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**(54) Title:** STATIC-DISSIPATIVE COATING TECHNOLOGY

**(57) Abstract:** The invention provides a glass sheet or another transparent substrate on which there is provided a static-dissipative coating. The static-dissipative coating includes a film comprising titania. The film comprising titania preferably is exposed so as to define an outermost face of the static-dissipative coating. The static-dissipative coating is characterized by an indoor dust collection factor of less than 0.145.

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# STATIC-DISSIPATIVE COATING TECHNOLOGY

## RELATED APPPLICATIONS

This application is an International PCT application claiming priority to U.S. provisional application No. 62/423,276, filed November 17, 2016, the entire contents of which are incorporated herein by reference.

## FIELD OF THE INVENTION

[0001] The present invention relates generally to coatings for glass and other substrates. More particularly, this invention relates to low-maintenance thin film coatings.

## BACKGROUND OF THE INVENTION

[0002] Various types of photocatalytic coatings are known. Self-cleaning coatings based on $TiO_2$, for example, have been studied widely and reported on in the scientific literature. Many past efforts have sought to maximize the photocatalytic properties of the coating, in some cases with the goal of providing a self-cleaning window. In such cases, high levels of photoactivity are desired.

[0003] Contrary to the goal of such research efforts, it can be advantageous to provide low-maintenance coatings that have lower levels of photoactivity than self-cleaning coatings and yet stay cleaner than uncoated glass, are easier to clean than uncoated glass, or both.

[0004] Anti-static coatings have been developed as one type of low-maintenance coating. These coatings are often based on a transparent conductive oxide ("TCO") coating. The TCO coating typically has considerable thickness, and a relatively high level of electrical conductivity. The thickness tends to be large enough that the coating imparts more than an optimal amount of visible reflection, absorption and surface roughness.

[0005] It would be desirable to provide a low-maintenance coating that comprises titania and has a small thickness, minimal optical impact, and is static dissipative so as to provide controlled dust collection properties.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0006] FIG. 1 is a broken-away schematic cross-sectional view of a substrate having a major surface with a static-dissipative coating in accordance with certain embodiments;

[0007] FIG. 2 is a broken-away schematic cross-sectional view of a substrate having a major surface with a static-dissipative coating in accordance with other embodiments;

[0008] FIG. 3 is a broken-away schematic cross-sectional view of a substrate having a first major surface with a static-dissipative coating and a second major surface with a functional coating in accordance with certain embodiments;

[0009] FIG. 4 is a partially broken-away schematic cross-sectional side view of a multiple-pane insulating glazing unit that includes an interior pane having a room-side surface with a static-dissipative coating in accordance with certain embodiments;

[0010] FIG. 5 is a partially broken-away schematic cross-sectional side view of a multiple-pane insulating glazing unit that includes an interior pane having a room-side surface with a static-dissipative coating in accordance with other embodiments; and

[0011] FIG. 6 is a schematic cross-sectional side view of a sputtering chamber used to deposit a static-dissipative coating in accordance with certain embodiments.

## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0012] The following detailed description is to be read with reference to the drawings, in which like elements in different drawings have like reference numerals. The drawings, which are not necessarily to scale, depict selected embodiments and are not intended to limit the scope of the invention. Skilled artisans will recognize that the examples provided herein have many useful alternatives that fall within the scope of the invention.

[0013] The invention provides a coated substrate. A wide variety of substrate types are suitable for use in the invention. In some embodiments, the substrate 10' is a sheet-like substrate having generally opposed first 16 and second 18 major surfaces. For example, the substrate 10' can be a sheet of transparent material (i.e., a transparent sheet). The substrate 10', however, is not required to be a sheet, nor is it required to be transparent.

[0014] For many applications, the substrate 10, 10’ will comprise a transparent (or at least translucent) material, such as glass or clear plastic. For example, the substrate 10, 10’ is a glass sheet (e.g., a window pane) in certain embodiments. A variety of known glass types can be used, and soda-lime glass will commonly be preferred. In certain preferred embodiments, the substrate 10, 10’ is part of a window, skylight, door, shower door, or other glazing. In some cases, the substrate 10, 10’ is part of an automobile windshield, an automobile side window, an exterior or interior rear-view mirror, or a roof panel. In other embodiments, the substrate 10, 10’ is a piece of aquarium glass, a plastic aquarium window, or a piece of greenhouse glass. In a further embodiment, the substrate 10, 10’ is a refrigerator panel, such as part of a refrigerator door or window. In still another embodiment, the substrate 10, 10’ is part of an oven door or window. In yet another embodiment, the substrate 10, 10’ is part of a switchable smart window, such as a switchable privacy window.

[0015] Substrates of various sizes can be used in the present invention. Commonly, large-area substrates are used. Certain embodiments involve a substrate 10, 10’ having a major dimension (e.g., a length or width) of at least about 0.5 meter, preferably at least about 1 meter, perhaps more preferably at least about 1.5 meters (e.g., between about 2 meters and about 4 meters), and in some cases at least about 3 meters. In some embodiments, the substrate 10’ is a jumbo glass sheet having a length and/or width that is between about 3 meters and about 10 meters, e.g., a glass sheet having a width of about 3.5 meters and a length of about 6.5 meters. Substrates having a length and/or width of greater than about 10 meters are also anticipated.

[0016] In some embodiments, the substrate 10, 10’ is a generally square or rectangular glass sheet. The substrate in these embodiments can have any of the dimensions described in the preceding paragraph and/or in the following paragraph. In one particular embodiment, the substrate 10, 10’ is a generally rectangular glass sheet having a width of between about 3 meters and about 5 meters, such as about 3.5 meters, and a length of between about 6 meters and about 10 meters, such as about 6.5 meters. In another embodiment, the substrate 10, 10’ is a generally square glass sheet having a width of between about 4 inches and 8 inches, such as about 6 inches.

[0017] Substrates of various thicknesses can be used in the present invention. In some embodiments, the substrate 10, 10' (which can optionally be a glass sheet) has a thickness of about 1-5 mm. Certain embodiments involve a substrate 10, 10' with a thickness of between about 2.3 mm and about 4.8 mm, and perhaps more preferably between about 2.5 mm and about 4.8 mm. In one particular embodiment, a sheet of glass (e.g., soda-lime glass) with a thickness of about 3 mm is used. In one group of embodiments, the thickness of the substrate is between about 4 mm and about 20 mm or perhaps between about 2 mm and about 19 mm. Thicknesses in this range, for example, may be useful for aquarium tanks (in which case, the substrate can optionally be glass or acrylic). When the substrate is float glass, it will commonly have a thickness of between about 4 mm and about 19 mm. In another group of embodiments, the substrate 10, 10' is a thin sheet having a thickness of between about 0.35 mm and about 1.9 mm. Embodiments of this nature can optionally involve the substrate 10, 10' being a sheet of display glass or the like.

[0018] The invention provides a substrate 10, 10' bearing a static-dissipative coating 50. The static-dissipative coating 50 includes a film 30 comprising titanium oxide (i.e., "titania"). Preferably, the film 30 comprising titania defines an outermost, exposed face of the static-dissipative coating 50. Reference is made to Figures 1 and 2.

[0019] The static-dissipative coating 50 provides the substrate 10, 10' with a combination of desirable optical properties and surprising low-maintenance properties. For example, it has a small thickness, minimal optical impact, and is static dissipative so as to provide controlled dust collection properties.

[0020] The present coating stays cleaner longer than uncoated glass, is easier to clean than uncoated glass, or both. Although the coating 50 may exhibit a level of photoactivity when activated by ultraviolet radiation, it does not rely on ultraviolet activation, or photocatalysis of organics, to provide low-maintenance properties. It is therefore well suited for indoor (e.g., room-side) applications.

