(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
05 December 2019 (05.12.2019)

WIPO | PCT

(10) International Publication Number
WO 2019/232402 A1

(51) International Patent Classification:
C03C 3/06 (2006.01)

(21) International Application Number:
PCT/US2019/034948

(22) International Filing Date:
31 May 2019 (31.05.2019)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/679,209 01 June 2018 (01.06.2018) US

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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))*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2019/232402 A1

(54) **Title:** CARBON-DOPED SILICON DIOXIDE GLASS AND METHODS OF MANUFACTURING THEREOF

(57) **Abstract:** A silica-based substrate includes a glass phase and a dispersed phase having carbon, such that the silica-based substrate has a thickness of at least 10 μm. Also disclosed is a method of forming a silica-based substrate, the method including contacting a porous silica soot preform with an organic solution having at least one hydrocarbon precursor to form a doped silica soot preform and heating the doped silica soot preform in an inert atmosphere to form the silica-based substrate.

CARBON-DOPED SILICON DIOXIDE GLASS AND METHODS OF MANUFACTURING THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Application Serial No. 62/679,209 filed on June 1, 2018 the contents of which are relied upon and incorporated herein by reference in their entirety as if fully set forth below.

BACKGROUND

1. Field

[0002] This disclosure relates to carbon-doped silicon dioxide glass and methods of manufacturing thereof.

2. Technical Background

[0003] Carbon-doped silicon dioxide (SiO_2) produces novel materials with unique optical and electronic properties. Besides the production of "black" glass with high optical absorption, carbon-doped SiO_2 exhibits improved electrical conductivity, chemical stability, and is a promising method to generate broad-band white light emission. Conventional technologies do not provide effective means for incorporating carbon in bulk SiO_2 materials, but rather, being limited to carbon-doped SiO_2 thin films using techniques such as chemical vapor deposition (CVD), ion implantation, magnetron sputtering, and carbonization/oxidation of porous silicon. Doping bulk-fused SiO_2 glass with carbon, however, remains a challenge due to the difficulty of controlling carbon dopants dispersion in SiO_2 or the reaction between carbon and SiO_2 during the consolidation of SiO_2 at high temperatures (e.g., greater than 1400°C).

[0004] The present application discloses improved carbon-doped silicon dioxide glass and methods of manufacturing thereof for incorporating carbon in bulk SiO_2 materials.

SUMMARY

[0005] In some embodiments, a silica-based substrate comprises a glass phase; a dispersed phase comprising carbon, wherein the silica-based substrate has a thickness of at least 10 μm.

[0006] In one aspect, which is combinable with any of the other aspects or embodiments, the carbon is at least one of: graphite carbon, silicon carbide, and amorphous carbon.

[0007] In one aspect, which is combinable with any of the other aspects or embodiments, the substrate comprises a carbon concentration in a range of 0.0001 wt.% (i.e., 1 ppm) to 1 wt.%.

[0008] In one aspect, which is combinable with any of the other aspects or embodiments, the carbon concentration in a range of 0.0001 wt.% (i.e., 1 ppm) to 0.25 wt.%.

[0009] In one aspect, which is combinable with any of the other aspects or embodiments, the dispersed phase comprises a first region having a first density and a second region having a second density, the first density being different from the second density.

[0010] In one aspect, which is combinable with any of the other aspects or embodiments, the dispersed phase comprises a first region having a first density and a second region having a second density, the first density being the same as the second density.

[0011] In one aspect, which is combinable with any of the other aspects or embodiments, the glass phase comprises a glassy domain having a carbon concentration of less than 0.01 wt.%.

[0012] In one aspect, which is combinable with any of the other aspects or embodiments, the glass phase comprises a glassy domain having a carbon concentration that is lower than the solubility of carbon in SiO_2.

[0013] In one aspect, which is combinable with any of the other aspects or embodiments, the carbon is positioned at a boundary of the glassy domain.

[0014] In one aspect, which is combinable with any of the other aspects or embodiments, the carbon is dispersed as a connected network to outline boundaries of the glassy domain.

[0015] In one aspect, which is combinable with any of the other aspects or embodiments, the carbon is dispersed as a disconnected network to outline boundaries of the glassy domain.

[0016] In one aspect, which is combinable with any of the other aspects or embodiments, the carbon is a nanostructure comprising at least one of nanoparticles, nanorods, nanowires, nanocylinders, or nanoribbons.

[0017] In one aspect, which is combinable with any of the other aspects or embodiments, the nanostructure has at least one dimension in a range of 20 nm to 200 nm.

[0018] In one aspect, which is combinable with any of the other aspects or embodiments, the nanostructure has at least one dimension in a range of 100 nm to 200 nm.

[0019] In one aspect, which is combinable with any of the other aspects or embodiments, the nanostructure has an aspect ratio in a range of 2 to 500.

[0020] In one aspect, which is combinable with any of the other aspects or embodiments, the nanostructure has an aspect ratio in a range of 5 to 100.

[0021] In one aspect, which is combinable with any of the other aspects or embodiments, the carbon is continuously dispersed in the glass phase.

[0022] In one aspect, which is combinable with any of the other aspects or embodiments, the carbon is not continuously dispersed in the glass phase.

[0023] In one aspect, which is combinable with any of the other aspects or embodiments, the carbon is uniformly distributed in the glass phase.

[0024] In one aspect, which is combinable with any of the other aspects or embodiments, the electrical resistivity is in a range of 3000 Ω•cm to 5000 Ω•cm.

[0025] In some embodiments, which is combinable with any of the other aspects or embodiments, an optical fiber, optical attenuator, fiber laser, or sensor comprises a substrate disclosed herein.

[0026] In some embodiments, a method of forming a silica-based substrate comprises contacting a porous silica soot preform with an organic solution comprising at least one hydrocarbon precursor to form a doped silica soot preform; heating the doped silica soot preform in an inert atmosphere to form the silica-based substrate.

[0027] In one aspect, which is combinable with any of the other aspects or embodiments, the porous silica soot preform has a porosity in a range of 25% to 75% and pore sizes in a range of 100 nm to 500 nm.

[0028] In one aspect, which is combinable with any of the other aspects or embodiments, the porosity is in a range of 55% to 65% and pore sizes in a range of 100 nm to 300 nm.

