



- (51) **International Patent Classification:**
C03C 17/00 (2006.01) *C03C 17/34* (2006.01)
C03C 17/245 (2006.01)
- (21) **International Application Number:**
PCT/GB2016/050401
- (22) **International Filing Date:**
17 February 2016 (17.02.2016)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
62/118,223 19 February 2015 (19.02.2015) 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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, 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))

(54) **Title:** A CHEMICAL VAPOUR DEPOSITION PROCESS FOR DEPOSITING AN IRON DOPED TIN OXIDE COATING AND A COATED GLASS ARTICLE FORMED THEREBY

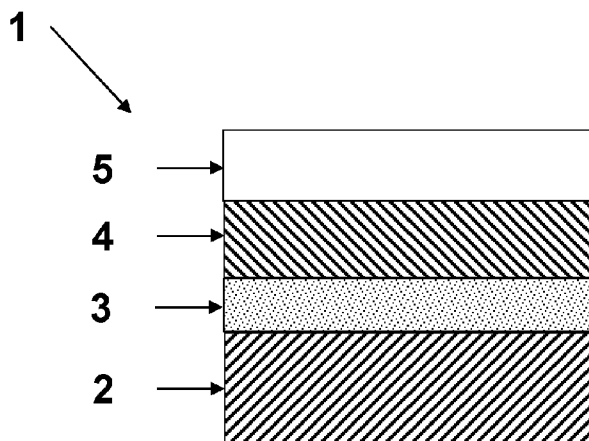


Fig. 1

(57) **Abstract:** A CVD process for depositing an iron doped tin oxide coating on a glass substrate and a glass article having an iron doped tin oxide coating are provided. According to the process, a gaseous mixture is formed comprising a tin-containing compound, water, oxygen, and an organic iron-containing compound. The gaseous mixture is directed toward and along the glass substrate, the mixture reacting over the glass substrate to deposit the iron doped tin oxide coating thereon. The glass article is suitable for a video display having predetermined resistivity and high visible light transmission.

A CHEMICAL VAPOUR DEPOSITION PROCESS FOR
DEPOSITING AN IRON DOPED TIN OXIDE COATING AND A COATED GLASS ARTICLE
FORMED THEREBY

5 BACKGROUND OF THE INVENTION

[0001] This invention relates in general to a chemical vapour deposition (CVD) process and a coated glass article formed thereby. In particular, this invention relates to a CVD process for depositing an iron doped tin oxide coating and a glass article having an iron doped tin oxide coating formed thereon.

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[0002] Tin oxide coatings are known to be deposited over glass substrates. It is also known to decrease the resistivity of a tin oxide coating by doping the coating with a material such as, for example, fluorine.

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[0003] WO200172652A1 (LOF/Varanasi) concerns a tin oxide coating having at least one dopant. Fluorine as a dopant is believed to substitute for oxygen thereby decreasing the sheet resistance. Niobium as a dopant is believed to substitute for tin, also decreasing sheet resistance. A combination of fluorine and niobium dopants also decreases sheet resistance.

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[0004] EP1624494A1 (AGC/Fukawa) discloses a transparent conductive substrate for a solar cell comprising a layer of tin oxide doped with a substance for exhibiting conductivity.

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[0005] However, for certain applications such as, for example, photovoltaic applications it may be desirable to increase the resistivity of the tin oxide coating. For these applications, it may also be desirable if the resistivity of the tin oxide coating is increased without decreasing the visible light transmission of the coating.

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[0006] Tin oxide coatings are also known in a flat screen video display. Such a video display is designed to be less obtrusive when the display is not in operation. One way to accomplish this objective is to conceal the video display by giving it the appearance of an object that might commonly appear in a room, such as a mirror. A known product for such an application is sold by Pilkington North America, Inc. as Pilkington MirrowiewTM. This product includes a clear glass substrate provided with a coating stack formed of a layer of silicon on the glass, a layer of silica on the layer of silicon, and a layer of tin oxide on the layer of silica,

providing a visible light transmittance (T_{vis}) of about 20% and a film side reflectance (R_f) of 70-75%.

[0007] WO 2015121632 discloses a coated glass article that has a mirror-like appearance
5 for concealing a video display when the display is not in use. The coated glass article permits a video image from the display to be bright and sharp when the display is in use and utilized in areas with high levels of natural light. The coating comprises an optional base layer of an oxide of silicon deposited over a major surface of the glass substrate, a first coating layer of an oxide of titanium, niobium or chromium deposited over the optional base
10 layer, a second coating layer of an oxide of silicon deposited over the first coating layer, and a third coating layer of an oxide of tin deposited over the second coating layer. The coated glass article exhibits a T_{vis} of 40% - 55% and an R_f of 40% - 60%.

[0008] In certain applications it may be desirable to achieve a predetermined resistivity for
15 such a coated glass article, for example to discharge an amount of static electricity which may occur during cleaning. It may be desirable that the coated glass article should have approximately similar T_{vis} to Pilkington MirroviewTM.

[0009] Therefore, it is desired to devise an improved process for depositing a doped tin
20 oxide coating with a high resistivity and high visible light transmission.

