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(54) Title: COLOR SHIFT IMPROVEMENT AFTER HEAT TREATMENT

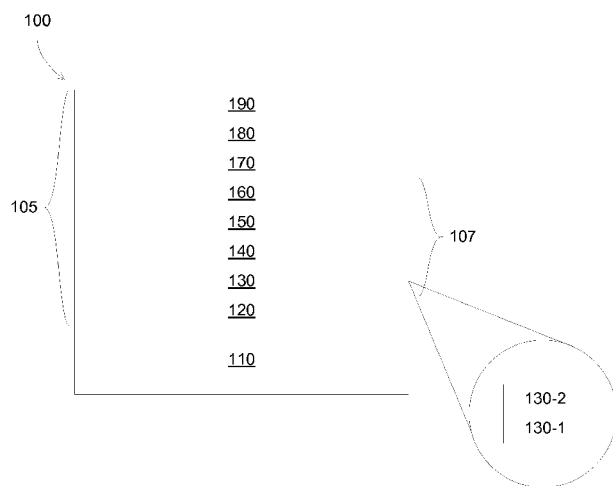


Fig. 1

(57) **Abstract:** Low emissivity panels can include a layer of AlZnSnO between a top dielectric layer and an upper protective layer. The low emissivity panels can also include Ni-Nb-based alloy such as NiNbTiO_x as barrier layer. The low emissivity panels have high light to solar gain, color neutral, together with similar observable color before and after a heat treatment process.



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COLOR SHIFT IMPROVEMENT AFTER HEAT TREATMENT

5 **FIELD OF THE INVENTION**

The present invention relates generally to films providing high transmittance and low emissivity, and more particularly to such films deposited on transparent substrates.

BACKGROUND OF THE INVENTION

10 Sunlight control glasses are commonly used in applications such as building glass windows and vehicle windows, typically offering high visible transmission and low emissivity. High visible transmission can allow more sunlight to pass through the glass windows, thus being desirable in many window applications. Low emissivity can block infrared (IR) radiation to reduce undesirable interior heating.

15 In low emissivity glasses, IR radiation is mostly reflected with minimum absorption and emission, thus reducing the heat transferred to and from the low emissivity surface. Low emissivity, or low-e, panels are often formed by depositing a reflective layer (e.g., silver) onto a substrate, such as glass. The overall quality of the reflective layer, such as with respect to texturing and crystallographic orientation, is important for achieving the desired performance,
20 such as high visible light transmission and low emissivity (i.e., high heat reflection). In order to provide adhesion, as well as protection, several other layers are typically formed both under and over the reflective layer. The various layers typically include dielectric layers, such as silicon nitride, tin oxide, and zinc oxide, to provide a barrier between the stack and both the substrate and the environment, as well as to act as optical fillers and function as anti-reflective coating layers to
25 improve the optical characteristics of the panel.

Low-emissivity coatings can also be engineered to provide desired shading properties. When sunlight reaches a window, a portion can pass through the window, a portion can be reflected, and a portion can be absorbed, (which can increase the temperature of various parts of the window). A portion of the absorbed heat can radiate to the inside of the building, thus
30 increasing the temperature of the air in the building. Thus, when sunlight is incident upon a glass window, in addition to lighting the interior of the building, the incident solar radiation can also pass through the window to increase the temperature of the building. Solar Heat Gain Coefficient (SHGC) is defined as the fractional amount of the solar energy that strikes a window that contributes to warming the building. Other terms can also be used, such as solar shading property
35 or Light to Solar Gain (LSG), which is used to describe the relationship between lighting and heating from solar irradiation. Light to Solar Gain is defined as the ratio of visible light transmission to solar heat gain coefficient. In the hot weather, it is desirable to have high LSG

glass. For example, commercial glass coatings are generally recommended to have LSG greater than 1.8.

There can be a tradeoff between having high visible transmittance and high light to solar gain. Transparent glass can provide high light transmittance but also high solar gain, (e.g., low light to solar gain). Dark glass can provide low solar gain, but also low light transmittance. Low emissivity coatings incorporating silver can provide significant improvements in terms of both visible light transmittance and light to solar gain properties. However, further improvement in light to solar gain is difficult; for example, low emissivity coatings having thicker silver layers, or having multiple silver layers, (e.g., double silver layer or triple silver layer), can reduce the solar heat gain, but at the expense of lower light transmission.

Another desired characteristic of the low-emissivity glass coatings is a color neutral property, (e.g., colorless glass). The glass coatings should not exhibit observable hues, (e.g., more red or blue than is desired).

Another desired characteristic of the low-emissivity glass coatings is temperature stability, (e.g., similar performance and appearance before and after heat treatment). Since glass can be tempered, (e.g., heating the glass to 600 - 700 °C), the appearance of the low-emissivity coatings can change significantly during the heat treatment process. To accommodate the tempering changes, low-emissivity coatings can be provided in a temperable version (e.g., heat treated) and a non-temperable version (non heat treated). This is inconvenient in a manufacturing environment since two separate types of inventory must be maintained. The film stack of the temperable version can be designed to have properties matching those of the non-temperable version.

It would be desirable to provide low-emissivity coatings that can provide high visible transmittance, high light to solar gain, color neutral, and thermal stability for color and optical performance.

SUMMARY OF THE DISCLOSURE

In some embodiments, methods, and coated panels fabricated from the methods, are disclosed to form multiple coatings, (e.g., one or more infrared reflective layers), with minimal color change before and after heat treatments. For example, by adding appropriate dielectric metal oxide layers between the barrier layers and the top protective layers, the color performance can be maintained regardless of high temperature processes.

In some embodiments, the dielectric metal oxide layers can include aluminum, zinc, tin, and oxygen, forming an aluminum zinc tin oxide such as AlZnSnO_x . The thickness of the metal oxide layers can be between 1 and 100 nm. Other elements may be substituted for the aluminum in the AlZnSnO . Examples of these other elements include lithium, sodium, magnesium, potassium, calcium, or titanium.