[0021] The static-dissipative coating 50 preferably provides the substrate 10, 10' with an indoor dust collection factor of less than 0.145. In preferred embodiments, the indoor dust collection factor is less than 0.142 but greater than 0.050, for example less than 0.140 but greater than 0.050. In some embodiments, the indoor dust collection factor is less than 0.128 but greater than 0.050. The indoor dust collection factor reflects the extent to which the coated surface collects dust under defined conditions that have been established to approximate common indoor air movement conditions.

[0022] Specifically, the indoor dust collection factor is the dust collected in grams for a given sample as calculated in accordance with the Glass Dust Hazing test method specified in the IBR JN 16775 Protocol, the contents of which are incorporated herein by reference. The purpose of the test is to determine the amount of dust that adheres to a glass surface oriented parallel to air flow. Dust-laden air is swept over the samples. The test is conducted using an air velocity of 1.1 miles/hour (100 feet/minute); a calibrated air flow meter is used. The duct size is 24 inches by 24 inches (stainless steel ducting), and the glass sample size is four inches by four inches. Each glass sample is tested with its coated side facing up. A dust aerosol generator capable of 10 to 50 mg dust per $m^3$ of air is used. The challenge aerosol is ISO 12103-1 A2 Fine Dust (silica dust); a dust concentration of 50 $mg/m^3$ is used. A suitable photometer for measuring dust concentration is the Thermo Electron Model DR-2000. The dust is neutralized using an ion generator to simulate natural conditions. The test area cleaning and setup involves wiping down the ducting with moistened wipes, and purging with HEPA filtered air. The test protocol is as follows. Turn on air flow, and set to the desired rate. Mount a cleaned glass sample in the duct with its coated major surface parallel to the air flow and two inches above the duct base. Inject ISO silica dust to the desired concentration. Neutralize the dust at the generator exit. Monitor dust concentration during exposure with the photometer. Conduct flow for 30 minutes using a stopwatch. Stop the flow. Wipe the test glass with a pre-weighed tack cloth (e.g., HDX Tack Cloth). Weigh the same tack clock after such wiping. An analytical balance accurate to 0.001 g, with span to 60 g, is used to determine the weight difference for the tack cloth, so as to determine the change in weight due to the dust that had accumulated on the coated glass surface and that was subsequently transferred to the tack cloth. The resulting dust collected by the sample (in grams) is the indoor dust collection factor.

[0023] In some embodiments, the static-dissipative coating 50 is on a surface of a substrate 10' mounted such that the coating is exposed to an indoor (e.g., room-side) environment, e.g., so as to be exposed to an ambient environment inside a building. Certain embodiments provide an IG unit having the static-dissipative coating 50 on an exterior surface (e.g., a #4 or #6 surface) that is destined to be exposed to an indoor environment.

[0024] While the present coating is particularly advantageous for indoor applications, it also offers advantages for use as a #1 surface coating (i.e., a coating on a surface destined to be exposed to an outdoor environment). For example, the static-dissipative coating 50 preferably provides the substrate 10, 10' with an outdoor dust collection factor of less than 0.036, for example less than 0.035. In preferred embodiments, the outdoor dust collection factor is less than 0.032 but greater than 0.010, for example less than 0.030 but greater than 0.010. In some embodiments, the outdoor dust collection factor is less than 0.028 but greater than 0.010. The outdoor dust collection factor reflects the extent to which the coated substrate collects dust under defined conditions that have been established to approximate common outdoor air movement conditions.

[0025] As with the indoor dust collection factor, the outdoor dust collection factor is the dust collected in grams for a given sample as calculated in accordance with the Glass Dust Hazing test method specified in the above-noted IBR JN 16775 Protocol. Here again, the purpose of the test is to determine the amount of dust that adheres to a glass surface oriented parallel to air flow when dust-laden air is swept over the samples. Measurement of the outdoor dust collection factor is conducted using an air velocity of 10.0 miles/hour (880 feet/minute) and a duct size of 12 inches by 12 inches (stainless steel ducting). The glass sample size is four inches by four inches, each glass sample is tested with its coated side facing up, a calibrated air flow meter is used, a dust aerosol generator capable of 10 to 50 mg dust per $m^3$ of air is used, the challenge aerosol is ISO 12103-1 A2 Fine Dust, a dust concentration of 50 $mg/m^3$ is used, and a suitable photometer for measuring dust concentration is the Thermo Electron Model DR-2000. The dust is neutralized using an ion generator to simulate natural conditions. The test area cleaning and setup involves wiping down the ducting with moistened wipes, and purging with HEPA filtered air. As with the indoor dust collection factor, the test protocol for the outdoor dust collection factor is as follows. Turn on air flow, and set to the desired rate. Mount a cleaned glass sample in the duct with its coated major surface parallel to the air flow and two inches above the duct base. Inject ISO silica dust to the desired concentration. Neutralize the dust at the generator exit. Monitor dust concentration during exposure with the photometer. Conduct flow for 30 minutes using a stopwatch. Stop the flow. Wipe the test glass with a pre-weighed tack cloth. Weigh the same tack clock after such wiping. An analytical balance accurate to 0.001 g, with span to 60 g, is used to determine the weight difference for the tack cloth, so as to determine the change in weight due to the dust that had accumulated on the coated glass surface and that was subsequently transferred to the tack cloth. The resulting dust collected by the sample (in grams) is the outdoor dust collection factor.

[0026] Thus, in some embodiments, the static-dissipative coating is on a #1 surface of a substrate 10 mounted such that the coating is exposed to an outdoor environment, e.g., so as to exposed to periodic contact with rain. Certain embodiments provide an IG unit having the static-dissipative coating 50 on an exterior surface (i.e., a #1 surface) that is destined to be exposed to an outdoor environment. Such an embodiment is shown in Figure 5.

[0027] The static-dissipative coating 50 of any embodiment of the present disclosure can optionally provide the substrate with a surface roughness $R_a$ in the range of between about 0.05 nm and about 5 nm, such as between 0.2 nm and 4 nm. Surface roughness is defined in terms of deviations from the mean surface level. In certain embodiments, the surface roughness is less than 0.25, or even less than 0.22, such as from 0.05 to 0.20. The surface roughness $R_a$ is the arithmetical mean surface roughness. This is the arithmetic average of the absolute deviations from the mean surface level. The arithmetical mean surface roughness of a coating is commonly represented by the equation: $R_a = 1/L \int_0^L |f(x)| dx$. The surface roughness $R_a$ can be measured in conventional fashion, e.g., using an Atomic Force Microscope (AFM) equipped with conventional software that gives $R_a$.

[0028] In addition to having a surface roughness in one or more of the ranges noted in the preceding paragraph, the static-dissipative coating 50 preferably provides the substrate 10, 10' with a wet dynamic coefficient of friction of less than 0.1, less than 0.075, or even less than 0.07. In some embodiments, the wet dynamic coefficient of friction of the coated surface is in the range of from about 0.01 to about 0.065, such as about 0.05. The wet dynamic coefficient of friction is measured as follows. The coated glass sample is placed horizontally in a test instrument (Mecmesin Multitest 2.5-i), covered with Windex, and a 2.5 ounce test puck is placed on top of the sample. The bottom of the puck has a piece of crock cloth on it in contact with the coated sample surface (the crock cloth is an ISO standard material commercially available from Testfabrics, Inc., of West Pittston, Pennsylvania USA). The puck is drawn across the coated surface, and the force required to do so is measured. As the puck is moving, the force is constant. This friction force is compared to the downward (gravitational) force of the puck to determine a coefficient of (wet) dynamic friction. The numbers reported herein are for fresh glass with the film 30 comprising titania in an un-activated-by-UV state.

[0029] The static-dissipative coating 50 preferably has a total thickness of less than 500 angstroms, or less than 350 angstroms, such as greater than 30 angstroms and less than 300 angstroms. In some cases, the thickness of the static-dissipative coating 50 is less than 250 angstroms, or even less than 200 angstroms, such as greater than 25 angstroms and less than 200 angstroms. In one embodiment, the thickness of the static-dissipative coating 50 is about 60 angstroms. In another embodiment, the thickness of the static-dissipative coating 50 is about 160 angstroms.