BRIEF SUMMARY OF THE INVENTION

[0010] According to a first aspect of the present invention, a process of manufacture of a
25 glass article is provided comprising the steps set out in claim 1.

The chemical vapour deposition process for forming a coated glass article comprises steps:
providing a glass substrate;
forming a gaseous mixture comprising a tin-containing compound, water, oxygen,
30 and an organic iron-containing compound; and
directing the gaseous mixture toward and along the glass substrate, and reacting the mixture over the glass substrate to deposit an iron doped tin oxide coating thereon.

[0011] Preferably, when the iron doped tin oxide coating is deposited, the temperature of the glass substrate is 752°F (400°C) or more. This allows coating during substrate formation.

5 [0012] Preferably, the glass substrate is moving at the time the iron doped tin oxide coating is deposited. This allows coating on a ribbon of glass in the float process.

[0013] Preferably, the mixture is reacted over the glass substrate at essentially atmospheric pressure. This eliminates a need for costly vacuum apparatus.

10 [0014] Preferably, the organic iron-containing compound is ferrocene or a derivative thereof.

[0015] Preferably, the iron doped tin oxide coating is the outermost layer of the coated glass article.

15 [0016] Preferably, the glass substrate is a soda-lime-silica glass. This reduces material cost.

[0017] Preferably, the iron doped tin oxide coating is formed over a previously deposited sodium diffusion barrier layer. The layer prevents sodium reaching the tin oxide coating.

20 [0018] Preferably, the sodium diffusion barrier layer is comprised of silica.

[0019] Preferably, the process further comprises feeding the gaseous mixture through a coating apparatus and discharging the gaseous mixture from the coating apparatus, wherein the coating apparatus is provided at a predetermined distance above and extends
25 transversely across the glass substrate.

[0020] Preferably, the tin-containing compound is a halogenated tin-containing compound.

[0021] Preferably the tin-containing compound is dimethyltin dichloride.

30 [0022] Preferably, the oxygen is in the form of molecular oxygen.

[0023] Preferably, the iron doped tin oxide coating exhibits a resistivity of at least 4×10^{-2} ohm-cm.

[0024] Preferably, the iron doped tin oxide coating exhibits a resistivity of at least 8×10^{-2} ohm-cm.

5 [0025] Preferably, the glass substrate comprises a glass ribbon in a float glass manufacturing process, the gaseous mixture is delivered to a coating apparatus provided at a predetermined distance above and extending transversely across the glass ribbon, the glass ribbon being surrounded by float bath atmosphere, and the gaseous mixture is discharged from the coating apparatus and the gaseous mixture is directed toward and
10 along the glass ribbon, the mixture reacting over the glass ribbon to form the iron doped tin oxide coating thereon.

[0026] According to a second aspect of the present invention, a coated glass article is provided comprising the features set out in claim 17.

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[0027] The coated glass article comprises a glass substrate and an iron doped tin oxide coating, wherein the coating exhibits a resistivity of at least 4×10^{-2} ohm-cm.

[0028] The inventors have found that iron when added as a dopant in a tin oxide coating
20 does not function as a conventional dopant to increase conductivity. Surprisingly, iron added to an otherwise undoped tin oxide coating simultaneously leads to higher sheet resistance and a decrease deposition rate, leading to a thinner coating and an increase in visible light transmission.

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BRIEF DESCRIPTION OF THE DRAWINGS

[0029] The above, as well as other advantages of the process will become readily apparent to those skilled in the art from the following detailed description when considered in the light
30 of the accompanying drawings in which Fig. 1 depicts a schematic view, in cross-section, of a coated glass article in accordance with certain embodiments of the invention and Fig. 2 depicts a schematic view, in vertical section, of an installation for practising the float glass process in accordance with certain embodiments of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0030] It is to be understood that the invention may assume various alternative orientations
5 and step sequences, except where expressly specified to the contrary. It is also to be
understood that the specific articles, apparatuses and processes described in the following
specification are simply exemplary embodiments of the inventive concepts. Hence, specific
dimensions, directions, or other physical characteristics relating to the embodiments
disclosed are not to be considered as limiting, unless expressly stated otherwise. Also,
10 although they may not be, like elements in the various embodiments described within this
section of the application may be commonly referred to with like reference numerals.

[0031] In an embodiment, a CVD process for depositing an iron doped tin oxide coating
(hereinafter also referred to as the "CVD process") is provided. The CVD process will be
15 described in connection with forming a coated glass article. In certain embodiments, the
coated glass article will be described for use in the manufacture of solar cells. It would be
understood by one of ordinary skill in the art that the coated glass article could be utilized as
a superstrate or substrate in the manufacture of solar cells. Furthermore, the coated glass
article described herein is not limited to solar cell applications. For example, the coated
20 glass article may be utilized in architectural glazings, electronics, and/or have automotive
and aerospace applications.

[0032] For describing certain embodiments, the iron doped tin oxide coating may be
designated herein by the chemical formula $\text{SnO}_2\text{:Fe}$ or abbreviated herein as TOFe. In an
25 embodiment, the iron doped tin oxide coating contains primarily tin, oxygen and iron.
However, the iron doped tin oxide coating may also contain trace contaminants of, for
example, carbon. Also, an iron doped tin oxide coating which is slightly oxygen deficient
may also be deposited by the CVD process and may be useful.