Disclosed herein are systems, methods, and apparatus for forming low-emissivity (low-E) panels. In some embodiments, methods of fabricating low emissivity panels are disclosed that may include providing a substrate, forming a bottom dielectric stack over the substrate, and forming a seed layer over the bottom dielectric stack. The methods may also include forming a
5 reflective layer over the seed layer, forming a barrier layer over the reflective layer, and forming a top dielectric stack over the barrier layer. The methods may further include applying a heat treatment to the low emissivity panels, where the low emissivity panels include the substrate, the bottom dielectric stack, the seed layer, the reflective layer, the barrier layer, and the top dielectric stack. In some embodiments, the bottom dielectric stack includes a first bottom dielectric layer
10 and a second bottom dielectric layer. The first bottom dielectric layer may include zinc tin oxide. The second bottom dielectric layer may include tin aluminum oxide. Moreover, the top dielectric stack may include a first top dielectric layer and a second top dielectric layer. The first top dielectric layer may include tin aluminum oxide. The second top dielectric layer may include zinc oxide. Furthermore, a glass side reflection of the low emissivity panels may change by less than
15 3% in response to the application of the heat treatment.

In some embodiments, forming the bottom dielectric stack may include reactive sputtering of a first bottom dielectric stack target that includes an alloy of zinc and tin followed by reactive sputtering of a second bottom dielectric stack target that includes an alloy of tin and aluminum. Furthermore, forming the top dielectric stack may include reactive sputtering of a first
20 top dielectric stack target that includes an alloy of tin and aluminum followed by reactive sputtering of a second top dielectric stack target that includes zinc.

In some embodiments, a color of a glass side reflection of the low emissivity panels may change by less than 3% in response to the application of the heat treatment. Further still, a color of a glass side reflection of the low emissivity panels may change by less than 2% in response to
25 the application of the heat treatment. Moreover, a glass side reflection of the low emissivity panels may change by less than 2% in response to the application of the heat treatment, and a transmission of the low emissivity panels may change by less than 3% in response to the application of the heat treatment.

In some embodiments, an atomic ratio of aluminum to tin in the first top dielectric layer is
30 between about 0.3 and 0.65. Moreover, an atomic ratio of aluminum to tin in the second bottom dielectric layer may be between about 0.3 and 0.65. The atomic ratio of zinc to tin in the first bottom dielectric layer may be between about 1.8 and 2.2.

Also disclosed herein are low emissivity panels that may include a substrate, a bottom dielectric stack formed over the substrate, a seed layer formed over the bottom dielectric stack
35 such that the bottom dielectric stack is formed between the seed layer and the substrate, and a reflective layer formed over the seed layer such that the seed layer is formed between the reflective layer and the bottom dielectric stack. The low emissivity panels may further include a

barrier layer formed over the reflective layer such that the reflective layer is formed between the barrier layer and the seed layer, and a top dielectric stack formed over the barrier layer such that the barrier layer is formed between the top dielectric stack and the reflective layer. In some embodiments, the bottom dielectric stack may include a first bottom dielectric layer and a second bottom dielectric layer. The first bottom dielectric layer may include zinc tin oxide. The second bottom dielectric layer may include tin aluminum oxide. The top dielectric stack may include a first top dielectric layer and a second top dielectric layer. The first top dielectric layer may include tin aluminum oxide. The second top dielectric layer may include zinc oxide. The low emissivity panels may be configured to have a glass-side reflection that changes by less than 3% in response to an application of a heat treatment to the low emissivity panels.

In some embodiments, the top dielectric stack has a thickness of between about 5 nm and 30 nm. Moreover, the bottom dielectric stack may have a thickness of between about 5 nm and 30 nm. In some embodiments, an atomic ratio of aluminum to tin in the first top dielectric layer is between about 0.3 and 0.65. Furthermore, the second top dielectric layer might include no metals other than zinc. The first bottom dielectric layer may be formed between the second bottom dielectric layer and the substrate. Moreover, an atomic ratio of aluminum to tin in the second bottom dielectric layer is between about 0.3 and 0.65, and an atomic ratio of zinc to tin in the first bottom dielectric layer is between about 1.8 and 2.2. In some embodiments, the low emissivity panels also include a bottom diffusion layer formed between the substrate and the bottom dielectric stack. A color of a glass side reflection of the low emissivity panels may change by less than 3% in response to the application of the heat treatment to the low emissivity panels.

BRIEF DESCRIPTION OF THE DRAWINGS

To facilitate understanding, identical reference numerals have been used, where possible, to designate identical elements that are common to the figures. The drawings are not to scale and the relative dimensions of various elements in the drawings are depicted schematically and not necessarily to scale.

The techniques of the present invention can readily be understood by considering the following detailed description in conjunction with the accompanying drawings, in which:

Fig. 1 illustrates a low emissivity transparent panel 100 according to some embodiments.

Figs. 2A - 2B illustrate physical vapor deposition (PVD) systems according to some embodiments.

Fig. 3 illustrates an exemplary in-line deposition system according to some embodiments.

Fig. 4 illustrates a low emissivity stack according to some embodiments.

Figs. 5A and 5B illustrate the transmission and reflection of the low emissivity stack before and after a high temperature heat treatment according to some embodiments.

Fig. 6 presents data for before and after a high temperature heat treatment in the format of a scorecard according to some embodiments.

Fig. 7 illustrates a flow chart for sputtering coated layers according to some embodiments.

5 Fig. 8 illustrates a flow chart for sputtering coated layers according to some embodiments.

Fig. 9 presents data for transmission versus wavelength according to some embodiments.

Fig. 10 presents data for a scorecard according to some embodiments.

10 **DETAILED DESCRIPTION OF THE DISCLOSURE**

A detailed description of one or more embodiments is provided below along with accompanying figures. The detailed description is provided in connection with such embodiments, but is not limited to any particular example. The scope is limited only by the claims and numerous alternatives, modifications, and equivalents are encompassed. Numerous
15 specific details are set forth in the following description in order to provide a thorough understanding. These details are provided for the purpose of example and the described techniques may be practiced according to the claims without some or all of these specific details. For the purpose of clarity, technical material that is known in the technical fields related to the embodiments has not been described in detail to avoid unnecessarily obscuring the description.

20 Before various embodiments are described in detail, it is to be understood that unless otherwise indicated, this invention is not limited to specific layer compositions or surface treatments. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to limit the scope of the present invention.

25 It must be noted that as used herein and in the claims, the singular forms “a,” “and” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a layer” includes two or more layers, and so forth.

Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper
30 and lower limit of that range, and any other stated or intervening value in that stated range, is encompassed within the invention. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges, and are also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in
35 the invention. The term “about” generally refers to $\pm 10\%$ of a stated value.