[0029] In one aspect, which is combinable with any of the other aspects or embodiments, the hydrocarbon precursor comprises at least one of (a) alkanes of the form C_nH_{2n+2}; (b) alkenes of the form C_nH_{2n}; (c) carboxylic acids, amines, or alcohols with an aliphatic group of at least 6 carbon atoms; (d) metal carboxylates; (e) graphite powder; amorphous carbon powder; paraffin wax; or phenolic resin; or (f) organic polymers; wherein $n > 6$.

[0030] In one aspect, which is combinable with any of the other aspects or embodiments, the hydrocarbon precursor comprises at least one of: icosane, octadecane, heptadecane, 1-octadecene, stearic acid, oleic acid, myristic acid, octanoic acid, oleylamine, trioctylamine, octadecenol, zinc stearate, zinc oleate, zinc acetate, polystyrene, or polyethylene.

[0031] In one aspect, which is combinable with any of the other aspects or embodiments, the organic solution comprises at least one of: hexane, heptane, toluene, benzene, acetone, methanol, ethanol, butanol, chloroform, dichloromethane, or water.

[0032] In one aspect, which is combinable with any of the other aspects or embodiments, the organic solution comprises at least one of zinc stearate and toluene or stearic acid and hexane.

[0033] In one aspect, which is combinable with any of the other aspects or embodiments, the step of contacting is conducted at or above a boiling point temperature of the organic solution.

[0034] In one aspect, which is combinable with any of the other aspects or embodiments, after the step of contacting, cooling the doped silica soot preform; and drying the doped silica soot preform in air.

[0035] In one aspect, which is combinable with any of the other aspects or embodiments, the organic solution has a concentration of the at least one hydrocarbon precursor in a range of 1 mg/mL to 100 mg/mL.

[0036] In one aspect, which is combinable with any of the other aspects or embodiments, the step of heating is conducted at a temperature in a range of 1000°C to 2000°C and for a time in a range of 0.1 hr to 10 hrs.

[0037] In one aspect, which is combinable with any of the other aspects or embodiments, the step of heating comprises decomposing the at least one hydrocarbon precursor into an amorphous carbon; and densifying the doped silica soot preform to form the silica-based substrate.

[0038] In one aspect, which is combinable with any of the other aspects or embodiments, the temperature is in a range of 1300°C to 1500°C the time is in a range of 1 hr to 3 hrs.

[0039] In one aspect, which is combinable with any of the other aspects or embodiments, the silica-based substrate has at least one length dimension less than a length dimension of the silica soot preform.

BRIEF DESCRIPTION OF THE DRAWINGS

[0040] The disclosure will become more fully understood from the following detailed description, taken in conjunction with the accompanying figures, in which:

[0041] FIG. 1 illustrates an OVD method for forming a soot preform, according to some embodiments.

[0042] FIG. 2 is an optical transmission spectrum through polished, carbon-doped (0.28 wt.%) SiO_2 glass (0.7 mm thickness).

[0043] FIG. 3 is a transmission electron microscopy (TEM) image of a 0.28 wt.% carbon-doped SiO_2 cross-section sample.

[0044] FIGS. 4(a) to 4(c) are energy dispersive spectroscopy (EDS) images of a 0.28 wt.% carbon-doped SiO_2 cross-section sample illustrating: dark areas of rod-like features (FIG. 4(a)), bright areas of rod-like features (FIG. 4(b)), and glassy domain (FIG. 4(c)). The EDS detect area is shown by the red circle.

[0045] FIG. 5 illustrates electrical resistivity characterization of 0.28 wt.% carbon-doped SiO_2 including DC curves (500), AC curves (502), and I-V curves (504).

[0046] FIG. 6 is a schematic of a carbon-doped SiO_2 material according to one embodiment showing a continuous glass phase and a dispersed carbon phase distributed substantially at glass grain boundaries or the glass phase interface.

DETAILED DESCRIPTION

[0047] Reference will now be made in detail to exemplary embodiments which are illustrated in the accompanying drawings. Whenever possible, the same reference numerals will be used throughout the drawings to refer to the same or like parts. The components in the drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the exemplary embodiments. It should be understood that the present application is not limited to the details or methodology set forth in the description or illustrated in the figures. It should also be understood that the terminology is for the purpose of description only and should not be regarded as limiting. Additionally, any examples set forth in this specification are not limiting and merely set forth some of the many possible embodiments of the claimed invention.

[0048] "Preform" refers to the porous solid product formed from vapor deposition of oxide soot and optional drying. "Blank" refers to the solid product formed from sintering or thermally consolidating a preform. "Dope," "dopant," and like terms refer to the addition of a conductive substance such as at least one carbon form from any suitable carbon precursor, to the pores or the interstitial surfaces of the pores of a porous glass preform or like article, for

the purpose of lowering the resistivity and increasing the conductivity of the resulting carbon doped glass. "Bulk" refers to porous silica soot preforms, doped silica soot preforms, silica-based substrates, or other like SiO_2 or carbon-doped SiO_2 materials having a thickness of at least 10 μm.

[0049] The present disclosure provides improved carbon-doped silicon dioxide glass and methods of manufacturing thereof for incorporating carbon in bulk SiO_2 materials. For example, in some embodiments, a carbon-doped SiO_2 glass exhibits an electrical resistivity in a range of 3000 Ω•cm to 5000 Ω•cm, which is about 15 orders of magnitude lower than that of pure fused silica (~10^{18} Ω•cm).

[0050] In a first step of forming the carbon-doped silicon dioxide glass, a porous silica soot preform was placed in contact with an organic solution comprising at least one hydrocarbon precursor to form a doped silica soot preform. The preform used in the solution doping process may be an outside vapor deposition (OVD) silica soot blank or silica soot pellets prepared by pressing SiO_2 nanoparticles.

[0051] For OVD processes, silica and doped silica particles are pyrogenically generated in a flame and deposited as soot. Silica soot preforms are formed layer-by-layer by deposition of the particles on the outside of a cylindrical target rod by traversing the soot-laden flame along the axis of the cylindrical target.

[0052] FIG. 1 illustrates an OVD method for forming a soot preform 100, according to some embodiments. A soot preform 100 is formed by depositing silica-containing soot 102 onto an outside of a rotating and translating mandrel or bait rod 106. Mandrel 106 is preferably tapered. Soot 102 is formed by providing glass precursor 110 in gaseous form to flame 112 of a burner 108 to oxidize it. Fuel 114 (e.g., methane (CH_4)) and combustion supporting gas 116 (e.g., oxygen (O_2)) are provided to burner 108 and ignited to form flame 112. Optional dopant compounds 118 (e.g., germanium (Ge), fluorine (F), etc.) may be included, if desired. Mass flow controllers (V) meter the dopant compound 118, silica glass precursor 110, fuel 114, and combustion supporting gas 116, to the burner 108. The dopant compound 118 and silica glass precursor 110 are oxidized in flame 112 to form a generally cylindrically-shaped soot region 104.