[0033] The CVD process comprises providing a substrate. The substrate is preferably glass.
The glass substrate has a deposition surface over which the iron doped tin oxide coating is
formed. In an embodiment, the glass substrate is a soda-lime-silica glass. However, the
CVD process is not limited to a soda-lime-silica glass substrate as, in other embodiments,
30 the glass substrate may be a borosilicate glass. Additionally, it may be preferable to utilize a

glass substrate having a low iron content in the CVD process. Thus, in certain embodiments, the CVD process is not limited to a particular substrate composition.

[0034] Further, in certain embodiments, the glass substrate is substantially transparent.

5 However, the invention is not limited to transparent glass substrates as translucent glass substrates may also be utilized in practicing the CVD process. Also, the transparency or absorption characteristics of the substrate may vary between embodiments. Additionally, the CVD process can be practiced utilizing clear or a colored glass substrate and is not limited to a particular glass substrate thickness.

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[0035] In certain embodiments, the glass substrate is heated when the iron doped tin oxide coating is deposited thereover. In an embodiment, the temperature of the glass substrate is 752°F (400°C) or more. Preferably, the temperature of the glass substrate is about 1100°F (593°C) or more. In another embodiment, the temperature of the glass substrate is between
15 about 1100°F (593°C) and 1400°F (760°C) when the iron doped tin oxide coating is deposited thereover.

[0036] The CVD process may be carried out in conjunction with the manufacture of the glass substrate. In an embodiment, the glass substrate may be formed utilizing the well-known
20 float glass manufacturing process. An example of a float glass manufacturing process is illustrated in the FIGURE. In this embodiment, the glass substrate may also be referred to as a glass ribbon. However, it should be appreciated that the CVD process can be utilized apart from the float glass manufacturing process or well after formation and cutting of the glass ribbon.

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[0037] In certain embodiments, the CVD process is a dynamic deposition process. In these embodiments, the glass substrate is moving at the time of forming the iron doped tin oxide coating. Preferably, the glass substrate moves at a predetermined rate of, for example, 3.175 m/min (125 in/min) or more as the iron doped tin oxide coating is being formed
30 thereover. In an embodiment, the glass substrate is moving at a rate of between 3.175 m/min (125 in/min) and 12.7 m/min (600 in/min) as the iron doped tin oxide coating is being formed.

[0038] Preferably, the iron doped tin oxide coating is deposited over the deposition surface of the glass substrate while the surface is at essentially atmospheric pressure. In this embodiment, the CVD process is an atmospheric pressure CVD (APCVD) process. However, the CVD process is not limited to being an APCVD process as, in other
5 embodiments, the iron doped tin oxide coating may be formed under low-pressure conditions.

[0039] The CVD process may comprise providing a source of a tin-containing compound, a source of water, a source of oxygen, and a source of an iron-containing compound.

10 Preferably, these sources are provided at a location outside the float bath chamber. Separate supply lines may extend from the sources of reactant (precursor) compounds. As used herein, the phrases "reactant compound" and "precursor compound" may be used interchangeably to refer to any or all of the tin-containing compound, water, oxygen, and iron-containing compound and/or used to describe the various embodiments thereof
15 disclosed herein.

[0040] The CVD process also comprises forming a gaseous mixture of the precursor compounds. As would be appreciated by those skilled in the art, the precursor compounds suitable for use in the gaseous mixture should be suitable for use in a CVD process. Such
20 compounds may at some point be a liquid or a solid but are volatile such that they can be vapourized for use in the gaseous mixture. In certain embodiments, the gaseous mixture includes precursor compounds suitable for forming the iron doped tin oxide coating at essentially atmospheric pressure. Once in a gaseous state the precursor compounds can be included in a gaseous stream and utilized to form the iron doped tin oxide coating.

25 [0041] For any particular combination of gaseous precursor compounds, the optimum concentrations and flow rates for achieving a particular deposition rate and iron doped tin oxide coating thickness may vary. However, in order to form an iron doped tin oxide coating as is provided by the CVD process described herein, the gaseous mixture may comprise the
30 tin-containing compound, water, oxygen, and iron-containing compound.

[0042] In an embodiment, the tin-containing compound is a halogenated compound. Preferable halogenated compounds include Cl- containing compounds. Preferred Cl- containing compounds for use as the tin-containing compound are dimethyltin dichloride

(DMT), tin tetrachloride (SnCl_4) and monobutyltin trichloride (MBTC). Other tin-containing compounds are also suitable for use in the gaseous mixture.

5 [0043] Additionally, the gaseous mixture may comprise water (H_2O) in the form of water vapour or steam. The concentration of water vapour in the gaseous mixture may vary to achieve a desired growth rate. However, it has been discovered that with the addition of high concentrations of water vapour higher coating deposition rates are achieved.

10 [0044] Oxygen may be provided in the gaseous mixture as a part of a gaseous composition such as air. More preferably, oxygen is provided in a substantially purified form. In either embodiment, the oxygen is in the form of molecular oxygen.

[0045] In an embodiment, the iron-containing compound is an organoiron compound. Preferably, the organoiron compound is ferrocene (Cp_2Fe) or a derivative such as
15 halogenated Cp_2Fe . However, other iron-containing compounds are suitable for use in the gaseous mixture.