The term “substrate” as used herein may refer to any workpiece on which formation or treatment of material layers is desired. Substrates may include, without limitation, float glass,

low-iron glass, borosilicate glass, display glass, alkaline earth boro-aluminosilicate glass, fusion drawn glass, flexible glass, specialty glass for high temperature processing, polyimide, plastics, polyethylene terephthalate (PET), etc. for either applications requiring transparent or non-transparent substrate functionality.

5 The term “horizontal” as used herein will be understood to be defined as a plane parallel to the plane or surface of the substrate, regardless of the orientation of the substrate. The term “vertical” will refer to a direction perpendicular to the horizontal as previously defined. Terms such as “above”, “below”, “bottom”, “top”, “side” (e.g. sidewall), “higher”, “lower”, “upper”, “over”, and “under”, are defined with respect to the horizontal plane. The term “on” means there
10 is direct contact between the elements. The term “above” will allow for intervening elements.

As used herein, a material (e.g. a dielectric material or an electrode material) will be considered to be “crystalline” if it exhibits greater than or equal to 30% crystallinity as measured by a technique such as x-ray diffraction (XRD).

15 The term “Solar Heat Gain Coefficient (SHGC)” is defined as the fractional amount of the solar energy that strikes a window that contributes to warming the building.

The term “Light to Solar Gain (LSG)” is defined as the ratio of visible light transmission to solar heat gain coefficient.

20 As used herein, the notation “Al-Zn-Sn-O” and “AlZnSnO” and AlZnSnO_x will be understood to be equivalent and will be used interchangeably and will be understood to include a material containing these elements in any ratio. Where a specific composition is discussed, the atomic concentrations (or ranges) will be provided. The notation is extendable to other materials and other elemental combinations discussed herein.

25 As used herein, the terms “film” and “layer” will be understood to represent a portion of a stack. They will be understood to cover both a single layer as well as a multilayered structure (i.e. a nanolaminate). As used herein, these terms will be used synonymously and will be considered equivalent.

30 In some embodiments, methods, and coated panels fabricated from the methods, are disclosed to form low emissivity coatings that can provide high visible transmission, high light to solar gain, and minimal color change before and after heat treatments. The low emissivity coatings can include one or more infrared reflective layers to increase the light to solar gain property. The low emissivity coatings can include material and thickness optimization to increase the visible transmission property. Further, the low emissivity coatings can include top dielectric metal oxide layers so that the color performance can be maintained regardless of high temperature processes.

35 In some embodiments, the second top dielectric metal oxide layer can include a metal oxide layer, such as an aluminum zinc tin oxide (e.g. AlZnSnO_x). The thickness of the second top

dielectric metal oxide layer can be between 1 and 100 nm (e.g., sufficient to protect the first top dielectric during the deposition of the upper protective layer).

In some embodiments, the low emissivity coatings can include a Ni-Nb-based alloy barrier layer for the infrared reflective layers. The Ni-Nb-based alloy barrier layer can include nickel, niobium, and oxygen, together with titanium, aluminum or chromium. For example, the
5 Ni-Nb-based alloy barrier layer can include a nickel niobium titanium oxide, such as NiNbTiO_x , with x between 10 and 30 at%. For example, the NiNbTiO_x layer can be sputtered deposited in a partial oxygen pressure, (e.g., in a mixture of oxygen and argon), to control the amount of oxygen content in the oxide barrier layer. The thickness of the Ni-Nb alloy barrier layer can be between 1
10 and 5 nm, (e.g., sufficient to protect the infrared reflective underlayer).

The low emissivity coatings have high visible light transmission and ability to control the solar gain, (either to achieve high solar gain for the cold weather, (e.g. SHGC >0.5), or to achieve low solar gain for hot weather, which requires high light to solar gain (e.g. LSG > 2)). Further, the low emissivity coatings can be thermally stable, (e.g. minimal color changes of the glass
15 coatings after a high temperature exposure), for example, $R_g \Delta E < 3$ (color change of glass side reflection).

In some embodiments, methods and apparatus for making coated panels are disclosed. The coated panels can include coated layers formed thereon, such as one or more low resistivity thin infrared reflective layers having a conductive material such as silver. The infrared reflective
20 layer(s) can include a conductive material, with the percentage of reflectance proportional to the conductivity. Thus, a metallic layer, for example silver, can be used as infrared reflective layer(s) in low emissivity coatings. To maintain the conductivity of the infrared reflective layer against oxidation from deposition of subsequent layers or from subsequent high temperature anneals, a barrier layer can be formed on the infrared reflective layer.

25 In some embodiments, improved coated transparent panels, such as a coated glass, that has acceptable visible light transmission and IR reflection are disclosed. Methods of producing the improved coated transparent panels, which include specific layers in a coating stack, are also disclosed.

The coated transparent panels can include a glass substrate or any other transparent
30 substrates, such as substrates made of organic polymers. The coated transparent panels can be used in window applications such as vehicle and building windows, skylights, or glass doors, either in monolithic glazings or multiple glazings, with or without a plastic interlayer or a gas-filled sealed interspace.

Fig. 1 illustrates a low emissivity transparent panel 100 according to some embodiments.
35 The low emissivity transparent panel can include a glass substrate 110 and a low emissivity (low-e) stack 105 formed over the glass substrate 110. In some embodiments, the glass substrate 110 is made of a glass, such as borosilicate glass, and has a thickness of, for example, between 1 and 10

millimeters (mm). The substrate 110 may be square or rectangular and about 0.5 – 2 meters (m) across. For example, for low-E applications, the substrate may be transparent. Specifically, a transparent glass substrate may be used for this and other applications. For purposes of this disclosure, the term "transparency" is defined as a substrate characteristic related to a visible light transmittance through the substrate. The term "translucent" is defined as a property of passing the visible light through the substrate and diffusing this energy within the substrate, such that an object positioned on one side of the substrate is not visible on the other side of the substrate. The term "opaque" is defined as a visible light transmittance of 0%. Some examples of suitable materials for substrate 102 include, but are not limited to, plastic substrates, such as acrylic polymers (e.g., polyacrylates, polyalkyl methacrylates, including polymethyl methacrylates, polyethyl methacrylates, polypropyl methacrylates, and the like), polyurethanes, polycarbonates, polyalkyl terephthalates (e.g., polyethylene terephthalate (PET), polypropylene terephthalates, polybutylene terephthalates, and the like), polysiloxane containing polymers, copolymers of any monomers for preparing these, or any mixtures thereof. Substrate 110 may be also made from one or more metals, such as galvanized steel, stainless steel, and aluminum. Other examples of substrate materials include ceramics, glass, and various mixtures or combinations of any of the above.