[0030] Figure 1 shows a substrate 10′ with a major surface 18 bearing a static-dissipative coating 50 according to one embodiment. In some cases, the static-dissipative coating 50 includes one or more other films beneath the film 30 comprising titania. In other cases, the static-dissipative coating 50 has only a single film 30, which is directly on (i.e., in contact with) the substrate 10′. In such cases, the static-dissipative coating 50 consists of the film 30 comprising titania.

[0031] Figure 2 shows a substrate 10′ with a major surface 18 bearing a static-dissipative coating 50 according to another embodiment. In Figure 2, the static-dissipative coating 50 includes both the film 30 comprising titania and a base film 20. In some cases, the static-dissipative coating 50 further includes one or more other films beneath the film 30 comprising titania. For example, one or more other films can be provided beneath the base film 20, between the base film 20 and the film 30 comprising titania, or both. In other cases, the static-dissipative coating 50 consists essentially of, or consists of, the base film 20 and the film 30 comprising titania.

[0032] The present coating 50 preferably has a level of electrical conductivity. However, even for embodiments where this is the case, the surface resistance of the coating 50 is relatively large. For example, the surface resistance preferred for the static-dissipative coating 50 is well above the typical range reported for anti-static coatings, which is $10^0$-$10^3$ ohm/square. By comparison, the present static-dissipative coating 50 preferably has a surface resistance of greater than $10^6$ ohms per square. In some cases, the surface resistance is greater than $10^6$ ohms per square but less than $10^{11}$ ohms per square. In certain preferred embodiments, the surface resistance is greater than $10^8$ ohms per square but less than $10^{11}$ ohms per square. Surface resistance can be measured in standard fashion using a surface resistivity meter. The noted surface resistance numbers reflect measurements taken at room temperature and 30% relative humidity.

[0033] The static-dissipative coating 50 preferably is devoid of a transparent conductive oxide layer (e.g., a layer formed of ITO, FTO, AZO, or any other electrically conductive oxide material) beneath the film 30 comprising titania. In any embodiment of the present disclosure, the static-dissipative coating 50 can optionally be devoid of any electrically conductive film (e.g., a layer formed of metal or TCO) beneath the film 30 comprising titania. In such cases, if desired a transparent conductive oxide layer or another electrically conductive film can still be provided on an opposite side of the substrate.

[0034] In some embodiments, the film 30 comprising titania includes $TiO_2$, TiO, or both. In some cases, the film 30 comprising titania consists essentially of (or consists of) titanium oxide. In such cases, the film comprising titania is devoid of any additional material, such as a dopant. In other cases, the film 30 comprising titania further includes a dopant. The optional dopant material can generally be present in an amount of up to ten atomic percent, e.g., about five atomic percent or less. As one example, the film 30 comprising titania can also include tungsten.

[0035] The film 30 comprising titania can be doped with a material, and to a level, that provide an electrical conductivity within one or more of the ranges noted above. In embodiments of this nature, the film 30 comprising titania preferably is doped with a material, and to a level, that provide the particular indoor and/or outdoor dust collection factors noted above. The dopant can be tungsten, niobium, silver, zirconium, tantalum, sodium, aluminum, zinc, chromium, vanadium, nitrogen, manganese, molybdenum, iron, nickel, calcium carbon, sulfur, boron, phosphorous, fluorine, or iodine, or mixtures or compound of these elements.

[0036] Additionally or alternatively, to provide a level of electrical conductivity, the film 30 comprising titania can include substoichiometric titanium oxide, i.e., $TiO_x$, where x is less than 2. The suboxide composition can be chosen to help provide an electrical conductivity within one or more of the ranges noted above. In embodiments of this nature, the suboxide composition preferably is chosen to help provide the particular indoor and/or outdoor dust collection factors noted above. In some cases, the film 30 consists essentially of (or consists of) $TiO_x$, where x is less than 2. For example, the film 30 can optionally consist essentially of (or consist of) $TiO_x$, where x is less than 2 but greater than 1.8. In these cases, the $TiO_x$ is devoid of an additional material such as a dopant.

[0037] In other cases, the film 30 comprising titania includes both tungsten (or another dopant selected from the list above) and $TiO_x$, where x is less than 2. For example, the film 30 comprising titania can optionally include both tungsten (or another dopant selected from the list above) and $TiO_x$, where x is less than 2 but greater than 1.8.

[0038] The film 30 comprising titania can be a homogenous film, a graded film, or another type of non-homogenous film. The thickness of the film 30 comprising titania preferably is less than 500 Å, such as greater than 30 angstroms and less than 300 angstroms. In some embodiments, the thickness of the film 30 comprising titania is less than 250 Å, such as less than 200 Å, less than 150 Å, or even less than 100 Å. The thickness of the film 30 comprising titania is greater than 25 Å, and preferably 30 Å or greater, such as in the range of 30-95 Å. In certain embodiments, the film 30 consists of titania (or titania doped with one or more of the materials noted above) at a thickness of 30-75 Å, such as about 60 Å. In some of these embodiments, the titania is substoichiometric titanium oxide.

[0039] When provided, the base film 20 can be any suitable thin film material that adheres well to both the substrate 10, 10' and the immediately overlying film (which may be the film 30 comprising titania). In cases where the substrate 10, 10' is soda-lime glass, the base film 20 preferably also protects the film 30 comprising titania from sodium ion diffusion. In cases where the base film 20 is omitted and the substrate 10, 10' is soda-lime glass, the surface of the substrate itself can optionally be treated to reduce, or perhaps deplete, the sodium ions in the surface area of the glass.

[0040] The base film 20 can be a transparent dielectric film. In certain embodiments, the base film comprises silica, alumina, or both. The base film 20 can optionally be a mixed film including two or more metals or semi-metals. In some cases, it is a mixed film comprising silica and alumina, or silica and titania, or silica, alumina and titania. Other materials can be used instead. In some embodiments, the base film consists essentially of (or consists of) silica, or consists essentially (or consists of) of alumina. In other embodiments, the base film consists essentially of (or consists of) silicon nitride, or consists essentially (or consists of) of silicon oxynitride. The base film 20 can be a substantially homogenous film or a graded film. When provided, the base film 20 can be deposited directly onto the substrate, with the film 30 comprising titania deposited directly onto the base film 20. This, however, is by no means required.

[0041] When provided, the base film 20 can optionally have a thickness of less than about 300 Å. In certain embodiments, the base film 20 has a thickness of less than 150 Å. As one example, the base film 20 can comprise silica at a thickness of about 100 Å.

[0042] In certain embodiments, the static-dissipative coating 50 is provided on one major surface of a substrate 10, 10' and another functional coating 80 is provided on an opposite major surface of the same substrate. Figure 3 shows one such embodiment. Here, the illustrated substrate 10' has one surface 18 bearing the static-dissipative coating 50 and another surface 16 bearing another functional coating 80. Functional coating 80 can be a single layer or a stack of layers. Various functional coatings can be used. For example, functional coating 80 can optionally be a low-emissivity coating comprising one or more infrared-reflective metallic films. Such metallic film(s) commonly comprise (e.g., are formed of) silver. Suitable low-emissivity coatings are described in U.S. Patent Nos.

9,376,853 and 7,192,648 and 7,060,359 and 7,101,810, the contents of which are incorporated herein by reference. When provided, functional coating 80 can alternatively be a transparent conductive oxide coating, i.e., a coating comprising at least one transparent conductive oxide layer, such as ITO, FTO, AZO, or the like. Suitable transparent conductive oxide coatings are described in U.S. Patent No. 9,453,365, the contents of which are incorporated herein by reference.