[0053] Porosity of the OVD soot blanks may be controlled by varying CH_4/O_2 flows in the deposition burners. Increasing the CH_4/O_2 flows to the burners will result in a decrease in the porosity of the soot preform, while decreasing the CH_4/O_2 flows will result in a corresponding

increase in the soot porosity. Porosity may also be modified by varying the speed at which the preform traverses through the deposition flame. In some embodiments, the porosity of the OVD soot blanks is in a range of 30% to 90%. In some embodiments, the porosity of the OVD soot blanks is in a range of 50% to 70%.

[0054] In some embodiments, the process for preparing an OVD soot blank is described in United States Patent No. 7,930,904, the entirety of which is herein incorporated by reference.

[0055] For silica soot pellets prepared by pressing SiO_2 nanoparticles, silica soot particles are compressed in a mold by a perpendicular or radial direction of pressure and then heat treated (up to 1200°C) to enhance soot body strength. The compressed silica soot pellets have an average particle size distribution in a range of 0.01 μm to 1.0 μm. In some embodiments, the average particle size distribution is in a range of 0.02 μm to 0.5 μm. In some embodiments, the average particle size distribution is in a range of 0.05 μm to 0.4 μm (e.g., 0.2 μm). Porosity of the compressed silica soot pellets may be controlled by varying silica soot particle size, doping silica nanoparticles, or altering compression pressure. In some embodiments, the porosity of the compressed silica soot pellets is in a range of 30% to 90%. In some embodiments, the porosity of the compressed silica soot pellets is in a range of 50% to 80%. In some embodiments, the porosity of the compressed silica soot pellets is in a range of 55% to 70%. In some embodiments, the compressed silica soot pellet has an average pore size in a range of 0.01 μm and 0.5 μm. In some embodiments, the compressed silica soot pellet has an average pore size in a range of 0.05 μm and 0.25 μm. In some embodiments, the compressed silica soot pellet has an average pore size in a range of 0.07 μm and 0.12 μm.

[0056] In some embodiments, the porous silica soot preform has a porosity in a range of 25% to 75% and pore sizes in a range of 100 nm to 500 nm. In some embodiments, the porous silica soot preform has a porosity in a range of 55% to 65% and pore sizes in a range of 100 nm to 300 nm.

[0057] After preparation of the porous silica soot preform (e.g., by OVD, compression, or similar techniques), the porous silica soot preform was placed in contact with an organic solution comprising at least one hydrocarbon precursor to form a doped silica soot preform. In some embodiments, the contacting step was conducted at or above a boiling point temperature of the organic solution.

[0058] The organic solution comprises at least one suitable hydrocarbon precursor capable of incorporation into porous silica soot preform. In some embodiments, appropriate hydrocarbon precursors include:

(a) alkanes of the form C_nH_{2n+2};

(b) alkenes of the form C_nH_{2n};

(c) carboxylic acids, amines, or alcohols with an aliphatic group of at least 6 carbon atoms;

(d) metal carboxylates;

(e) graphite powder; amorphous carbon powder; paraffin wax; or phenolic resin; or

(f) organic polymers;

wherein $n > 6$.

[0059] For example, the organic solution may include high boiling point alkane and alkenes such as icosane, octadecane, heptadecane, 1-octadecene, or the like. Other examples of the at least one hydrocarbon precursor include stearic acid, oleic acid, myristic acid, octanoic acid, oleylamine, trioctylamine, octadecenol. Metal carboxylates hydrocarbon precursors may include at least one transition metal (e.g., titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), etc.), post-transition metal (e.g., aluminum (Al)), alkali metal, or alkaline earth metal. Organic polymers may include polystyrene, polyethylene, polypropylene, or the like.

[0060] Moreover, the organic solution may also include a solvent comprising at least one of hexane, heptane, toluene, benzene, acetone, methanol, ethanol, butanol, chloroform, dichloromethane, or water. In some embodiments, the organic solution comprises a zinc stearate hydrocarbon precursor and toluene. In some embodiments, the organic solution comprises a stearic acid hydrocarbon precursor and hexane. In some embodiments, the organic solution comprises a salt, ester, or other suitable derivatives of the hydrocarbon precursors disclosed herein (e.g., for stearic acid: an alkyl stearate ester).

[0061] Concentration of the hydrocarbon precursor in the organic solvent may be varied in a range of 1 mg/mL to 100 mg/mL. This concentration range was found to produce a uniform hydrocarbon dopant distribution inside the porous silica soot preform and avoids unwanted migration and pooling of the dopant at a surface of the porous silica soot preform during solvent evaporation. Factors involved in determining whether the hydrocarbon dopant is uniformly distributed in the porous silica soot preform include (1) solubility differences of the

precursor at different temperatures in the organic solvent, and (2) chemical interaction of the precursor with the porous silica soot preform surface.

[0062] With respect to (1), in the instance where the organic solution comprises zinc stearate hydrocarbon precursor and toluene, for example, the solubility of zinc stearate in toluene is greater than 100 mg/mL at 110°C (approximate boiling point of toluene) while less than 1 mg/mL at room temperature (e.g., 25°C). Thus, there is a greater amount of hydrocarbon precursor available for entry into the porous silica soot preform at elevated temperatures. When the soak of the porous silica soot preform in the hot, concentrated organic solution is complete, the preform is quickly cooled down, thereby allowing the precursor to precipitate inside the preform, rather than diffusing to the preform surface during solvent evaporation. With respect to (2), strong interaction (i.e., Lewis acid-base interactions) of the hydrocarbon precursor (for example, the hydroxide (-OH) group when a stearic acid precursor is used or the Zn^{2+} ion when a zinc stearate precursor is utilized) with the contacting surface of the porous silica soot preform prevents diffusion of the hydrocarbon precursor to the silica surface during solvent evaporation.