The low-e stack 105 can include a lower protective layer 120, an infrared reflective stack 107, a first top dielectric layer 170, a second top dielectric layer 180, and an upper protective layer 190. The infrared reflective stack 107 can include a bottom dielectric layer 130, a seed layer 140, a reflective layer 150, and a barrier layer 160. The infrared reflective stack 107 can be repeated for multiple reflective layer applications such as "double-silver (e.g. two reflective stacks)" or "triple silver (e.g. three reflective stacks)" low-e stacks. Some layers can be optional, and other layers can be added, such as interface layers or adhesion layers. Exemplary details as to the functionality provided by each of the layers 120-190 are provided below.

The various layers in the low-e stack 105 may be formed sequentially (i.e., from bottom to top) on the substrate 110 using a physical vapor deposition (PVD) and/or reactive (or plasma enhanced) sputtering processing tool. For example, the layers can be sputtered deposited using different processes and equipment, for example, the targets can be sputtered under direct current (DC), pulsed DC, alternate current (AC), radio frequency (RF) or any other suitable conditions. In some embodiments, the low-e stack 105 is formed over the entire glass substrate 110. However, in some embodiments, the low-e stack 105 may only be formed on isolated portions of the substrate 110.

The lower protective layer (e.g. a first layer) 120 is formed on the upper surface of the glass substrate 110. The lower protective layer 120 can include silicon nitride, silicon oxynitride, or other nitride material such as silicon zirconium nitride, to protect the other layers in the stack 105 from diffusion of contaminants from the substrate 110 or to improve the haze reduction

properties. In some embodiments, the lower protective layer 120 is made of silicon nitride and has a thickness of, for example, between about 5 nm to 50 nm, such as 25 nm. In some embodiments, silicon nitride may be doped with aluminum and/or zirconium. The dopant concentration may be between about 0% to 20% by weight. In some embodiments, silicon nitride may be partially oxidized. Silicon nitride diffusion layers may be silicon-rich, such that their compositions may be represented by the following expression, Si_xN_y , where the X-to-Y ratio is between about 0.8 and 1.0. The refractive index lower protective layer 120 may be between about 2.0 and 2.5 or, more specifically, between about 2.15 to 2.25.

In addition to protecting stack 100 from the environment, lower protective layer 120 may help with adhering bottom dielectric layer 130 to substrate 110. Without being restricted to any particular theory, it is believed that deposition of bottom dielectric layer 130 and subsequent heat treatment of this layer results in heat-induced mechanical stresses at the interfaces of bottom dielectric layer 130. These stresses may cause delamination of bottom dielectric layer 130 from other layers and coating failure. A particular example is a titanium oxide layer deposited directly onto the glass substrate. However, when silicon nitride lower protective layer 120 is provided between bottom dielectric layer 130 and substrate 110, the adhesion within this multi-layer stack remains strong as evidenced by improved durability, especially after heat treatment.

The bottom dielectric layer (e.g. a second layer) 130 is formed above the lower protective layer 120 and above the substrate 110. The bottom dielectric layer 130 may include a single layer or may include multiple layers (e.g. 130-1, 130-2). The bottom dielectric oxide layer is preferably a metal or metal alloy oxide layer and can serve as an antireflective layer. The bottom dielectric oxide layer 130 may enhance the crystallinity of the reflective layer 150, for example, by enhancing the crystallinity of a seed layer 140 for the reflective layer 150, as is described in greater detail below.

As stated above, bottom dielectric layer 130 may include several layers. For example, bottom dielectric layer 130 may include a first bottom dielectric layer 130-1 and a second bottom dielectric layer 130-2. First bottom dielectric layer may be a layer that is formed between the second bottom dielectric layer and the substrate. In some embodiments, the first bottom dielectric layer may directly interface the second bottom dielectric layer and lower protective layer 120. First bottom dielectric layer 130-1 may include a material that is a metal oxide, such as zinc tin oxide. In some embodiments, an atomic ratio of zinc to tin in the first bottom dielectric layer is between about 1.8 and 2.2. Applicants have determined that if this ratio is too high or too low, the zinc tin oxide is no longer amorphous and experiences undesirable color changes when a heat treatment is applied. Accordingly, an atomic ratio of zinc to tin in the first bottom dielectric layer is preferably between about 1.8 and 2.2.

Bottom dielectric layer 130 may further include a second bottom dielectric layer 130-2. In some embodiments, the second bottom dielectric layer may be formed between reflective layer

150 and the first bottom dielectric layer. The second bottom dielectric layer may directly interface the first bottom dielectric layer and seed layer 140. The second bottom dielectric layer may also include a material that is a metal oxide. In some embodiments, the second bottom dielectric layer 130-2 may include tin aluminum oxide. A ratio of aluminum to tin in the second
5 bottom dielectric layer may be between about 0.3 and 0.65.

In some embodiments, one or both of the bottom dielectric layers may include dopants, such as Al, Ga, In, Mg, Ca, Sr, Sb, Bi, Ti, V, Y, Zr, Nb, Hf, or Ta. The bottom dielectric layers can each include different dielectric materials with similar refractive indices or different materials with different refractive indices. The relative thicknesses of the bottom dielectric layers can be
10 varied to optimize thermal-management performance, aesthetics, and/or durability of the coated article.

The seed layer (e.g. a third layer) 140 can be used to provide a seed layer for the IR reflective layer. For example, a zinc oxide layer deposited before the deposition of a silver reflective layer can provide a silver layer with lower resistivity, which can improve its reflective
15 characteristics. The seed layer 140 can include a metal such as titanium, zirconium, and/or hafnium, or a metal alloy such as zinc oxide, nickel oxide, nickel chrome oxide, nickel alloy oxides, chrome oxides, or chrome alloy oxides.

In some embodiments, the seed layer 140 can be made of a metal, such as titanium, zirconium, and/or hafnium, and has a thickness of, for example, 50 Å or less. Generally, seed
20 layers are relatively thin layers of materials formed on a surface (e.g., a substrate) to promote a particular characteristic of a subsequent layer formed over the surface (e.g., on the seed layer). For example, seed layers may be used to affect the crystalline structure (or crystallographic orientation) of the subsequent layer, which is sometimes referred to as "templating." More particularly, the interaction of the material of the subsequent layer with the crystalline structure of
25 the seed layer causes the crystalline structure of the subsequent layer to be formed in a particular orientation.