[0046] The precursor compounds can be mixed without undergoing ignition and premature reaction. Thus, in certain embodiments, the CVD process comprises mixing the precursor
20 compounds to form the gaseous mixture. Preferably, the CVD process comprises mixing the tin-containing compound, water, oxygen, and iron-containing compound to form the gaseous mixture. However, the gaseous mixture may also comprise one or more inert gases utilized as carrier or diluent gas. Suitable inert gases include nitrogen (N_2), helium (He) and mixtures thereof. Thus, the CVD process may comprise providing a source of the
25 one or more inert gases from which separate supply lines may extend.

[0047] In certain embodiments, the gaseous mixture is fed through a coating apparatus and discharged from the coating apparatus utilizing one or more gas distributor beams prior to forming the iron doped tin oxide coating. Preferably, the gaseous mixture is formed prior to
30 being fed through the coating apparatus. For example, the precursor compounds may be mixed in a feed line connected to an inlet of the coating apparatus. In other embodiments, the gaseous mixture may be formed within the coating apparatus.

[0048] The gaseous mixture is directed toward and along the glass substrate. Utilizing a coating apparatus aids in directing the gaseous mixture toward and along the glass substrate. Preferably, the gaseous mixture is directed toward and along the glass substrate in a laminar flow.

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[0049] Preferably, the coating apparatus extends transversely across the glass substrate and is provided at a predetermined distance thereabove. The coating apparatus is preferably located at, at least, one predetermined location. When the CVD process is utilized in conjunction with the float glass manufacturing process, the coating apparatus is preferably provided within the float bath section thereof. However, the coating apparatus may be provided in the annealing Lehr, and/or in the gap between the float bath and the annealing Lehr.

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[0050] It is desirable that the gaseous mixture be kept at a temperature below the thermal decomposition temperature of the precursor compounds to prevent pre-reaction and formation of the iron doped tin oxide coating before the mixture reaches the deposition surface of the glass substrate. Within the coating apparatus, the gaseous mixture is maintained at a temperature below that at which it reacts to form the iron doped tin oxide coating and is delivered to a location near the deposition surface of the glass substrate, the glass substrate being at a temperature above the reaction temperature. The gaseous mixture reacts at or near the deposition surface to form the iron doped tin oxide coating thereover. The CVD process results in the deposition of a high quality coating on the glass substrate. In particular, the iron doped tin oxide coating formed using the CVD process exhibits excellent coating thickness uniformity. An additional feature of the CVD process is that it allows for the formation of iron doped tin oxide coatings at commercial viable deposition rates under dynamic deposition conditions.

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[0051] In an embodiment, the iron doped tin oxide coating is a pyrolytic coating.

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[0052] Advantageously, the iron doped tin oxide coating exhibits a sheet resistance and a resistivity which is higher than an undoped tin oxide (SnO_2) coating. Additionally, the glass article having the iron doped tin oxide coating formed thereover may exhibit a higher total visible light transmittance than a glass article having only an undoped tin oxide (SnO_2) coating formed thereover. For describing the coated glass article, total visible light

transmittance refers to the percentage of visible light which passes through the glass article as measured from the side of the glass article where the deposition surface of the glass substrate is located.

- 5 [0053] In an embodiment, the iron doped tin oxide coating is formed directly on the glass substrate. Thus, the coated glass article resulting from utilizing the CVD process may be of a glass/TOFe arrangement. However, the CVD process described herein may be utilized in combination with one or more additional coating layers to achieve a desired coating stack. The additional coating layer(s) may be formed before or after forming the iron doped tin
10 oxide coating. The additional coating layer(s) may be formed in conjunction of the float glass manufacturing process or as part of another manufacturing process. Also, the additional coating layer(s) may be formed by pyrolysis or by another coating deposition process, and/or by utilizing one or more additional coating apparatuses.
- 15 [0054] For example, in an embodiment, the iron doped tin oxide coating may be formed directly on a tin oxide coating. In this embodiment, the tin oxide coating has been previously deposited over the deposition surface of the glass substrate. Preferably, in this embodiment, the tin oxide coating comprises a dopant material such as, for example, fluorine. As known to those skilled in the art, when a fluorine dopant is included in a tin
20 oxide coating, the resistivity of the tin oxide coating is decreased. In this embodiment, the iron doped tin oxide coating may be formed directly on the fluorine doped tin oxide ($\text{SnO}_2\text{:F}$) coating at a thickness of 75 nanometers or less.

- [0055] The fluorine doped tin oxide coating may be formed shortly before forming the iron
25 doped tin oxide coating. In an embodiment, the fluorine doped tin oxide coating is formed in conjunction with the float glass manufacturing process. In this embodiment, the deposition of the fluorine doped tin oxide coating preferably takes place in the float bath section. However, it should be appreciated that the fluorine doped tin oxide coating may be formed utilizing another manufacturing process. When the fluorine doped tin oxide coating is
30 formed in conjunction with the float glass manufacturing process, the fluorine doped tin oxide coating may be formed by CVD, utilizing a coating apparatus and/or at essentially atmospheric pressure. However, as should be appreciated, the fluorine doped tin oxide coating may be formed utilizing another deposition process, under low-pressure conditions, and without the use of a coating apparatus.