[0063] In some embodiments, the doped silica soot preform may be formed during preparation of the porous silica soot preform. For example, SiO_2 nanoparticles may be mechanically and uniformly mixed (e.g., mechanic mill, vortexing, ball milling, jetting, and like methods, or combinations thereof) with the hydrocarbon precursor and then pressed to form a doped silica soot preform pellet. In some examples, the mixing is a dry mixing process. In some examples, the mixing is a wet mixing process whereby silica nanoparticles are mixed with hydrocarbon precursor and an organic solvent. In some examples, silica nanoparticles are mixed with hydrocarbon precursor in solution and then precipitated out.

[0064] After the porous silica soot preform was contacted with an organic solution comprising at least one hydrocarbon precursor to form the doped silica soot preform, the doped silica soot preform was cooled and dried in air. As explained above, the cooling and drying steps serve to precipitate out the precursor inside the preform rather than diffusing to the preform surface during solvent evaporation.

[0065] Subsequently, the cooled and dried doped silica soot preform was consolidated by heating in an inert atmosphere to form the silica-based substrate. In some embodiments, the heating was conducted at a temperature in a range of 1000°C to 2000°C. In some embodiments, the heating was conducted at a temperature in a range of 1200°C to 1800°C. In

some embodiments, the heating was conducted at a temperature in a range of 1300°C to 1500°C. In some embodiments, the heating was conducted for a time in a range of 0.1 hr to 10 hrs. In some embodiments, the heating was conducted for a time in a range of 0.5 hr to 5 hrs. In some embodiments, the heating was conducted for a time in a range of 1 hr to 3 hrs. In some embodiments, the heating was conducted at a temperature in a range of 1300°C to 1500°C and for a time in a range of 1 hr to 3 hrs. To minimize loss of carbon precursors during the heating-up process, the heating ramp rate may be at least 5°C/minute or at least 10°C/minute.

[0066] After the doped silica soot preform was cooled and dried in air, the heating step resulted in decomposition of the uniformly distributed hydrocarbon precursor into an amorphous carbon, graphite carbon, silicon carbide, or combination thereof, and densified the doped silica soot preform to form the silica-based substrate such that the silica-based substrate has at least one length dimension less than a length dimension of the porous silica soot preform.

EXAMPLES

1. Process for making carbon-doped SiO_2 glass

[0067] Low-volatility bulky hydrocarbon compounds, such as zinc stearate and stearic acid, are used as hydrocarbon precursors dissolved in toluene and hexane, respectively, to dope OVD silica soot blanks (i.e., porous silica soot preform). The OVD silica soot blanks have a porosity in a range of 55% to 65% with pore sizes in a range of 100 nm to 300 nm. Furthermore, the test OVD silica soot blanks were cylindrically configured, having a diameter of about 1.5 inches and a length of about 1.0 inch.

[0068] In some implementations, the OVD silica soot blanks were soaked in a boiling zinc stearate/toluene solution at about 110°C for a time in a range of 1 hrs to 10 hrs. In some implementations, the OVD silica soot blanks were soaked in a boiling stearic acid/hexane solution at about 68°C for a time in a range of 1 hrs to 10 hrs. The doped OVD silica soot blank is then cooled to room temperature and dried in air for approximately 24-48 hours. The doping level was tuned by varying the concentration of the hydrocarbon precursor in their respective organic solvents. In some implementations, a concentration of 50 mg/mL of zinc stearate was used in 100 mL of solution. Carbon-doped SiO_2 glass was obtained by heating

(i.e., consolidating) the hydrocarbon precursor-doped OVD silica soot blank in helium (He) or argon (Ar) or nitrogen (N_2) at 1500°C for a time in a range of 1.5 hrs to 2.5 hrs.

[0069] In some embodiments, the carbon-doped SiO_2 glass has a carbon concentration in a range of 0.0001 wt.% (1 ppm) to 1 wt.%. In some embodiments, the carbon-doped SiO_2 glass has a carbon concentration in a range of 0.0001 wt.% (1 ppm) to 0.25 wt.%.

2. Characterization of carbon-doped SiO_2 glass

[0070] A carbon-doped SiO_2 glass substrate was prepared according to the process described in Example 1. After consolidating, the carbon-doped SiO_2 glass substrate was a densified black glass measured as having a diameter of about 1.0 inches and a length of about 0.6 inch. LECO combustion elemental analysis determined a carbon dopant concentration as being about 0.28 wt.%.

[0071] FIG. 2 is an optical transmission spectrum through polished, carbon-doped (0.28 wt.%) SiO_2 glass having a thickness of about 0.7 mm. The absorption of carbon dopants causes strong optical attenuation (of less than 2% transmission) in a wide wavelength range of 250 nm to 2500 nm. In other words, light having a wavelength in a range of 250 nm to 2500 nm has a transmission of less than 2% through black glass having a 0.28 wt.% carbon dopant concentration. Such black glass maintains its color after heat treatment in air at 900°C for about 4 hours. The heat treatment at 900°C was used to determine the thermal stability of the carbon-doped SiO_2 glass.

[0072] FIG. 3 is a transmission electron microscopy (TEM) image of a 0.28 wt.% carbon-doped SiO_2 cross-section sample and suggests uniform carbon distributions of the carbon dopant shaped as rod-like nanostructures outlining glassy domain boundaries. In some implementations, the rod-like nanostructures have a length in a range of 20 nm to 200 nm. The rod-like nanostructures of FIG. 3 have a length in a range of 100 nm to 200 nm and a width of a few nm wide. In some implementations, the rod-like nanostructures have an aspect ratio in a range of 2 to 500. In some implementations, the rod-like nanostructures have an aspect ratio in a range of 5 to 100. In some implementations the nanostructures may be at least one of nanoparticles, nanorods, nanowires, nanocylinders, or nanoribbons.

[0073] Microstructural analysis by electron energy loss spectroscopy reveals that brighter regions of the rod-like nanostructures of FIG. 3 may contain silicon carbide, while darker

regions of the rod-like nanostructures in FIG. 3 may contain amorphous carbon and graphite carbon.

[0074] FIG. 6 illustrates a schematic of a carbon-doped SiO_2 material showing a continuous glass phase and a dispersed carbon phase distributed substantially at glass grain boundaries 610 (i.e., glass phase interface). Taking FIGS. 3 and 8 together, it is shown that the dispersed carbon phase 620 may form connected network to outline boundaries 610 of the glassy domain 600. In other words, the glass phase comprises a glassy domain 600 having a carbon concentration of less than 0.01 wt.% and a boundary 610 of the glassy domain 600 which does have carbon 620. In some embodiments, the dispersed carbon phase may form a disconnected network to outline boundaries of the glassy domain. The carbon may be continuously dispersed in the glass phase, or the carbon may not be continuously dispersed in the glass phase, or the carbon may be a combination of continuously and not continuously dispersed in the glass phase.