[0043] In the embodiment of Figure 4, substrate 10′ is a transparent pane (e.g., a glass sheet) that is part of a multiple-pane insulating glazing unit 110. Typically, the insulating glazing unit 110 has an exterior pane 10 and an interior pane 10′ separated by at least one between-pane space 800. At least one spacer 900 (which can optionally be part of a sash) is commonly provided to separate the panes 10 and 10′. The spacer 900 can be secured to the interior surfaces of each pane using an adhesive or seal 700. In some cases, an end sealant 600 is also provided. In the illustrated embodiment, the exterior pane 10 has an exterior surface 12 (the #1 surface) and an interior surface 14 (the #2 surface). The interior pane 10′ has an interior surface 16 (shown as a #3 surface) and an exterior surface 18 (shown as a #4 surface), which is the room-side surface. The IG unit can optionally be mounted in a frame (e.g., a window frame) such that the exterior surface 12 of the exterior pane 10 is exposed to an outdoor environment 77 while the exterior surface 18 of the interior pane 10′ is exposed to a room-side interior environment. Interior surfaces 14 and 16 are both exposed to the atmosphere in the between-pane space 800 of the insulating glazing unit. While Figure 4 shows a double-pane IG unit, other embodiments provide a triple-pane IG unit having the static-dissipative coating 50 on the #6 surface, the #1 surface, or both.

[0044] The IG unit 110 can be filled with a conventional insulative gas mix (e.g., argon and air), or it can be a vacuum IG unit. In other embodiments, it is a switchable smart glazing, such as a privacy glazing switchable between transparent and opaque states.

[0045] When it is desired to provide a room-side surface of a window or other glazing with low-maintenance properties, the static-dissipative coating 50 can be provided quite advantageously. Thus, in the embodiment of Figure 4, the exterior surface 18 of pane 10′ has the static-dissipative coating 50. The static-dissipative coating 50 shown in Figure 4 can be in accordance with any embodiment of the present disclosure. Of course, skilled artisans would understand that the static-dissipative coating 50 can be provided on the exterior surface 12 of pane 10 in other embodiments, as illustrated in Figure 5.

[0046] With continued reference to Figure 4, it is to be appreciated that the interior surface 14 of pane 10 can optionally have a functional coating, such as a low-emissivity coating. Additionally or alternatively, the interior surface 16 of pane 10′ can optionally have a functional coating, such as a low-emissivity coating or a transparent conductive coating. Moreover, while Figure 4 shows a double-pane IG unit, it can alternatively have three or more panes. Further, the static-dissipative coating 50 can additionally or alternatively be provided on the #1 surface of the IG unit 110.

[0047] Methods for producing a substrate 10, 10’ bearing a static-dissipative coating 50 are also provided. In such methods, each film of the coating 50 can be deposited using any of a variety of well-known coating techniques. Suitable coating techniques include, but are not limited to, sputter deposition, chemical vapor deposition (CVD), plasma enhanced chemical vapor deposition, pyrolytic deposition, sol-gel deposition, and wet chemical deposition. In preferred embodiments, the coating 50 is deposited by sputtering. Sputtering is well known in the present art.

[0048] Figure 6 schematically depicts an exemplary magnetron sputtering chamber 200 that can be used to deposit a static-dissipative coating 50. Magnetron sputtering chambers and related equipment are commercially available from a variety of sources (e.g., Leybold). Useful magnetron sputtering techniques and equipment are described in U.S. Pat. No. 4,166,018, issued to Chapin, the teachings of which are incorporated herein by reference. The sputtering chamber 200 shown in Figure 6 includes a base (or "floor") 220, a plurality of side walls 222, and a ceiling (or "top lid" or "cover") 230, together bounding a sputtering cavity 202. In Figure 6, two upper targets 280a, 280b are shown mounted above the path of substrate travel 45. The substrate 10′ is conveyed along the path of substrate travel 45 during film deposition, optionally over a plurality of spaced-apart transport rollers 210. In Figure 6, two upper targets are provided in the illustrated sputtering chamber, although this is by no means required. For example, a single sputtering target (cylindrical or planar) can alternatively be provided in the sputtering chamber. As another possibility, the target(s) could be lower targets positioned below the path of substrate travel and adapted for upwardly sputter depositing the static-dissipative coating 50 onto a bottom surface of the substrate.

[0049] In certain embodiments, a method of depositing a static-dissipative coating 50 is provided. The method includes depositing the film 30 comprising titania onto a major surface of a substrate. The sputtering chamber of Figure 6 can be used to deposit the film 30. Thus, targets 280a, 280b can be titanium-containing targets. In some cases, the titanium-containing targets 280a, 280b have a sputterable material that consists of metallic titanium. In other cases, the titanium-containing targets 280a, 280b have a sputterable material that includes both metallic titianium and a metallic dopant, such as tungsten. In still other cases, the targets have a sputterable material comprising substoichiometric titanium oxide, and the sputtering is carried out in an inert gas atmosphere or a gas atmosphere with little or no oxygen.

[0050] As noted above, the film 30 can in some cases comprise substoichiometric $TiO_x$, where x is less than 2. In such cases, a sputtering chamber as shown in Figure 6 can be used, and the targets 280a, 280b can each have a sputterable material comprising titanium. For example, the targets each have a sputterable material comprising substoichiometric titanium oxide, and an inert (or weakly oxygen) atmosphere can be used in the chamber. In such cases, different levels of oxygen can be used in the sputtering chamber. More will be said of this later. In other cases, the targets 280a, 280b each have a sputterable material consisting of metal titanium, and an oxygen-containing atmosphere is used for sputter-depositing the film 30.

[0051] In some embodiments, the targets 280a and 280b each have a titanium-containing sputterable material, and they are sputtered under conditions selected to deposit a film 30 comprising substoichiometric $TiO_x$, where x is less than 2. This may involve sputtering in an inert gas atmosphere or a gas atmosphere with little or no oxygen. Metallic titanium targets, for example, can be sputtered in an atmosphere comprising between 10% to 35% argon with the remainder being oxygen (e.g., in an atmosphere comprising between 15% to 25% argon with the remainder being oxygen, or perhaps in an atmosphere comprising between 17% to 23% argon with the remainder being oxygen, such as about 20% argon with the remainder being oxygen).

[0052] In certain embodiments, the sputterable material consists essentially of titanium metal and tungsten metal. For example, an alloy target comprising both titanium and tungsten can be used. Alternatively, one could use a metal titanium target provided with strips (or the like) of metal tungsten. Another possibility is a metal alloy target with tungsten metal strips attached. When metal targets are sputtered, an oxygen atmosphere (optionally with a small amount of nitrogen) can be used. In other cases, the sputterable material comprises both titanium oxide and tungsten oxide. In these cases, an inert atmosphere or slight oxygen atmosphere (optionally with a small amount of nitrogen) can be used. In certain embodiments, the sputterable material comprises titanium monoxide, titanium dioxide, and tungsten oxide. In these embodiments, a weakly oxygen atmosphere (optionally containing a small amount of nitrogen) can be used. Or, the targets could be sputtered in an inert atmosphere, e.g., if the resulting film is not required to be deposited in fully oxidized form. In certain cases, the sputterable material is characterized by a metal-only atomic ratio of between about 0.01 and 0.34, this ratio being the number of tungsten atoms in the sputterable material divided by the number of titanium atoms in the sputterable material.

[0053] A target with sputterable material comprising both titanium and tungsten can be prepared using a number of different methods. In some embodiments, a target is prepared by plasma spraying titanium oxide together with tungsten metal onto a target base in an atmosphere that is oxygen deficient and does not contain oxygen-containing compounds. During the plasma spraying process, the action of the plasma on the titanium oxide causes the titanium oxide to lose some oxygen atoms from their lattices. These oxygen atoms are believed to combine with the metal tungsten to form tungsten oxide, as tungsten has a high electrochemical potential. The titanium oxide sprayed onto the backing tube may thus comprise titanium monoxide, titanium dioxide, and tungsten oxide. The sputterable target may, as just one example, be a cylindrical rotary target having a backing tube with a length of at least 24 inches. In such cases, the sputterable material is carried on an exterior wall of the backing tube. Such a cylindrical target is adapted to rotate about a central axis to which the exterior wall of the backing tube is substantially parallel. Alternatively, hot isostatic pressing may be used to form a target. Other target forming methods can also be used. Suitable targets are also commercially available, from a number of well-known suppliers, such as Soleras Advanced Coatings BVBA, of Deinze, Belgium.