[0056] In other embodiments, the iron doped tin oxide coating may be formed over a previously deposited sodium diffusion barrier layer or a color suppression interlayer. Known sodium diffusion barriers such as, for example, a silica (SiO_2) coating are suitable for use with the CVD process. Also, known color suppression interlayers are suitable for use with the CVD process.

[0057] In certain preferred embodiments, the iron doped tin oxide coating is formed as the outermost layer of the coated glass article.

[0058] In other embodiments, additional coating layer(s) are formed after forming the iron doped tin oxide coating. For example, additional coating layer(s) of thin-film photovoltaic materials, or other semiconductor materials, may be formed over the iron doped tin oxide coating so as to provide a desired coating stack. The photovoltaic materials, or other semiconductor materials, may be formed over the coated glass article during the manufacturing of solar cells.

[0059] As discussed, above, the CVD process may be carried out in conjunction with the manufacture of the glass substrate in the well-known float glass manufacturing process. The float glass manufacturing process is typically carried out utilizing a float glass installation such as the installation 10 depicted in Fig. 2. However, it should be understood that the float glass installation 10 described herein is only illustrative of such installations.

[0060] As illustrated in Fig. 2, the float glass installation 10 may comprise a canal section along which molten glass 19 is delivered from a melting furnace, to a float bath section 11 wherein the glass substrate is formed. In this embodiment, the glass substrate will be referred to as a glass ribbon 8. The glass ribbon 8 is a preferred substrate over which the iron doped tin oxide coating is deposited. However, it should be appreciated that the glass substrate is not limited to being a glass ribbon.

[0061] The glass ribbon 8 advances from the bath section 11 through an adjacent annealing lehr 12 and a cooling section 13. The float bath section 11 includes: a bottom section 14 within which a bath of molten tin 15 is contained, a roof 16, opposite side walls (not depicted) and end walls 17. The roof 16, side walls and end walls 17 together define an

enclosure 18 in which a non-oxidizing atmosphere is maintained to prevent oxidation of the molten tin 15.

[0062] In operation, the molten glass 19 flows along the canal 20 beneath a regulating twee 21 and downwardly onto the surface of the tin bath 15 in controlled amounts. On the molten tin surface, the molten glass 19 spreads laterally under the influence of gravity and surface tension, as well as certain mechanical influences, and it is advanced across the tin bath 15 to form the glass ribbon 8. The glass ribbon 8 is removed from the bath section 11 over lift out rolls 22 and is thereafter conveyed through the annealing Lehr 12 and the cooling section 13 on aligned rolls. The deposition of the iron doped tin oxide coating preferably takes place in the float bath section 11, although it may be possible for deposition to take place further along the glass production line, for example, in the gap 28 between the float bath 11 and the annealing Lehr 12, or in the annealing Lehr 12.

[0063] As illustrated in Fig. 2, a coating apparatus 9 is shown within the float bath section 11. The coating apparatus 9 may be utilized in forming the iron doped tin oxide coating. However, depending on the thickness of the iron doped tin oxide coating desired and/or the need for additional coating layer(s), one or more additional coating apparatuses (not depicted) may be provided.

[0064] A suitable non-oxidizing atmosphere, generally nitrogen or a mixture of nitrogen and hydrogen in which nitrogen predominates, is maintained in the float bath section 11 to prevent oxidation of the molten tin 15 comprising the float bath. The atmosphere gas is admitted through conduits 23 operably coupled to a distribution manifold 24. The non-oxidizing gas is introduced at a rate sufficient to compensate for normal losses and maintain a slight positive pressure, on the order of between about 0.001 and about 0.01 atmosphere above ambient atmospheric pressure, so as to prevent infiltration of outside atmosphere. For purposes of the describing the invention, the above-noted pressure range is considered to constitute normal atmospheric pressure.

[0065] The iron doped tin oxide coating is preferably formed at essentially atmospheric pressure. Thus, the pressure of the float bath section 11, annealing Lehr 12, and/or in the gap 28 between the float bath 11 and the annealing Lehr 12 may be essentially atmospheric pressure.

[0066] Heat for maintaining the desired temperature regime in the float bath section 11 and the enclosure 18 is provided by radiant heaters 25 within the enclosure 18. The atmosphere within the lehr 12 is typically atmospheric air, as the cooling section 13 is not enclosed and the glass ribbon 8 is therefore open to the ambient atmosphere. The glass ribbon 8 is subsequently allowed to cool to ambient temperature. To cool the glass ribbon 8, ambient air may be directed against the glass ribbon 8 as by fans 26 in the cooling section 13. Heaters (not depicted) may also be provided within the annealing lehr 12 for causing the temperature of the glass ribbon 8 to be gradually reduced in accordance with a predetermined regime as it is conveyed therethrough.

EXAMPLES

[0067] In TABLE 1, examples within the scope of the invention are Ex 1-Ex 4. Ex 1-Ex 4 are for illustrative purposes only and are not to be construed as a limitation on the invention. A comparative process, not considered to be a part of the invention, is described below and illustrated by examples C1 and C1A.

