire document                                                                                                  | 1-29                  |
| A             | US 2018/0118610 A1 (Asahi Glass Company, Limited) 03 May 2018 (03.05.2018); entire document                                                                                          | 1-29                  |
| A, P          | WO 2019/172937 A1 (Hewlett-Packard Development Company, LLC) 12 September 2019 (12.09.2019)                                                                                          | 8, 19-29              |
| A, P          | CN 109553435 A (Wanda Quartz Co., Ltd.) 02 April 2019 (02.04.2019); entire document                                                                                                  | 8, 19-29              |
| A, E          | US 2019/0070748 A1 (Corning Incorporated) 07 March 2019 (07.03.2019); entire document                                                                                                | 1-29                  |