[0054] When the film 30 comprising titania is deposited by sputtering one or more targets comprising substoichiometric $TiO_x$, the sputtering is preferably carried out using argon, a mixture of argon and oxygen, a mixture of nitrogen and argon, a mixture of nitrogen and oxygen, or a mixture of oxygen, nitrogen, and argon. If the plasma gas does not contain oxygen, e.g., if pure argon is used, then the coating will not be fully oxidized when deposited. In contrast, if the plasma gas contains oxygen, then the reduced form(s) of titanium oxide may be converted during the sputtering process into the transparent form, which is stoichiometric or at least substantially stoichiometric. A film comprising titania and tungsten oxide can be produced in this way. The degree of transparency of the film will depend upon the amount of oxygen in the plasma gas. An exemplary gas mixture to form transparent film is about 20% by volume argon and about 80% by volume of oxygen.

[0055] EXAMPLE 1 (CONTROL)

A coating consisting of 60 angstroms of $TiO_2$ was deposited onto a major surface of a soda-lime glass sheet. The coating was deposited by pulsed DC sputtering, at a power of 5 kW, a frequency of 50 kHz, a voltage of 379, and an amperage of 13.19. Two passes of the substrate were made under a metallic titanium target. The conveyance speed was 29.43 inches per minute. The following process parameters were used: 100% $O_2$ gas, flow rate of 610 sccm, and pressure of 4.5 mtorr. The surface resistance of the resulting coating was about 3.5 x $10^{11}$ ohms/square. The resulting film was deposited as fully stoichiometric $TiO_2$.

[0056] EXAMPLE 2

A static-dissipative coating consisting of 62 angstroms of substoichiometric titanium oxide ($TiO_x$, where x is 1.8 or higher and less than 2) was deposited onto a major surface of a soda-lime glass sheet. The coating was deposited by pulsed DC sputtering, at a power of 5 kW, a frequency of 50 kHz, a voltage of 371, and an amperage of 13.49. Two passes of the substrate were made under a metallic titanium target. The conveyance speed was 25.89 inches per minute. The following process parameters were used: 20% argon/80% $O_2$ gas mix, argon flow rate of 153 sccm, oxygen flow rate of 438 sccm, and pressure of 4.5 mtorr. The surface resistance of the resulting coating was about 1.8 x $10^{10}$ ohms/square.

[0057] EXAMPLE 3

A static-dissipative coating consisting of 60 angstroms of substoichiometric titanium oxide ($TiO_x$ where x= 1.8 or higher) was deposited onto a major surface of a soda-lime glass sheet. The coating was deposited by pulsed DC sputtering, at a power of 5 kW, a frequency of 50 kHz, a voltage of 363, and an amperage of 13.79. Two passes of the substrate were made under a metallic titanium target. The conveyance speed was 24.87 inches per minute. The following process parameters were used: 50% argon/50% $O_2$ gas mix, argon flow rate of 305 sccm, oxygen flow rate of 305 sccm, and pressure of 4.5 mtorr. The surface resistance of the resulting coating was about 5.8 x $10^9$ ohms/square. The value x in Example 3 is lower than the value x in Example 2.

[0058] RESULTS

[0059] In dust collection testing, Example 2 performed about 12% better than Example 1, while Example 3 performed about 7% better than Example 1. Thus, both Example 2 and Example 3 exhibited better dust collection properties than Example 1 (Control). The surface resistance of Example 3 was smaller than that of Example 2. Surprisingly, even though Example 3 was more electrically conductive (and had a lower x value for the $TiO_x$) than in than Example 2, Example 2 exhibited better dust collection properties than Example 3.

[0060] Thus, certain embodiments of the invention provide a static-dissipative coating 50 that includes a film 30 comprising substoichiometric titanium oxide film produced by sputtering in an atmosphere comprising a mix of oxygen gas and inert gas (such as argon), where the sputtering gas mix comprises about 10-35% inert gas (e.g., argon) and about 65-90% oxygen gas, such as 15-25% inert gas (e.g., argon) and 75-85% oxygen gas. This particular type of substoichiometric titanium oxide can be used as the film 30 comprising titania in any embodiment of the present disclosure.

[0061] While certain preferred embodiments of the invention have been described, it should be understood that various changes, adaptations and modifications can be made without departing from the spirit of the invention and the scope of the appended claims.

EXEMPLARY EMBODIMENTS:

1. A transparent substrate on which there is provided a static-dissipative coating, the static-dissipative coating including a film comprising titania over a base film, the film comprising titania being exposed so as to define an outermost face of the static-dissipative coating, the static-dissipative coating characterized by an indoor dust collection factor of less than 0.145.

2. The transparent substrate of claim 1 wherein the indoor dust collection factor is less than 0.142 but greater than 0.050.

3. The transparent substrate of claim 2 wherein the indoor dust collection factor is less than 0.140 but greater than 0.050.

4. The transparent substrate of claim 1 wherein the static-dissipative coating is characterized by an outdoor dust collection factor of less than 0.036.

5. The transparent substrate of claim 4 wherein the outdoor dust collection factor is less than 0.035.

6. The transparent substrate of claim 5 wherein the outdoor dust collection factor is less than 0.032 but greater than 0.010.

7. The transparent substrate of claim 6 wherein the outdoor dust collection factor is less than 0.030 but greater than 0.010.

8. The transparent substrate of claim 1 wherein the static-dissipative coating has a surface resistance of greater than $10^6$ ohms per square.

9. The transparent substrate of claim 8 wherein the surface resistance of the static-dissipative coating is greater than $10^6$ ohms per square but less than $10^{11}$ ohms per square.

10. The transparent substrate of claim 9 wherein the surface resistance of the static-dissipative coating is greater than $10^8$ ohms per square but less than $10^{11}$ ohms per square.

11. The transparent substrate of claim 10 wherein the surface resistance of the static-dissipative coating is greater than $10^9$ ohms per square but less than $10^{10}$ ohms per square.

12. The transparent substrate of claim 11 wherein the surface resistance of the static-dissipative coating is greater than $3.0 \times 10^9$ ohms per square but less than $7.0 \times 10^9$ ohms per square.

13. The transparent substrate of claim 1 wherein the static-dissipative coating has a thickness of less than 500 angstroms.

14. The transparent substrate of claim 13 wherein the thickness of the static-dissipative coating is greater than 30 angstroms and less than 300 angstroms.

15. The transparent substrate of claim 1 wherein the film comprising titania is in contact with the base film.

16. The transparent substrate of claim 1 wherein the static-dissipative coating is devoid of a transparent conductive oxide film beneath the film comprising titania.

17. The transparent substrate of claim 1 wherein the static-dissipative coating is devoid of an electrically conductive film beneath the film comprising titania.

18. The transparent substrate of claim 1 wherein the static-dissipative coating consists of the film comprising titania and the base film.

19. The transparent substrate of claim 1 wherein the film comprising titania comprises substoichiometric $TiO_x$, where x is less than 2.

20. The transparent substrate of claim 19 wherein the film comprising titania comprises substoichiometric $TiO_x$, where x is less than 2 but greater than 1.8.

21. The transparent substrate of claim 20 wherein the substoichiometric $TiO_x$ is a film produced by sputtering in an atmosphere comprising a mix of oxygen gas and inert gas, where the mix comprises about 10-35% inert gas and about 65-90% oxygen gas.

22. The transparent substrate of claim 1 wherein the film comprising titania has a thickness in the range of between 25 Å and 250 Å.

23. The transparent substrate of claim 1 wherein the static-dissipative coating has a surface roughness in the range of between about 0.1 nm and about 5 nm.