[0068] The following experimental conditions are applicable to C1, C1A and Ex 1-Ex 4.

[0069] A laboratory furnace having a coating apparatus including a 10-inch wide bi-directional coater was provided. The coating apparatus was utilized to direct gaseous precursor compounds to the deposition surface of a glass substrate in order to form a coating by chemical vapour deposition. Prior to forming the coating, the precursor compounds were vapourized and mixed to form a gaseous mixture. The amounts of the individual gaseous precursor compounds in the gaseous mixtures of C1, C1A and Ex 1-Ex 4 are as listed in TABLE 1. Each gaseous precursor mixture also comprised inert gases which made up the balance of the gaseous mixture. The total flow of each gaseous mixture is listed in TABLE 1 and expressed in standard liters per minute (slpm).

[0070] The glass substrates utilized in each of C1, C1A and Ex 1-Ex 4 were of a soda-lime-silica glass composition. Each glass substrate was heated to approximately 1166°F prior to forming the coating. The coater, at the reactor face, or portion nearest the glass surface,

was at a temperature of approximately 450°F. The line speed, i.e. the speed that the glass substrate moved beneath the coater portion of the coating apparatus, from which the gaseous precursor compounds were delivered, was 200 inches/minute. Thus, it should be appreciated that each glass substrate was moving at the time the coatings of C1, C1A and Ex 1-Ex 4 were deposited thereon.

[0071] As noted above, examples C1 and C1A are illustrative of the same comparative deposition process. It should also be noted that the coated glass of C1 was formed prior to forming the coated glass articles of Ex 1-Ex 4. Additionally, it should be noted that the coated glass of C1A was formed after forming the coated glass articles of Ex 1-Ex 4. Thus, the results provided in TABLE 1 for examples C1 and C1A illustrate the repeatability of the comparative deposition process.

[0072] The coated glass articles of C1 and C1A are each of a glass/SnO₂ arrangement and the coated glass articles of Ex 1-Ex 4 are each of a glass/SnO₂:Fe arrangement. The coating thickness of the SnO₂ coatings of C1 and C1A are reported in TABLE 1. The coating thickness of the SnO₂:Fe coatings of Ex 1-Ex 4 are also reported in TABLE 1. The coating thicknesses were estimated by optical modelling using both the transmission spectra and reflection spectra of the coated glass articles of C1 and C1A and of the coated glass articles of Ex 1-Ex 4. In TABLE 1, the coating thickness of the SnO₂ coatings of C1 and C1A and the coating thickness of the SnO₂:Fe coatings of Ex 1-Ex 4 are reported in nanometers (nm).

[0073] The total visible light transmittance (% T_{vis}), sheet resistance (R_s), and resistivity (ρ) of the coated glass articles of C1, C1A and Ex 1-Ex 4 are also reported in TABLE 1. The total visible light transmittance is expressed as a percentage and was measured using a spectrophotometer.

[0074] The sheet resistance was measured using a four point probe and is expressed in ohm/sq, rounded down. The resistivity was calculated by multiplying the sheet resistance by the coating thickness and is expressed in ohm-cm, rounded down to three decimal places.

TABLE 1

Ref	Total Flow	% DMT	% O ₂	% H ₂ O	% Cp ₂ F _e	Thickness (nm)	% Tvis	Sheet res. R _s (ohm/sq)	Resistivity Rho (ohm.cm)
C1	42	3.2	42.7	35.4	0.0	324.8	81.27	320	0.010
Ex 1	42	3.2	42.7	35.4	0.04	274.9	85.59	3,521	0.096
Ex 2	42	3.2	42.7	35.4	0.06	271.5	85.78	6,904	0.187
Ex 3	42	3.2	42.7	35.4	0.08	261.4	85.02	11,730	0.307
Ex 4	42	3.2	42.7	35.4	0.10	260.1	84.03	114,440	2.975
C1A	42	3.2	42.7	35.4	0.0	300.7	83.51	564	0.017

[0075] As shown by Ex 1-Ex 4, the CVD process provides an improved process over the comparative deposition process illustrated by C1 and C1A. For example, the sheet resistance of the coated glass article of Ex 1 was 3521.00 ohm/sq. In stark contrast, the sheet resistances for the coated glass articles of C1 and C1A were only 320.20 ohm/sq. and 564.60 ohm/sq., respectively. Additional improvements in sheet resistance are illustrated by Ex 2-Ex 4 where it was observed that as the percentage of iron-containing compound in the gaseous precursor mixture increased, the sheet resistance and resistivity of the resulting coated glass articles increased. In accordance with the invention, the iron doped tin oxide coating preferably exhibits a resistivity of at least 4×10^{-2} ohm-cm, and more preferably a resistivity of at least 8×10^{-2} ohm-cm.

[0076] Additionally, as illustrated in Table 1, the coated glass articles provided by Ex 1-Ex 4 exhibited a higher total visible light transmittance than the coated glass articles of C1 and C1A. In fact, the coated glass articles provided by Ex 1-Ex 4 all exhibited a total visible light transmittance of 84% or more.

[0077] Thus, as illustrated by Ex 1-Ex 4 and discussed above, the CVD process described herein provides improvements over the comparative deposition process illustrated by C1 and C1A.