For example, a metal seed layer is used to promote growth of the reflective layer in a particular crystallographic orientation. In some embodiments, the metal seed layer is a material with a hexagonal crystal structure and is formed with a (002) crystallographic orientation which
30 promotes growth of the reflective layer in the (111) orientation when the reflective layer has a face centered cubic crystal structure (e.g., silver), which is preferable for low-e panel applications.

In some embodiments, the crystallographic orientation can be characterized by X-ray diffraction (XRD) technique, which is based on observing the scattered intensity of an X-ray beam incident upon the layer, (e.g., the silver layer or seed layer), as a function of the scattered
35 angles. For example, a zinc oxide seed layer can show a pronounced (002) peak and higher orders in a θ - 2θ diffraction pattern. This suggests that zinc oxide crystallites with the respective planes oriented parallel to the substrate surface are present.

In some embodiments, the terms "silver layer having (111) crystallographic orientation", or "zinc oxide seed layer having (002) crystallographic orientation" include a meaning that there is a (111) crystallographic orientation for the silver layer or a (002) crystallographic orientation for the zinc oxide seed layer, respectively. The crystallographic orientation can be determined by
5 observing pronounced crystallography peaks in an XRD characterization.

In some embodiments, the seed layer 140 can be continuous and covers the entire substrate. Alternatively, the seed layer 140 may not be formed in a completely continuous manner. The seed layer can be distributed across the substrate surface such that each of the seed layer areas is laterally spaced apart from the other seed layer areas across the substrate surface and
10 do not completely cover the substrate surface. For example, the thickness of the seed layer 140 can be a monolayer or less, such as between 2.0 and 4.0 Å, and the separation between the layer sections may be the result of forming such a thin seed layer (i.e., such a thin layer may not form a continuous layer).

The IR reflective layer (e.g. a fourth layer) 150 is formed above the seed layer 140. The
15 IR reflective layer can be a metallic, reflective film, such as silver, gold, or copper. In general, the IR reflective layer includes a good electrical conductor, blocking the passage of thermal energy. In some embodiments, the IR reflective layer 150 is made of silver and has a thickness of between about 7nm to about 20nm. Because the IR reflective layer 150 is formed on the seed layer 140, the growth of the silver IR reflective layer 150 in a (111) crystalline orientation is
20 promoted (e.g. due to the (002) crystallographic orientation of the seed layer 140), which offers low sheet resistance, leading to low panel emissivity.

Because of the promoted (111) textured orientation of the IR reflective layer 150, the conductivity and emissivity of the IR reflective layer 150 is improved. As a result, a thinner reflective layer 150 may be formed that still provides sufficient reflective properties and visible
25 light transmission. Additionally, the reduced thickness of the IR reflective layer 150 allows for less material to be used in each panel that is manufactured, thus improving manufacturing throughput and efficiency, increasing the usable life of the target (e.g., silver) used to form the reflective layer 150, and reducing overall manufacturing costs.

Further, the seed layer 140 can provide a barrier between the bottom dielectric layer 130
30 and the IR reflective layer 150 to reduce the likelihood of any reaction of the material of the reflective layer 150 and the oxygen in the bottom dielectric layer 130, especially during subsequent heating processes. As a result, the resistivity of the reflective layer 150 may be reduced, thus increasing performance of the reflective layer 150 by lowering the emissivity.

In some embodiments, barrier layers can be formed on an infrared reflective layer to
35 protect the infrared reflective layer from impurity diffusion, together with exhibiting good adhesion and good optical properties, for example, during the fabrication process.

The barrier layer (e.g. a fifth layer) 160 is formed above the IR reflective layer 150. The barrier layer 160 can include at least one of nickel, niobium, titanium, aluminum, or chromium, and oxygen. The silver layer should be as pure as possible to maintain its low emissivity performance. The layer immediately on top of the silver layer (e.g., the barrier layer) can be important in protecting the silver from oxidation, such as during oxygen reactive sputtering processes in the deposition of subsequent layers. In addition, this barrier layer can protect the silver layer against reaction with oxygen diffusion during the glass tempering process, or during long term use where the panel may be exposed to moisture or the environment.

In some embodiments, barrier layer 160 may be formed from a partially oxidized alloy of at least nickel, titanium, and niobium. Barrier layer 160 may be formed from a quaternary alloy that includes nickel, chromium, titanium, and aluminum. The concentration of each metal in this alloy is selected to provide adequate transparency and oxygen diffusion blocking properties. In some embodiments, a combined concentration of nickel and chromium in the barrier layer is between about 20% by weight and 50% by weight or, more specifically, between about 30% by weight and 40% by weight. A weight ratio of nickel to chromium in the alloy may be between about 3 and 5 or, more specifically, about 4. A weight ratio of titanium to aluminum is between about 0.5 and 2, or more, specifically about 1. In some embodiments, the concentration of nickel in the barrier layer is between about 5% and 10% by weight, the concentration of chromium - between about 25% and 30% by weight, the concentration of titanium and aluminum - between about 30% and 35% by weight each. This composition of barrier layer 160 may be achieved by using one or more sputtering targets containing nickel, chromium, titanium, and aluminum, controlling concentration of these metals in the sputtering targets, and controlling power levels applied to each sputtering target. For example, two sputtering targets may be used. The first target may include nickel and chromium, while the second target may include titanium and aluminum. The weight ratio of nickel to chromium in the first target may be about 4, while the weight ratio of titanium to aluminum in the second target may be about 1. These weight ratios may be achieved by using corresponding alloys for the entire target, target inserts made from different materials, or other features allowing combination of two or more materials in the same target. The two targets may be exposed to different power levels. In the above example, the first target may be exposed to twice smaller power than the second target to achieve the desired composition. The barrier can be deposited substantially free of oxygen (e.g., predominantly as a metal) in the inert environment (e.g., argon environment). Alternatively, some oxidant (e.g., 15% by volume of O₂ in Ar) may be used to oxidize the four metals. The concentration of oxygen in the resulting barrier layer may be between about 0% and 5% by weight.

In some embodiments, nickel, chromium, titanium, and aluminum are all uniformly distributed throughout the barrier layer, (i.e., its entire thickness and coverage area). Alternatively, the distribution of components may be non-uniform. For example, nickel and

chromium may be more concentrated along one interface than along another interface. In some embodiments, a portion of the barrier layer near the interface with the reflective layer includes more nickel for better adhesion to the reflective layer. In some embodiments, substantially no other components other than nickel, chromium, titanium, and aluminum are present in barrier layer 160.