24. The transparent substrate of claim 1 wherein the static-dissipative coating has a wet dynamic coefficient of friction of less than 0.07.

25. The transparent substrate of claim 24 wherein the wet dynamic coefficient of friction of the static-dissipative coating is less than 0.06.

26. An insulating glass unit comprising two spaced-apart panes bounding a between-pane space, wherein one of the panes has an interior surface that is exposed to an interior of a building and that bears a static-dissipative coating, the static-dissipative coating including a film comprising titania over a base film, the film comprising titania being exposed so as to define an outermost face of the static-dissipative coating, the static-dissipative coating characterized by an indoor dust collection factor of less than 0.145.

27. The insulating glass unit of claim 26 wherein the indoor dust collection factor is less than 0.142 but greater than 0.050.

28. The insulating glass unit of claim 27 wherein the indoor dust collection factor is less than 0.140 but greater than 0.050.

29. The insulating glass unit of claim 26 wherein the static-dissipative coating is characterized by an outdoor dust collection factor of less than 0.036.

30. The insulating glass unit of claim 29 wherein the outdoor dust collection factor is less than 0.035.

31. The insulating glass unit of claim 30 wherein the outdoor dust collection factor is less than 0.032 but greater than 0.010.

32. The insulating glass unit of claim 31 wherein the outdoor dust collection factor is less than 0.030 but greater than 0.010.

33. The insulating glass unit of claim 26 wherein the static-dissipative coating has a surface resistance of greater than $10^6$ ohms per square.

34. The insulating glass unit of claim 33 wherein the surface resistance of the static-dissipative coating is greater than $10^8$ ohms per square but less than $10^{11}$ ohms per square.

35. The insulating glass unit of claim 34 wherein the surface resistance of the static-dissipative coating is greater than $10^9$ ohms per square but less than $10^{10}$ ohms per square.

36. The insulating glass unit of claim 35 wherein the surface resistance of the static-dissipative coating is greater than $3.0 \times 10^9$ ohms per square but less than $7.0 \times 10^9$ ohms per square.

37. The insulating glass unit of claim 26 wherein the static-dissipative coating has a thickness of less than 500 angstroms.

38. The insulating glass unit of claim 37 wherein the thickness of the static-dissipative coating is greater than 30 angstroms and less than 300 angstroms.

39. The insulating glass unit of claim 26 wherein the film comprising titania is in contact with the base film.

40. The insulating glass unit of claim 26 wherein the static-dissipative coating is devoid of a transparent conducting oxide film beneath the film comprising titania.

41. The insulating glass unit of claim 26 wherein the static-dissipative coating is devoid of a conductive film beneath the film comprising titania.

42. The insulating glass unit of claim 26 wherein the static-dissipative coating consists of the film comprising titania and the base film.

43. The insulating glass unit of claim 26 wherein the film comprising titania comprises substoichiometric $TiO_x$, where x is less than 2.

44. The insulating glass unit of claim 43 wherein the film comprising titania comprises substoichiometric $TiO_x$, where x is less than 2 but greater than 1.8.

45. The insulating glass unit of claim 44 wherein the substoichiometric $TiO_x$ is a film produced by sputtering in an atmosphere comprising a mix of oxygen gas and inert gas, where the mix comprises about 10-35% inert gas and about 65-90% oxygen gas.

46. The insulating glass unit of claim 26 wherein the film comprising titania film has a thickness in the range of between about 25 Å and about 250 Å.

47. The insulating glass unit of claim 26 wherein the static-dissipative coating has a surface roughness in the range of between about 0.1 nm and about 5 nm.

48. The insulating glass unit of claim 26 wherein the static-dissipative coating has a wet dynamic coefficient of friction of less than 0.07.

49. The insulating glass unit of claim 48 wherein the wet dynamic coefficient of friction of the static-dissipative coating is less than 0.06.

50. A glass sheet on which there is provided a static-dissipative coating, the static-dissipative coating including a film comprising titania, the film comprising titania being exposed so as to define an outermost face of the static-dissipative coating, and the film comprising titania comprises substoichiometric $TiO_x$, where x is less than 2 but greater than 1.8, the substoichiometric $TiO_x$ being a film produced by sputtering in an atmosphere comprising a mix of oxygen gas and inert gas, where the mix comprises about 10-35% inert gas and about 65-90% oxygen gas, the static-dissipative coating characterized by an indoor dust collection factor of less than 0.145.