- 5 [0078] Based on the same experiments, the inventors modelled examples and comparative examples at a constant coating thickness, so as to correct for the decrease in deposition rate. The inventors have found that iron added to an otherwise undoped tin oxide coating so as to achieve a constant coating thickness, nominally 300 nm. Results are shown in Table 2.

10 TABLE 2

Ref	Cp2Fe(%)	Transmission (%)
C1-M	0.0	85.38
Ex 1-M	0.04	83.37
Ex 2-M	0.06	83.11
Ex 3-M	0.08	82.81
Ex 4-M	0.10	82.52
C1A-M	0.0	84.80

[0079] The inventors believe that comparative example C1A and corresponding C1A-M have residual traces of ferrocene precursor from Ex 4 and corresponding Ex 4-M, so that some iron doping occurs.

15

[0080] As illustrated in Fig. 1, a coated article 1 according to the invention may comprise a glass substrate 2, a high refractive index layer 3, a low refractive index layer 4 and a high resistivity layer 5.

- 20 [0081] An example of a coated glass article according to the invention comprises a glass substrate provided with a coating stack formed of a layer of silicon on the glass, a layer of silica on the layer of silicon, and a layer of iron doped tin oxide on the silica, providing a visible light transmittance of about 20% and a film side reflectance of 70-75%. The iron doped tin oxide coating exhibits a resistivity of at least 4×10^{-2} ohm-cm, which may be
- 25 suitable for discharging static electricity in certain applications where the coated glass article is used as a video display. A coated glass article according to the invention may also be suitable as a mirror.

WHAT IS CLAIMED IS:

1. A chemical vapour deposition process for forming a coated glass article,
5 comprising:
 providing a glass substrate;
 forming a gaseous mixture comprising a tin-containing compound, water, oxygen,
 and an organic iron-containing compound; and
 directing the gaseous mixture toward and along the glass substrate, and reacting the
10 mixture over the glass substrate to deposit an iron doped tin oxide coating thereon.
2. The process of claim 1, wherein when the iron doped tin oxide coating is
deposited, the temperature of the glass substrate is 752°F (400°C) or more.
- 15 3. The process of claim 1, wherein the glass substrate is moving at the time the
iron doped tin oxide coating is deposited.
4. The process of claim 1, wherein the mixture is reacted over the glass
substrate at essentially atmospheric pressure.
20
5. The process of claim 1, wherein, the organic iron-containing compound is
ferrocene or a derivative of ferrocene.
6. The process of claim 1, wherein the iron doped tin oxide coating is the
25 outermost layer of the coated glass article.
7. The process of claim 1, wherein the glass substrate is a soda-lime-silica
glass.
- 30 8. The process of claim 1, wherein the iron doped tin oxide coating is formed
over a previously deposited sodium diffusion barrier layer.
9. The process of claim 8, wherein the sodium diffusion barrier layer is
comprised of silica.

10. The process of claim 1, further comprising feeding the gaseous mixture through a coating apparatus and discharging the gaseous mixture from the coating apparatus, wherein the coating apparatus is provided at a predetermined distance above
5 and extends transversely across the glass substrate.

11. The process of claim 1, wherein the tin-containing compound is a halogenated tin-containing compound.

10 12. The process of claim 1, wherein the tin-containing compound is dimethyltin dichloride.

13. The process of claim 1, wherein the oxygen is in the form of molecular oxygen.
15

14. The process of claim 1, wherein the iron doped tin oxide coating exhibits a resistivity of at least 4×10^{-2} ohm-cm.

15. The process of claim 1, wherein the iron doped tin oxide coating exhibits a
20 resistivity of at least 8×10^{-2} ohm-cm.

16. The process of claim 1, wherein the glass substrate comprises a glass ribbon in a float glass manufacturing process, the gaseous mixture is delivered to a coating apparatus provided at a predetermined distance above and extending transversely across
25 the glass ribbon, the glass ribbon being surrounded by float bath atmosphere, and the gaseous mixture is discharged from the coating apparatus and the gaseous mixture is directed toward and along the glass ribbon, the mixture reacting over the glass ribbon to form the iron doped tin oxide coating thereon.

30 17. A coated glass article comprising a glass substrate and an iron doped tin oxide coating, wherein the iron doped tin oxide coating exhibits a resistivity of at least 4×10^{-2} ohm-cm.