Barrier layer 160 may be amorphous metal. For purposes of this disclosure, an amorphous metal may be an amorphous material if the crystalline phase composes less than 5% of the material by volume. Barrier layer 160 may be a layer of a material, such as NiTiNb which may be configured to have a thickness between about 1.5nm and 5nm. In one example, barrier layer 160 has a thickness of 2.4nm. Barrier layer 160 may be formed using a deposition technique, such as sputtering. During the forming process, a small amount of oxygen may be mixed with Argon to create a layer of NiTiNb oxide having an oxygen content between 10% to 30% by atomic weight. In some embodiments, barrier layer 160 may have a thickness of between about 1 Angstrom and 100 Angstroms or, more specifically, between about 5 Angstroms and 30 Angstroms, and even between about 10 Angstroms and 20 Angstroms.

Without being restricted to any particular theory, it is believed that when the barrier layer is exposed to oxygen (e.g., during deposition of the top dielectric), some metals of the barrier layer (e.g., Cr, Ti, and Al) will be easily oxidized thereby consuming oxygen and preventing oxygen from penetrating through the barrier layer and reaching the reflective layer. As such, the barrier layer may be considered as a scavenging layer.

In addition to the oxygen diffusion barrier property, there are other desirable properties for the barrier layer. For example, since the barrier layer is placed directly on the silver layer, low or no solubility of the barrier material in silver is desirable to minimize reactivity between the barrier layer and silver at the interface. The reaction between the barrier layer and silver can introduce impurities in the silver layer, potentially reducing the conductivity.

First top dielectric layer (e.g. a sixth layer) 170 is formed above the barrier layer 160 which can function as an antireflective film stack, including a single layer or multiple layers having different functional purposes. The first top dielectric layer 170 can serve to reduce the reflection of visible light. The first top dielectric layer 170 can be selected based on transmittance, index of refraction, adherence, chemical durability, and thermal stability. In some embodiments, the first top dielectric layer 170 includes aluminum tin oxide (AlSnO), offering high thermal stability properties. The first top dielectric layer 170 can also include titanium dioxide, silicon nitride, silicon dioxide, silicon oxynitride, niobium oxide, silicon zirconium nitride, tin oxide, zinc oxide, or any other suitable dielectric material. First top dielectric layer 170 may be a layer that is formed between second top dielectric layer 180 and reflective layer 150. In some embodiments, first top dielectric layer 170 may directly interface second top dielectric layer 180 and barrier layer 160. First top dielectric layer 170 may include a material

that is a metal oxide, such as tin aluminum oxide. In some embodiments, an atomic ratio of aluminum to tin in first top dielectric layer 170 is between about 0.3 and 0.65.

The second top dielectric layer (e.g. a seventh layer) 180 can be used to provide a proper thickness to the low-e stack, (e.g. to provide an antireflective property). The second top dielectric layer preferably has high visible light transmittance. In some embodiments, the second top dielectric layer 180 is made of tin oxide or zinc oxide and has a thickness of, for example, between 3nm and 60nm, such as between 3nm and 20nm. In some embodiments, the second top dielectric layer 180 is made of aluminum zinc tin oxide (AlZnSnO) and has a thickness of, for example between 3nm and 60nm, such as between 3nm and 20nm. The second top dielectric layer may be used to tune the optical properties of the low-e panel 100. For example, the thickness and refractive index of the second top dielectric layer may be used to increase the layer thickness to a multiple of the incoming light wavelengths, effectively reducing the light reflectance and improving the light transmittance.

An upper protective layer (e.g. an eighth layer) 190 is formed above the second top dielectric layer 180 and can be used for protecting the total film stack, to protect the panel from physical or chemical abrasion. The upper protective layer 190 can be an exterior protective layer, such as silicon nitride, silicon oxynitride, titanium oxide, tin oxide, zinc oxide, niobium oxide, or silicon zirconium nitride.

Some of the benefits of using AlSnO as the first top dielectric layer 170 are described in co-owned and co-pending U.S. Patent Application 14/139,350, filed on December, 23, 2013, which claims priority to U.S. Provisional Patent Application No. 61/778,758, filed on March 13, 2013; U.S. Patent Application No. xx/xxx,xxx, filed on March, xx, 2014, entitled "*High LSG Low-Emissivity Coating with Minimal Color Change During Heat Treatment*", and having Attorney Docket No. IM1084_US_V, which claims priority to U.S. Provisional Patent Application No. 61/778,758, filed on March 13, 2013; each of which is herein incorporated by reference for all purposes.

The AlSnO first top dielectric layer 170 will react with the silicon nitride upper protective layer 190 and degrade the overall performance of the stack. Without being limited by theory, it is believed that the tin in the AlSnO upper oxide layer reacts with the nitrogen during the deposition of the overlying silicon nitride layer and forms SnO_xN_y . Additionally, color changes were observed between the as coated stack and the heat treated stack. A thin layer of ZnO can be inserted between the AlSnO first top dielectric layer 170 and the silicon nitride upper protective layer 190. However, color changes were observed between the as coated stack and the heat treated stack due to the low crystallization temperature of the ZnO layer, resulting in a color change after heat treatment. As discussed herein, a layer of AlZnSnO can be used as the second top dielectric 180 between the first top dielectric layer 170 and the silicon nitride upper protective

layer 190. The AlZnSnO layer remains amorphous after the heat treatment and results in minimal color change after the heat treatment.

In some embodiments, adhesion layers can be used to provide adhesion between layers. The adhesion layers can be made of a metal alloy, such as nickel-titanium, and have a thickness of, for example, 30 Å.

Depending on the materials used, some of the layers of the low-e stack 105 may have some elements in common. An example of such a stack may use a zinc-based material in the oxide dielectric layers 130 and 170. As a result, a relatively low number of different sputtering targets can be used for the formation of the low-e stack 105.

Further, in the fabrication of low emissivity coated panels, high temperature processes can be used to anneal the deposited films or to temper the substrate. The high temperature processes can have adverse effects on the low emissivity coating, such as changing the structure or the optical properties, (e.g., index of refraction n or absorption coefficient k), of the coated films. Thus thermal stability with respect to optical properties is desirable.

In some embodiments, the coating can include multiple infrared reflective stacks 107, such as a double or triple infrared reflective stacks with two or three infrared reflective silver layers.