[0075] Moreover, FIG. 3 illustrates dark 300 and bright 302 features indicating that the dispersed carbon phase may comprise varying densities (brighter features indicate a higher density area). The higher density bright 302 features comprise silicon carbide, while the lower density dark 300 features comprise amorphous carbon and graphite carbon. Thus, in some implementations, the dispersed carbon phase comprises a first region having a first density and a second region having a second density, the first density being different from the second density. In some implementations, the dispersed carbon phase comprises a first region having a first density and a second region having a second density, the first density being the same as the second density.

[0076] FIGS. 4(a) to 4(c) are energy dispersive spectroscopy (EDS) images of a 0.28 wt.% carbon-doped SiO_2 cross-section sample illustrating: dark areas of rod-like features (FIG. 4(a)), bright areas of rod-like features (FIG. 4(b)), and glassy domain (FIG. 4(c)). The EDS detect area is shown by the circle. The Cu signal is from the TEM grids, and Ga signal is from TEM sample preparation with FEI Quanta 3D FEG 600 Focused Ion Beam. EDS analysis suggests the presence of carbon at both the dark area (i.e., 300 from FIG. 3) and bright area (i.e., 302 from FIG. 3) in these rod-like features, however, no carbon is detected from in the glassy domain (FIG. 4(c)). This indicates that carbon dopants are mostly distributed at boundaries of the glassy domain.

[0077] FIG. 5 illustrates electrical resistivity characterization of 0.28 wt.% carbon-doped SiO_2 including DC curves (500), AC curves (502), and I-V curves (504). Measurements are made in cryostat in vacuum. AC, DC, and I-V methods are used to evaluate consistency of the carbon-doped SiO_2 electrical behavior. The measured electrical resistivity of 3000 Ω•cm to 5000 Ω•cm (i.e., equaling a conductivity in a range of about33 mS/m to 20 mS/m) is about 15 orders of magnitude lower than the resistivity of pure fused silica (about 10^{18} Ω•cm). This indicates that carbon dopants form connected networks inside SiO_2 glass to enable electrical conduction (i.e., such a low electrical resistivity, comparatively), which is consistent with the carbon distribution studies of FIGS. 3 to 4(c).

[0078] Thus, as provided herein, carbon-doped silicon dioxide glass and methods of manufacturing thereof is described having a lowered electrical resistivity and increased conductivity. Conventional techniques for carbon-doping SiO_2 are often limited to thin film materials. The present disclosure describes low-cost, solution-based methods for producing carbon-doped bulk SiO_2 glass as a promising means for developing silica-based specialty glass and fibers, optical fibers, optical attenuators, fiber lasers, or sensors. Carbon dopant distribution is uniform within the SiO_2 bulk layer which leads to improved electrical and optical properties.

[0079] As utilized herein, the terms "approximately," "about," "substantially", and similar terms are intended to have a broad meaning in harmony with the common and accepted usage by those of ordinary skill in the art to which the subject matter of this disclosure pertains. It should be understood by those of skill in the art who review this disclosure that these terms are intended to allow a description of certain features described and claimed without restricting the scope of these features to the precise numerical ranges provided. Accordingly, these terms should be interpreted as indicating that insubstantial or inconsequential modifications or alterations of the subject matter described and claimed are considered to be within the scope of the invention as recited in the appended claims.

[0080] As utilized herein, "optional," "optionally," or the like are intended to mean that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event or circumstance occurs and instances where it does not occur. The indefinite article "a" or "an" and its corresponding definite article "the" as used herein means at least one, or one or more, unless specified otherwise.

[0081] References herein to the positions of elements (e.g., "top," "bottom," "above," "below," etc.) are merely used to describe the orientation of various elements in the FIGURES. It should be noted that the orientation of various elements may differ according to other exemplary embodiments, and that such variations are intended to be encompassed by the present disclosure.

[0082] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for the sake of clarity.

[0083] It will be apparent to those skilled in the art that various modifications and variations can be made without departing from the spirit or scope of the claimed subject matter. Accordingly, the claimed subject matter is not to be restricted except in light of the attached claims and their equivalents.

What is claimed is:

1. A silica-based substrate comprising:
a glass phase;
a dispersed phase comprising carbon,
wherein the silica-based substrate has a thickness of at least 10 μm.

2. The substrate of claim 1, wherein the carbon is at least one of: graphite carbon, silicon carbide, and amorphous carbon.

3. The substrate of claim 1 or claim 2, wherein the substrate comprises a carbon concentration in a range of 0.0001 wt.% to 1 wt.%.

4. The substrate of any one of claims 1-3, wherein the carbon concentration in a range of 0.0001 wt.% to 0.25 wt.%.

5. The substrate of any one of claims 1-4, wherein the dispersed phase comprises a first region having a first density and a second region having a second density, the first density being different from the second density.

6. The substrate of any one of claims 1-4, wherein the dispersed phase comprises a first region having a first density and a second region having a second density, the first density being the same as the second density.

7. The substrate of any one of claims 1-6, wherein the glass phase comprises a glassy domain having a carbon concentration of less than 0.01 wt.%.

8. The substrate of any one of claims 1-7, wherein the carbon is positioned at a boundary of the glassy domain.

9. The substrate of any one of claims 1-7, wherein the carbon is dispersed as a connected network to outline boundaries of the glassy domain.

10. The substrate of any one of claims 1-7, wherein the carbon is dispersed as a disconnected network to outline boundaries of the glassy domain.

11. The substrate of any one of claims 1-10, wherein the carbon is a nanostructure comprising at least one of nanoparticles, nanorods, nanowires, nanocylinders, or nanoribbons.

12. The substrate of any one of claims 1-11, wherein the nanostructure has at least one dimension in a range of 20 nm to 200 nm.