1/2

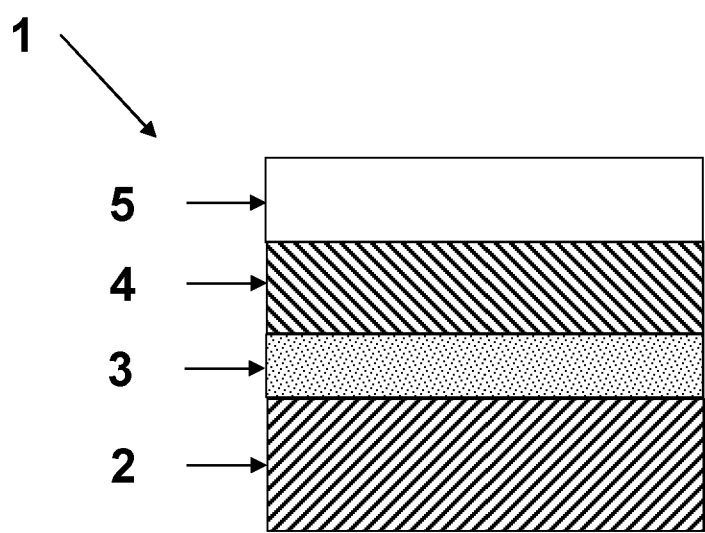


Fig. 1

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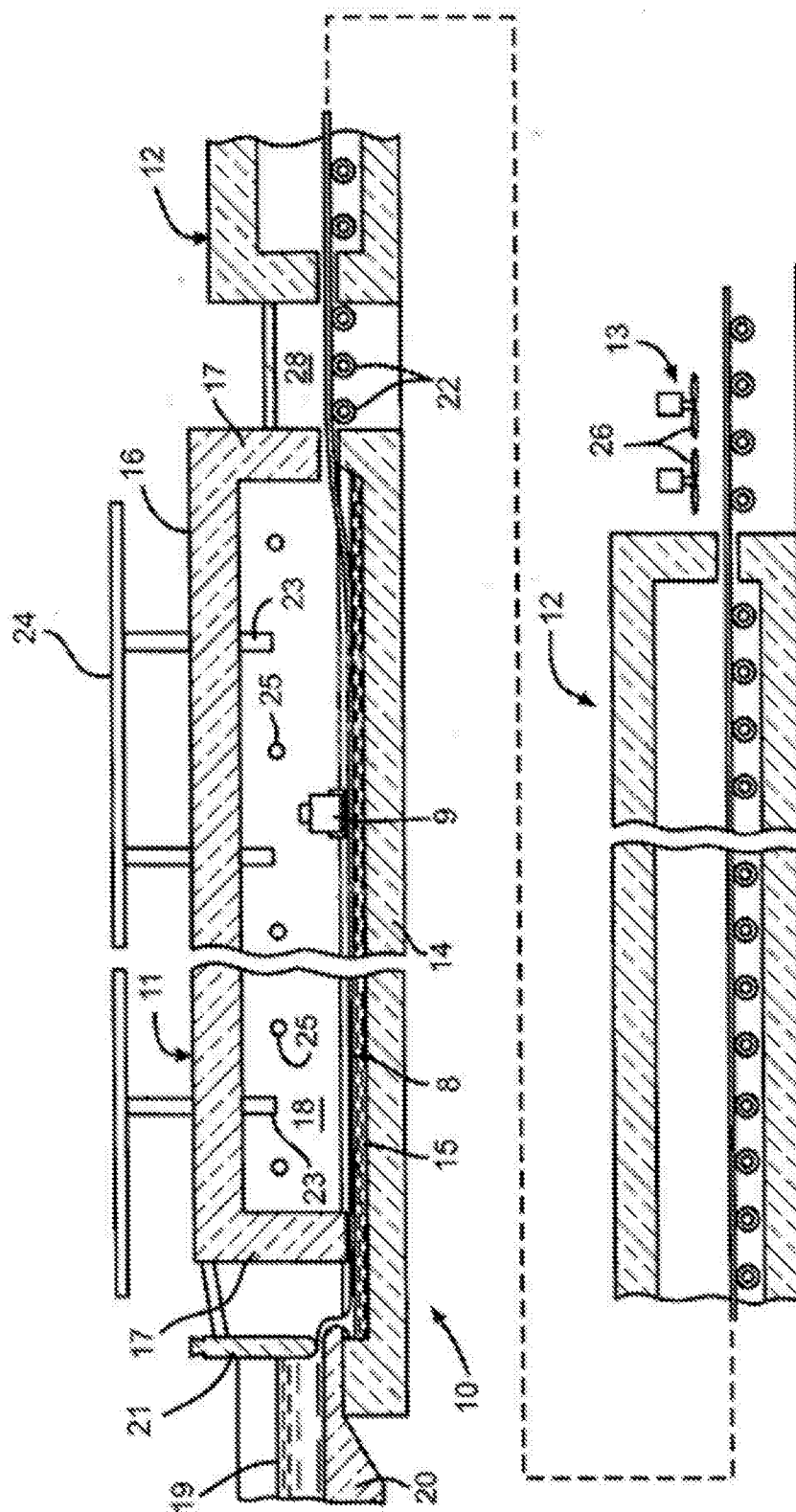


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2016/050401

A. CLASSIFICATION OF SUBJECT MATTER

INV. C03C17/00 C03C17/245 C03C17/34
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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	the whole document in particular page 3 (line 55) to 4 (line 78) and figure 4	1-16
X	US 6 387 514 B1 (LEGRAND PHILIPPE [BE]) 14 May 2002 (2002-05-14) the whole document in particular examples 5-7 (tables 1-2) and 22-24 (table 3).	1-17
A	US 6 218 018 B1 (MCKOWN CLEM [US] ET AL) 17 April 2001 (2001-04-17) the whole document	1-17
A	US 6 521 295 B1 (REMINGTON JR MICHAEL P [US]) 18 February 2003 (2003-02-18) the whole document	1-17



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

6 May 2016

Date of mailing of the international search report

13/05/2016

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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