In some embodiments, the effects of the deposition process of the layers deposited above the silver IR reflective layer on the quality of the silver IR reflective layer are disclosed. Since the silver IR reflective layer is desirably thin, (e.g. less than 20 nm, to provide high visible light transmission), the quality of the silver IR reflective layer can be affected by the deposition of the subsequently deposited layers, such as the barrier layer or the antireflective layer.

In some embodiments, sputter deposition processes, which can be applied for a barrier layer deposited on an IR reflective layer, are disclosed. For example, the barrier layer can protect the IR reflective layer from being oxidized. The barrier layer can function as an antireflective layer. The materials of the barrier layer can reduce reaction for the IR reflective underlayer such as oxidation, preventing resistivity and emissivity degradation.

In some embodiments, the alloy barrier layer can be sputtered from an alloyed target, or co-sputtered from different elemental targets onto the same substrate. The process may include oxygen to make the film oxidized, or may be in pure Ar (which will deposit a metallic barrier layer) followed by an exposure to an oxygen ambient, (e.g., during a subsequent metal oxide layer deposition or a subsequent oxidation anneal process).

Figs. 2A - 2B illustrate physical vapor deposition (PVD) systems according to some embodiments. In Fig. 2A, a PVD system, also commonly called sputter system or sputter deposition system, 200 includes a housing that defines, or encloses, a processing chamber 240, a substrate 230, a target assembly 210, and reactive species delivered from an outside source through a gas inlet 220. During deposition, the target is bombarded with argon ions, which

releases sputtered particles toward the substrate 230. The sputter system 200 can perform blanket deposition on the substrate 230, forming a deposited layer that covers the whole substrate, (e.g., the area of the substrate that can be reached by the sputtered particles generated from the target assembly 210).

5 The materials used in the target of target assembly 210 may include nickel, niobium and titanium for the barrier layer, silver for the IR reflective layer, and other metals for other layers. Additionally, the materials used in the targets may include oxygen, nitrogen, or a combination of oxygen and nitrogen in order to form the oxides, nitrides, and oxynitrides of the metals described above. The different targets can be used to deposit different layers in the low-e coating stack, in
10 addition to the barrier layer. Additionally, although only one target assembly 210 is shown, additional target assemblies may be used. As such, different combinations of targets may be used to form the dielectric layers described above. For example, in some embodiments in which the dielectric material is zinc-tin-oxide, the zinc and the tin may be provided by separate zinc and tin targets, or they may be provided by a single zinc-tin alloy target. A target assembly 210 can
15 include a silver target to sputter deposit a silver layer on substrate 230. The target assembly 210 can include a metal or metal alloy target, and together with reactive species of oxygen and/or nitrogen to sputter deposit a metal alloy oxide layer, a metal alloy nitride layer, or a metal alloy oxynitride layer.

 The sputter deposition system 200 can include other components, such as a substrate
20 support for supporting the substrate. The substrate support can include a vacuum chuck, electrostatic chuck, or other known mechanisms. The substrate support can be capable of rotating around an axis thereof that is perpendicular to the surface of the substrate. In addition, the substrate support may move in a vertical direction or in a planar direction. It should be appreciated that the rotation and movement in the vertical direction or planar direction may be
25 achieved through known drive mechanisms which include magnetic drives, linear drives, worm screws, lead screws, a differentially pumped rotary feed through drive, etc.

 In some embodiments, the substrate support includes an electrode which is connected to a power supply to provide a RF or DC bias to the substrate, or to provide a plasma environment in the processing chamber 240. The target assembly 210 can include an electrode which is connected
30 to a power supply to generate a plasma in the process housing. The target assembly 210 is preferably oriented towards the substrate 230.

 The sputter deposition system 200 can also include a power supply coupled to the target electrode. The power supply provides power to the electrodes, causing material to be sputtered from the target. During sputtering, inert gases, such as argon or krypton, may be introduced into
35 the processing chamber 240 through the gas inlet 220. In embodiments in which reactive sputtering is used, reactive gases may also be introduced, such as oxygen and/or nitrogen, which

interact with particles ejected from the targets to form oxides, nitrides, and/or oxynitrides on the substrate.

The sputter deposition system 200 can also include a control system (not shown) having a processor and a memory, which is in operable communication with the other components and
5 configured to control the operation thereof in order to perform the methods described herein.

Fig. 2B shows a sputter system having co-sputtering targets according to some embodiments. A sputter deposition chamber 205 can include two target assemblies 212 and 214 disposed in a plasma environment 245, containing reactive species delivered from an outside source 225. For example, the target assemblies 212 and 214 can include the metal elements of the
10 alloy base oxide layer, (e.g., Al and Sn), together with reactive species of oxygen to deposit a base layer of an alloy of aluminum-tin-oxide on substrate 230. This configuration serves as an example, and other sputter system configurations can be used, such as a single target having an alloy material.

In some embodiments, methods and apparatus for making low emissivity panels,
15 including forming an IR reflective layer formed under or over a barrier structure that includes an alloy of nickel titanium niobium oxide are disclosed. The panels can exhibit optimal IR reflectance, improved color neutrality, thermal stability, and durability due to the barrier layer protecting the IR reflective layer while not degrading the low emissivity coating characteristics.

In some embodiments, methods and apparatus for making low emissivity panels,
20 including forming an AlZnSnO layer between an upper oxide layer and an upper protective layer are disclosed. The panels can exhibit optimal IR reflectance, improved color neutrality, thermal stability, and durability due to the barrier layer protecting the IR reflective layer while not degrading the low emissivity coating characteristics. Other elements may be substituted for the aluminum. Examples of these other elements include lithium, sodium, magnesium, potassium,
25 calcium, or titanium.

In some embodiments, methods for making low emissivity panels in large area coaters are disclosed. A transport mechanism can be provided to move a substrate under one or more sputter targets, to deposit a conductive layer underlayer before depositing a barrier layer, an antireflective layer, together with other layers such as a surface protection layer.

30 In some embodiments, in-line deposition systems, including a transport mechanism for moving substrates between deposition stations are disclosed.

Fig. 3 illustrates an exemplary in-line deposition system according to some embodiments. A transport mechanism 370, such as a conveyor belt or a plurality of rollers, can transfer substrate 330 between different sputter deposition stations. For example, the substrate can be positioned at
35 station #1, having a target assembly 310A, then transferred to station #2, having target assembly 310B, and then transferred to station #3, having target assembly 310C. The station #1 having target assembly 310A can be a silver deposition station, sputtering an IR reflective layer including

silver. The station #2 having target assembly 310B can be a barrier deposition station, sputtering a metallic oxide alloy. As shown, the station #2 includes a single target assembly 310B.