13. The substrate of claim 12, wherein the nanostructure has at least one dimension in a range of 100 nm to 200 nm.

14. The substrate of any one of claims 1-11, wherein the nanostructure has an aspect ratio in a range of 2 to 500.

15. The substrate of claim 14, wherein the nanostructure has an aspect ratio in a range of 5 to 100.

16. The substrate of any one of claims 1-15, wherein the carbon is continuously dispersed in the glass phase.

17. The substrate of any one of claims 1-15, wherein the carbon is not continuously dispersed in the glass phase.

18. The substrate of any one of claims 1-17, wherein the carbon is uniformly distributed in the glass phase.

19. The substrate of any one of claims 1-18, wherein the electrical resistivity is in a range of 3000 Ω•cm to 5000 Ω•cm.

20. An optical fiber, optical attenuator, fiber laser, or sensor comprising the substrate of any one of claims 1-19.

21. A method of forming a silica-based substrate, the method comprising:

contacting a porous silica soot preform with an organic solution comprising at least one hydrocarbon precursor to form a doped silica soot preform;

heating the doped silica soot preform in an inert atmosphere to form the silica-based substrate.

22. The method of claim 21, wherein the porous silica soot preform has a porosity in a range of 25% to 75% and pore sizes in a range of 100 nm to 500 nm.

23. The method of claim 21 or claim 22, wherein the porosity is in a range of 55% to 65% and pore sizes in a range of 100 nm to 300 nm.

24. The method of any one of claims 21-23, wherein the hydrocarbon precursor comprises at least one of:

(a) alkanes of the form C_nH_{2n+2};
(b) alkenes of the form C_nH_{2n};
(c) carboxylic acids, amines, or alcohols with an aliphatic group of at least 6 carbon atoms;
(d) metal carboxylates;
(e) graphite powder; amorphous carbon powder; paraffin wax; or phenolic resin; or
(f) organic polymers;

wherein $n > 6$.

25. The method of any one of claims 21-24, wherein the hydrocarbon precursor comprises at least one of: icosane, octadecane, heptadecane, 1-octadecene, stearic acid, oleic acid, myristic acid, octanoic acid, oleylamine, trioctylamine, octadecenol, zinc stearate, zinc oleate, zinc acetate, polystyrene, or polyethylene.

26. The method of any one of claims 21-25, wherein the organic solution comprises at least one of: hexane, heptane, toluene, benzene, acetone, methanol, ethanol, butanol, chloroform, dichloromethane, or water.

27. The method of any one of claims 21-26, wherein the organic solution comprises at least one of zinc stearate and toluene or stearic acid and hexane.

28. The method of any one of claims 21-27, wherein the step of contacting is conducted at or above a boiling point temperature of the organic solution.

29. The method of any one of claims 21-28, wherein after the step of contacting,
cooling the doped silica soot preform; and
drying the doped silica soot preform in air.

30. The method of any one of claims 21-29, wherein the organic solution has a concentration of the at least one hydrocarbon precursor in a range of 1 mg/mL to 100 mg/mL.

31. The method of any one of claims 21-30, wherein the step of heating is conducted at a temperature in a range of 1000°C to 2000°C and for a time in a range of 0.1 hr to 10 hrs.

32. The method of any one of claims 21-31, wherein the step of heating comprises:
decomposing the at least one hydrocarbon precursor into an amorphous carbon; and
densifying the doped silica soot preform to form the silica-based substrate.

33. The method of claim 31, wherein the temperature is in a range of 1300°C to 1500°C the time is in a range of 1 hr to 3 hrs.

34. The method of any one of claims 21-33, wherein the silica-based substrate has at least one length dimension less than a length dimension of the silica soot preform.