*FIG. 1*

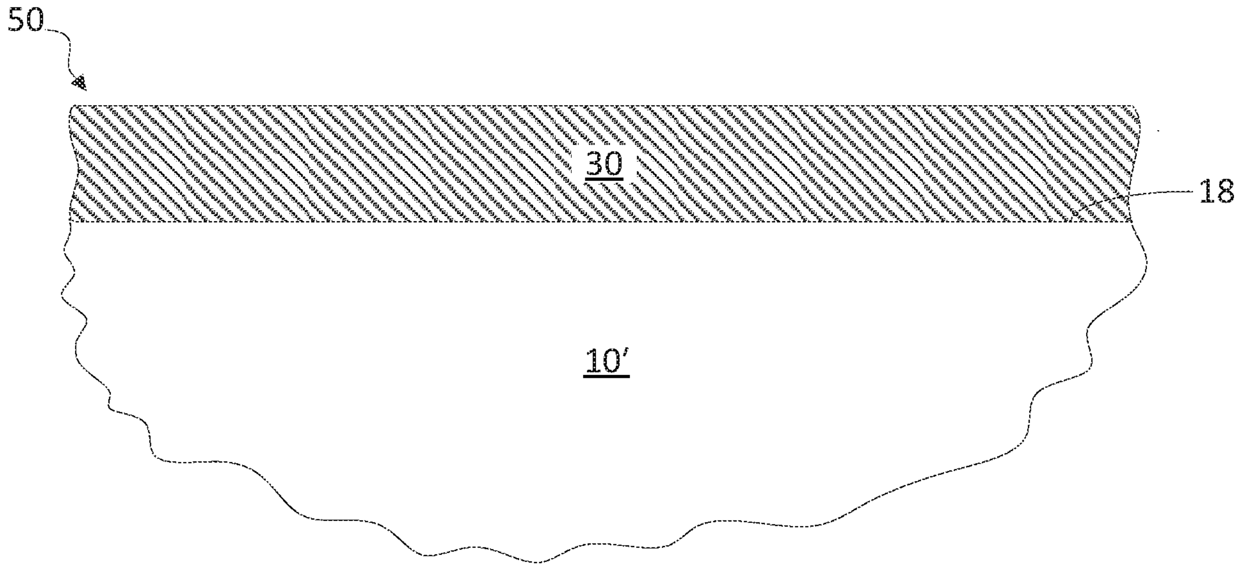


FIG. 2

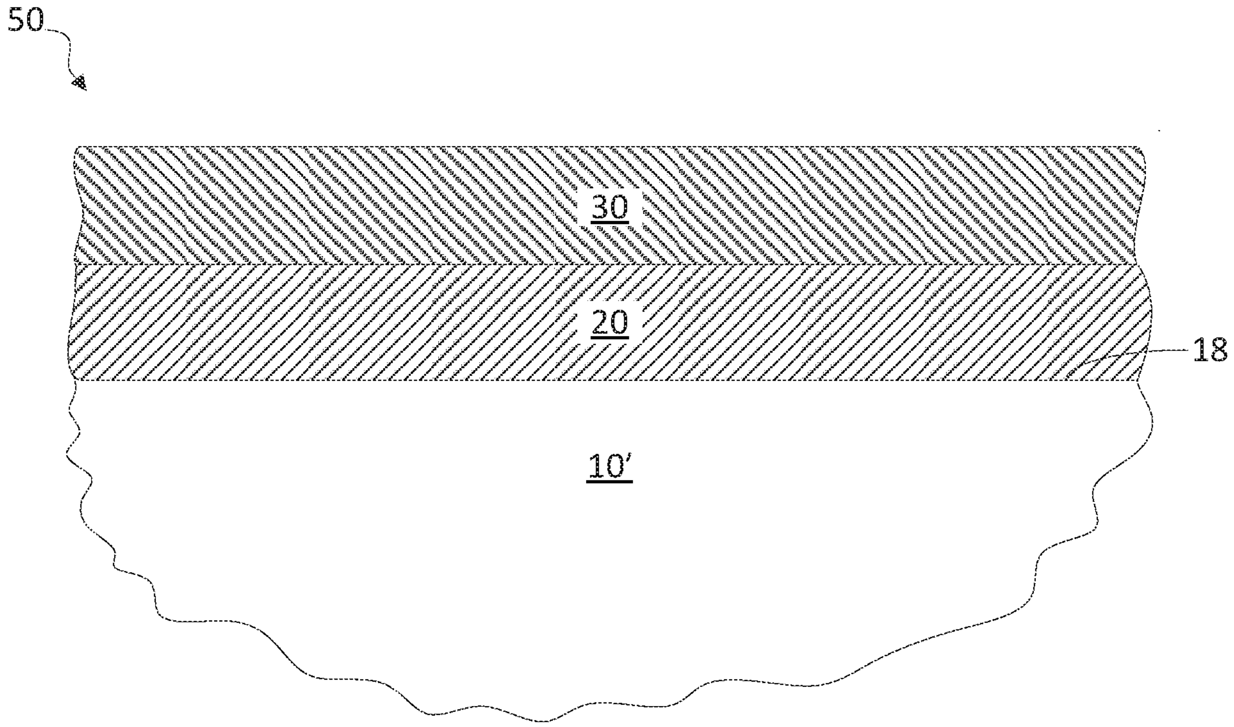


FIG. 3

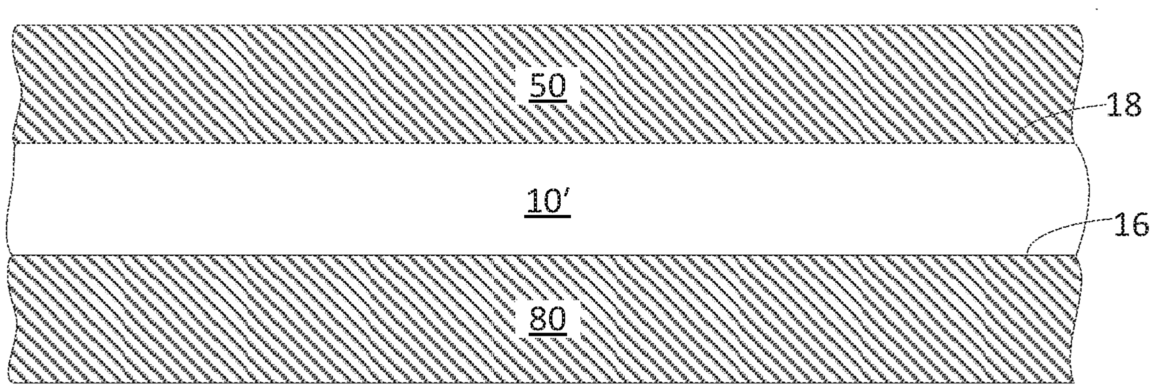


*FIG. 4*

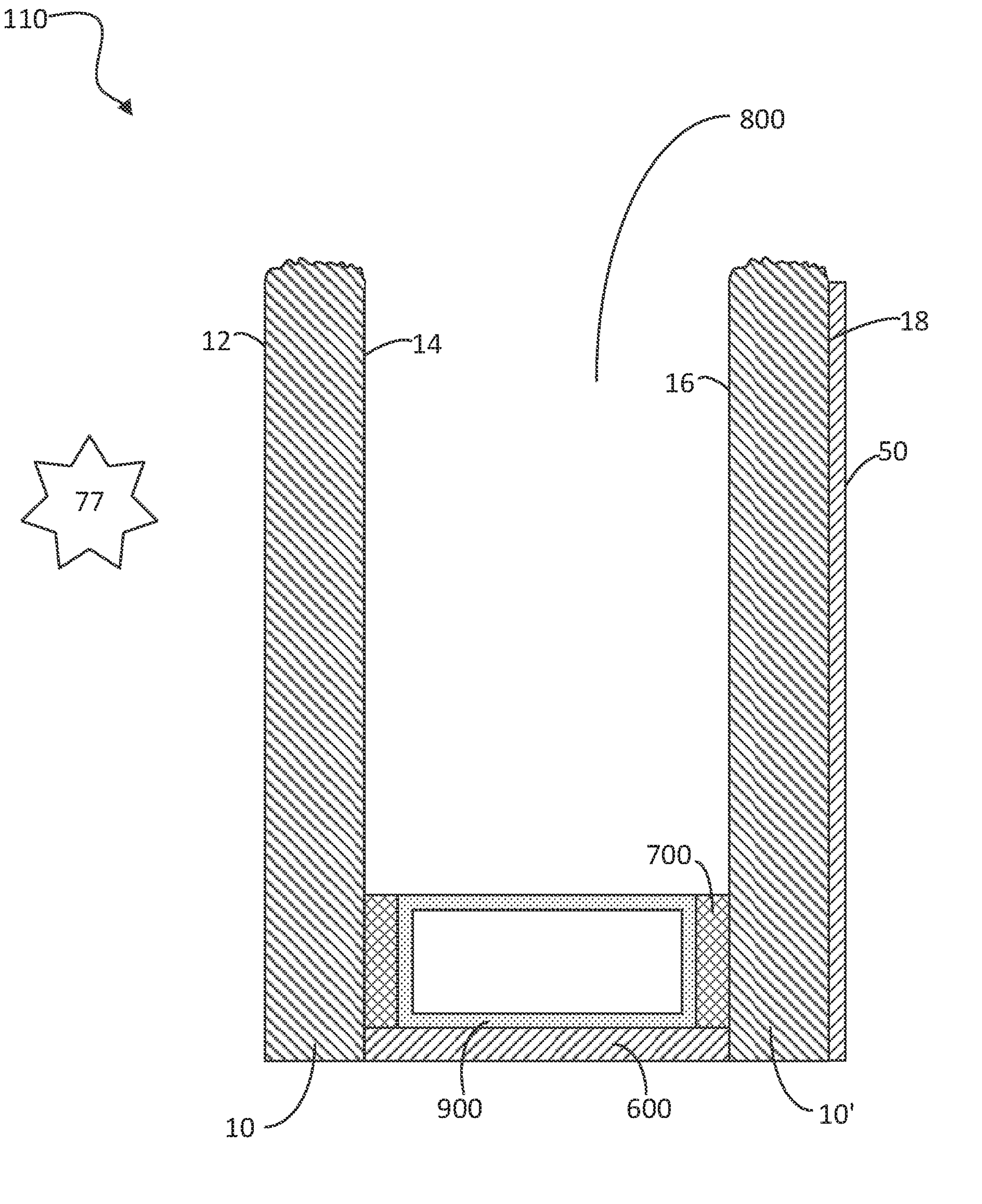


*FIG. 5*

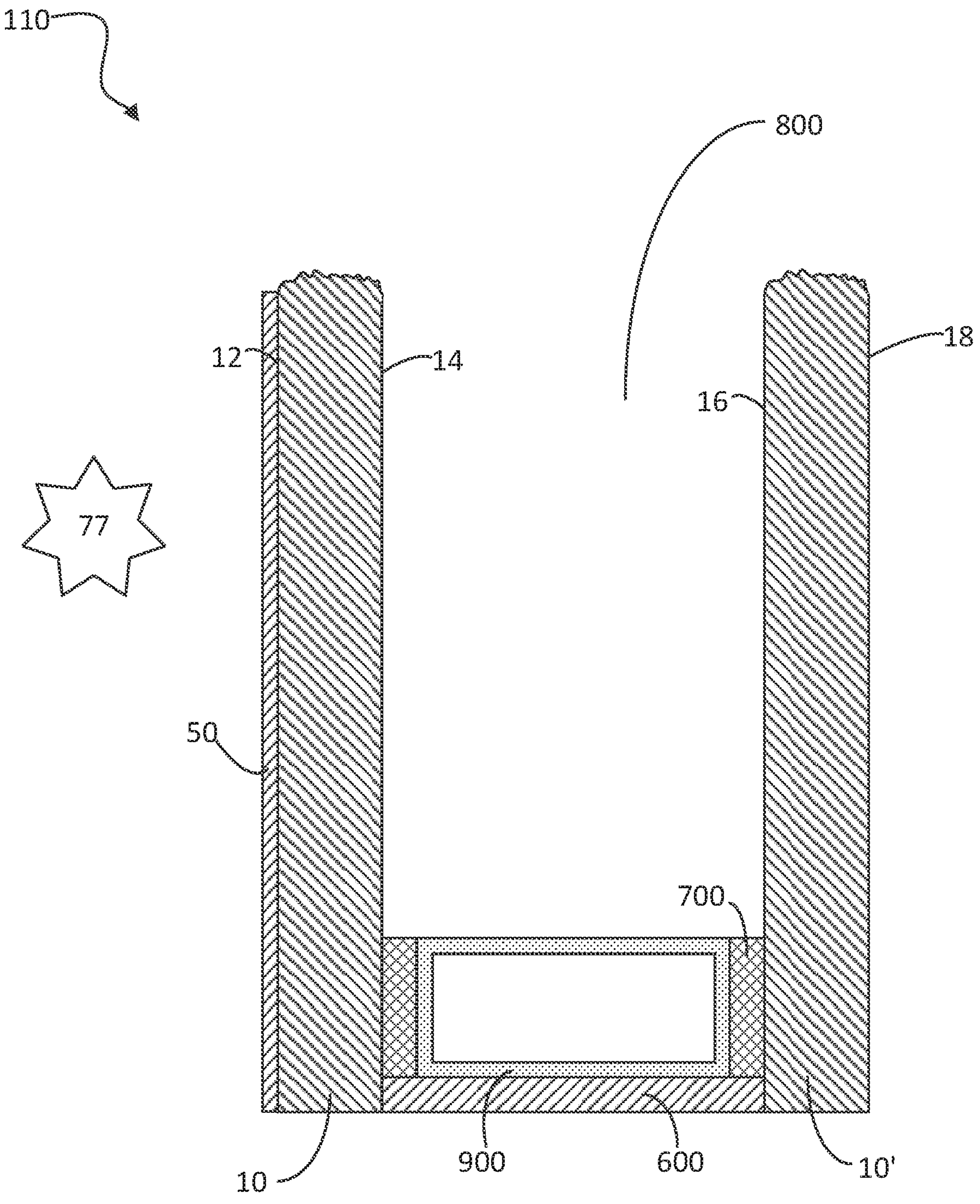
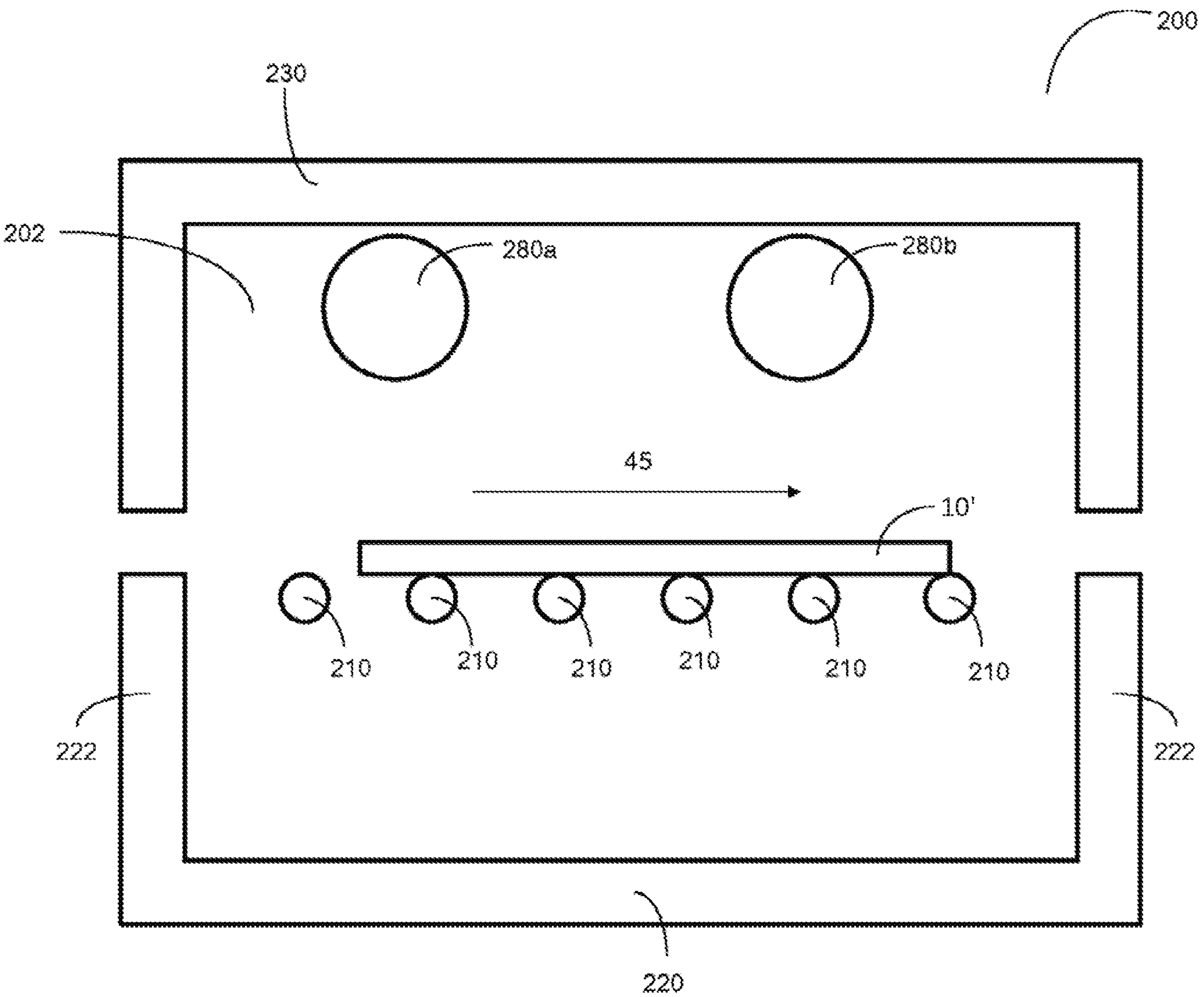


*FIG. 6*



# INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/061919

**A. CLASSIFICATION OF SUBJECT MATTER**
INV. C03C17/00 C03C17/34 C03C17/245 C23C14/00 C23C14/08
C23C14/34
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 C23C

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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| X | WO 2009/036263 A2 (CARDINAL CG CO [US]; MYLI KARI [US]; KRISKO ANNETTE [US]; GERMAN JOHN) 19 March 2009 (2009-03-19)<br>abstract<br>page 1, line 12 - line 19<br>page 7, line 24 - page 13, line 31<br>page 14, line 12 - line 16<br>tables 1-4<br>page 18, line 5 - page 19, line 7<br>page 24, line 15 - page 25, line 20<br>page 26, lines 9-14<br>example 2<br>figures 7-8<br>----- | 1-50 |

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"E" earlier application or patent but published on or after the international filing date

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"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 |
|---|---|
| 19 March 2018 | 28/03/2018 |

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

3

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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| A | US 2005/258030 A1 (FINLEY JAMES J [US] ET AL) 24 November 2005 (2005-11-24)<br>the whole document<br>----- | 1-50 |

3

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