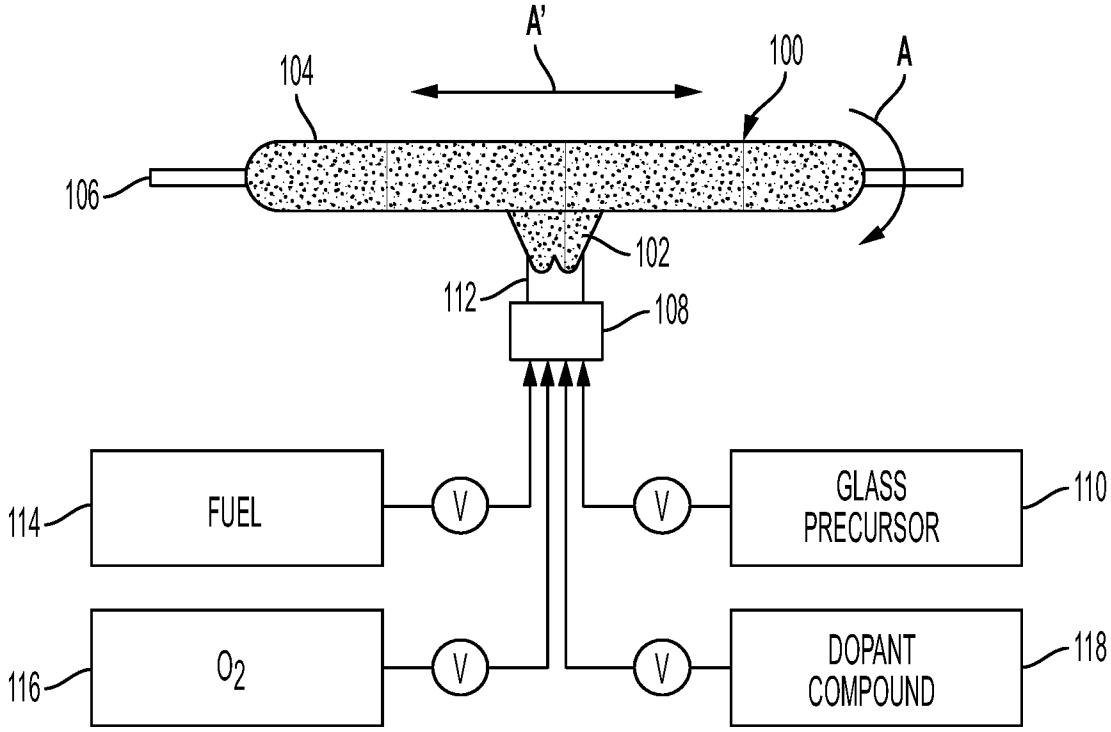

A'
A
104
100
106
102
112
108
114
FUEL
V
V
GLASS PRECURSOR
110
116
O_2
V
V
DOPANT COMPOUND
118

FIG. 1

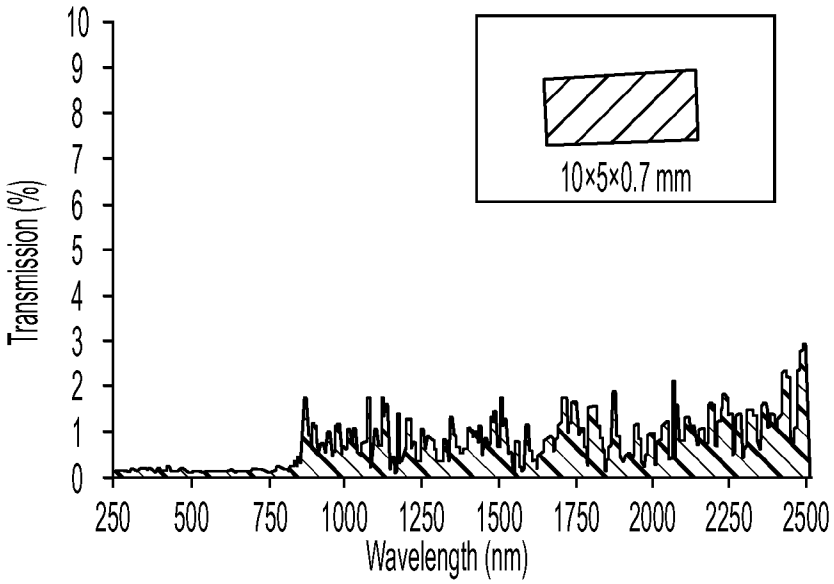

10×5×0.7 mm
Transmission (%)
0
1
2
3
4
5
6
7
8
9
10
250
500
750
1000
1250
1500
1750
2000
2250
2500
Wavelength (nm)

FIG. 2

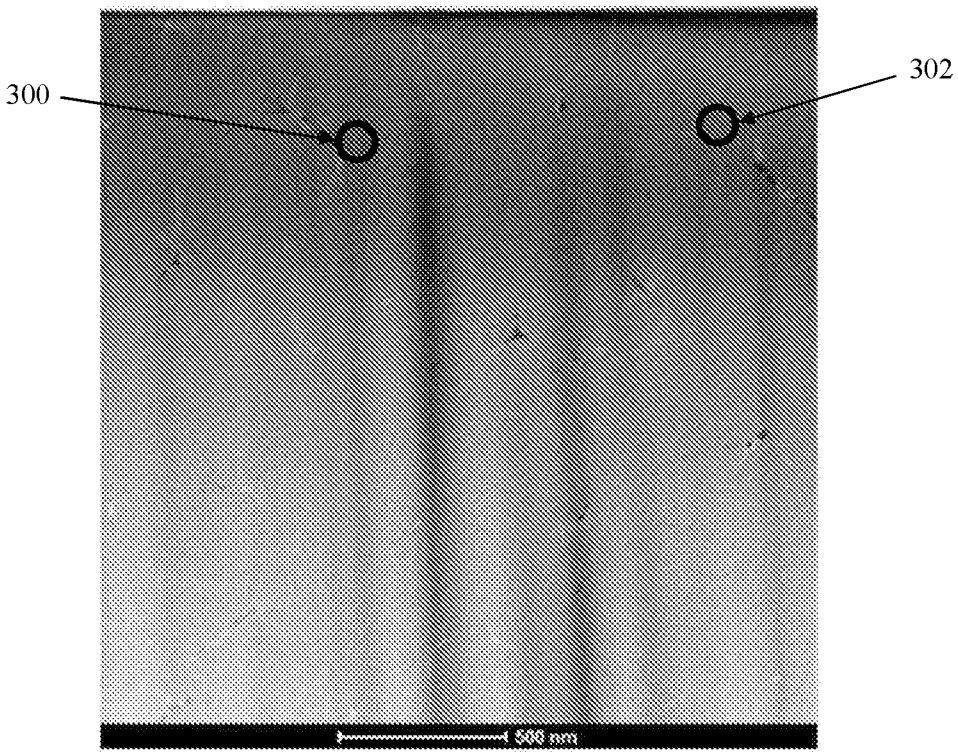


FIG. 3

FIG. 4A

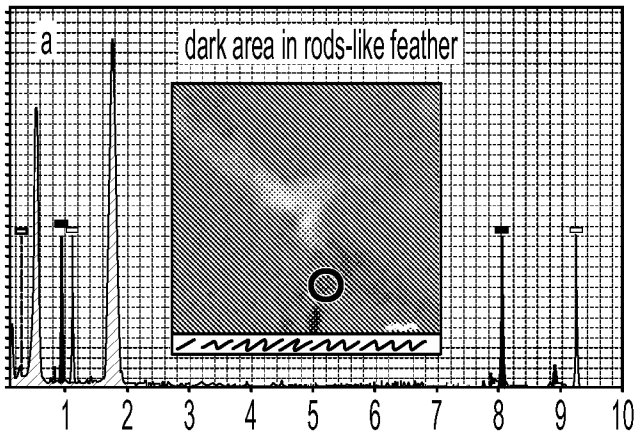
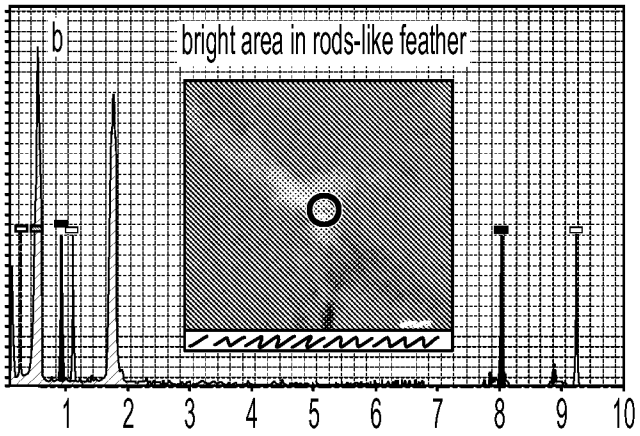


FIG. 4B



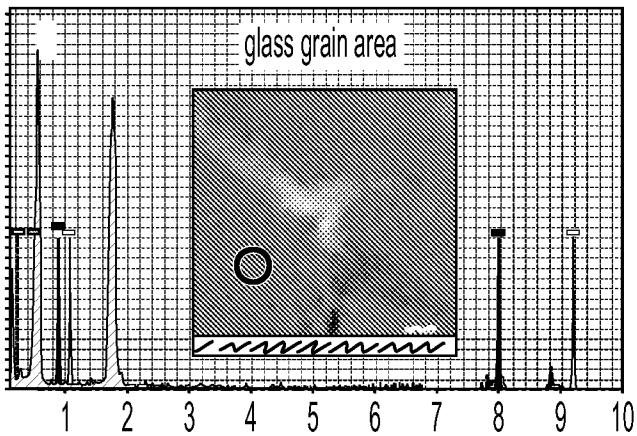


FIG. 4 C

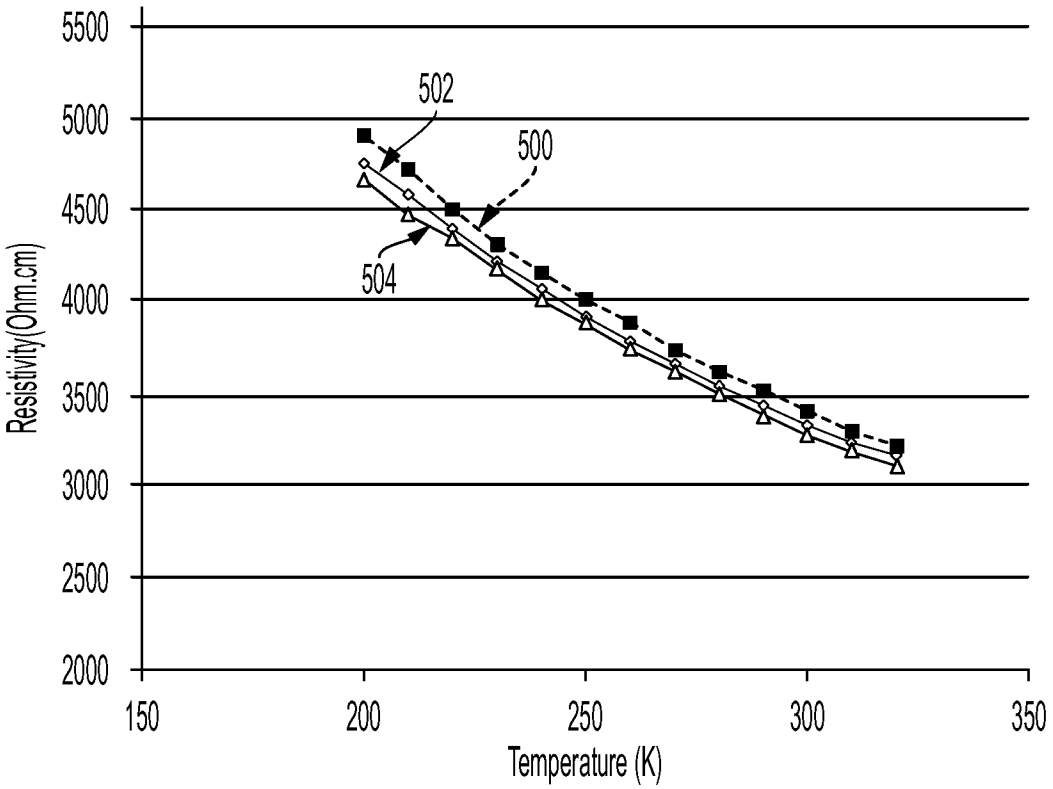

5500
5000
4500
4000
3500
3000
2500
2000
Resistivity(Ohm.cm)
150
200
250
300
350
Temperature (K)
502
500
504

FIG. 5

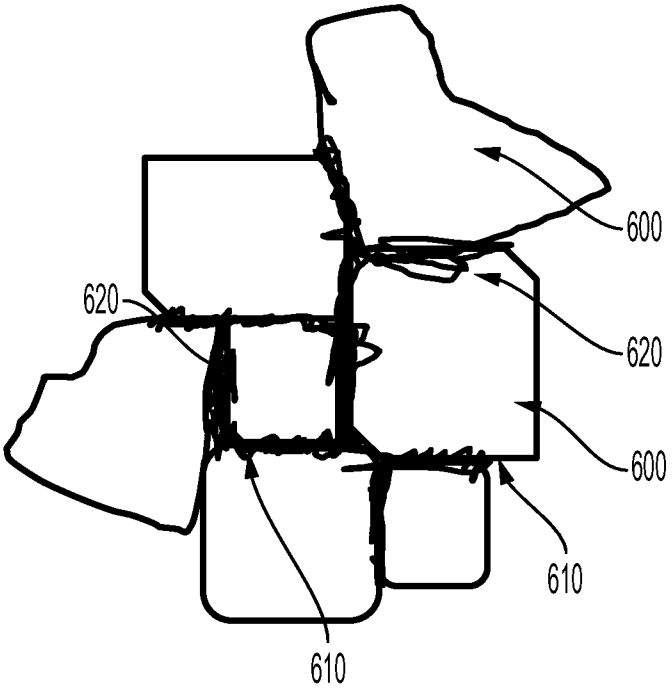


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/034948

A. CLASSIFICATION OF SUBJECT MATTER
INV. C03C3/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 2011 121153 B3 (HERAEUS QUARZGLAS [DE]) 21 March 2013 (2013-03-21) paragraph [0012] - paragraph [0015] paragraph [0002] paragraph [0038] - paragraph [0049] -----	1-4,20
A	NING, J. ET AL: MATERIAL SCIENCES AND ENGENEERING, vol. A357, 19 March 2013 (2013-03-19), pages 392-396, XP002794097, page 393 -----	1-34
A	US 7 930 904 B2 (CORNING INC [US]) 26 April 2011 (2011-04-26) cited in the application claims -----	1-34

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 September 2019	18/10/2019

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Friederich, Pierre

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2019/034948

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 102011121153 B3	21-03-2013	CN 103987670 A	13-08-2014
		DE 102011121153 B3	21-03-2013
		EP 2791070 A1	22-10-2014
		JP 6058693 B2	11-01-2017
		JP 2015505809 A	26-02-2015
		KR 20140095560 A	01-08-2014
		US 2014349830 A1	27-11-2014
		WO 2013087678 A1	20-06-2013
US 7930904 B2	26-04-2011	CN 104238001 A	24-12-2014
		EP 1949153 A1	30-07-2008
		JP 2009515217 A	09-04-2009
		KR 20080066991 A	17-07-2008
		US 2007104437 A1	10-05-2007
		US 2009032983 A1	05-02-2009
		WO 2007055881 A1	18-05-2007