However, other configurations can be used, such as co-sputtering system utilizing multiple targets. The station #3 having target 310C assembly can be used to deposit other layers, such as an antireflective layer or a protection layer.

In some embodiments, methods, and coated panels fabricated from the methods, are disclosed to form multiple coatings, (e.g., multiple infrared reflective layers), with minimal color change before and after heat treatments. The methods can include forming a second top dielectric layer between a first top dielectric layer and an upper protective layer to improve the thermal stability, such as color resistance to thermal exposures. The second top dielectric layers can include a metal oxide layer, such as an aluminum zinc tin oxide (AlZnSnO) layer. In some embodiments, some or all of the aluminum in the AlZnSnO second top dielectric layer can be replaced by one or more of lithium, sodium, magnesium, potassium, calcium, or titanium.

Fig. 4 illustrates an example of a low emissivity stack 400 according to some embodiments. In Fig. 4, a low emissivity stack 400 includes a second top dielectric layer (e.g. the seventh layer) 480 acting as a spacer to separate a first top dielectric layer 470 and an upper protective layer 490. The low emissivity stack in Fig. 4 is similar to the low emissivity stack discussed previously with respect to Fig. 1. The substrate 410, the lower protective layer 420, the bottom dielectric layer(s) 430, the seed layer 440, the IR reflective layer 450, the barrier layer, 460, the first top dielectric layer 470, and the upper protective layer 490, have the same composition options and properties as discussed previously.

In some embodiments, first top dielectric layer 470 includes AlSnO. The thickness of the AlSnO layer can be between 5nm and 100 nm.

In some embodiments, a second top dielectric layer 480 is formed above the first top dielectric layer 470. The second top dielectric layer 480 is operable to protect the first top dielectric layer from a subsequently deposited upper protective layer 490. In some embodiments, the second top dielectric layer comprises AlZnSnO. In some embodiments, some or all of the aluminum in the AlZnSnO second top dielectric layer 480 can be replaced by one or more of lithium, sodium, magnesium, potassium, calcium, or titanium.

In some embodiments, a low emissivity stack is provided, which can have high visible light transmission, high light to solar gain, color neutrality, and small color change after thermal cycles. The low emissivity stack can include a lower protection layer (e.g. a first layer), such as silicon nitride, on a glass substrate. The thickness of the silicon nitride can be between 10 and 30 nm. Above the silicon nitride layer is formed an infrared reflective stack. The infrared reflective stack can include (from top to bottom) a barrier layer (e.g. a fifth layer), such as NiNbTiO_x, formed above an infrared reflective layer (e.g. a fourth layer), such as silver, formed above a seed layer (e.g. a third layer), such as ZnO, formed above a bottom dielectric layer (e.g. a second

layer), such as AlSnO or Zn_2SnO_x . The thickness of the NiNbTiO_x barrier layer can be between 1 and 5 nm. The thickness of the silver layer can be between 7 and 12 nm. The thickness of the ZnO seed layer can be between 3 and 10 nm. The thickness of the AlSnO or Zn_2SnO_x bottom dielectric layer can be between 10 and 40 nm. Additional infrared reflective stacks can be formed above the first infrared reflective stack. Above the infrared reflective stack(s) is a first top dielectric layer (e.g. a sixth layer), such as AlSnO. The thickness of the AlSnO first top dielectric layer can be between 10 and 40 nm. Above the first top dielectric layer is formed a second top dielectric layer (e.g. a seventh layer), such as AlZnSnO. The thickness of the AlZnSnO second top dielectric layer can be between 3 and 60 nm. In some embodiments, some or all of the aluminum in the AlZnSnO second top dielectric layer can be replaced by one or more of lithium, sodium, magnesium, potassium, calcium, or titanium. Above the second top dielectric layer is an upper protective layer (e.g. an eighth layer), such as silicon nitride. The thickness of the silicon nitride upper protective layer can be between 10 and 30 nm.

Optical properties of the low emissivity stacks were measured before and after the heat treatment. Figs. 5A and 5B illustrate the transmission and reflection of the low emissivity stacks before and after a high temperature heat treatment according to some embodiments. Fig. 5A presents data for the low emissivity stacks without the use of the AlZnSnO second top dielectric layer (e.g. a ZnO second top dielectric layer was used). Fig. 5B presents data for the low emissivity stacks with the use of the AlZnSnO second top dielectric layer. The solid and dashed curves 510 show the transmission response through the low emissivity stack. High transmission, (e.g., maximum above 80 %), can be achieved for the visible light range, (e.g., between 400 and 750 nm). The solid and dashed curves 520 show the reflection response from the coating side ("F" series in the chart legend). Low reflection, (e.g., minimum below 5 %), can be achieved for the visible light range, (e.g., between 400 and 750 nm). High reflection, (e.g., maximum above 90 %), can be achieved for the infrared range, (e.g., between 800 and 2300 nm – not shown). The solid and dashed curves 530 show the reflection response from the glass side ("G" series in the chart legend). Low reflection, (e.g., minimum below 10 %), can also be achieved for the visible light range, (e.g., between 400 and 750 nm). High reflection, (e.g., maximum above 80 %), can be achieved for the infrared range, (e.g., between 800 and 2300 nm – not shown).

The solid curves represent the optical spectra for the as-coated low emissivity stack. The dashed curves represent the optical spectra for the high temperature heat treated low emissivity stack. As can be seen, there is minimum difference between the optical spectra of the transmission and reflection of the low emissivity stack before and after the heat treatment when the AlZnSnO second top dielectric layer is used.

Other characteristics of the low emissivity stack are shown in Fig. 6. "AC" represents data for the as-coated low emissivity stack. "HT" represents data for the low emissivity stack after a high temperature treatment (e.g. tempering). The columns labeled "no" present data for

the low emissivity stack without the AlZnSnO second top dielectric layer (e.g. silicon nitride in direct contact with AlSnO first top dielectric layer). The columns labeled “with” present data for the low emissivity stack with the AlZnSnO second top dielectric layer. Data are presented for monolithic coated stacks. Due to the distribution of cones in the eye, the color observance can depend on the observer's field of view. Standard (colorimetric) observer is used, which was taken to be the chromatic response of the average human viewing through a 2 degree angle, due to the belief that the color-sensitive cones reside within a 2 degree arc of the fovea. Thus the measurements are shown for the 2 degree Standard Observer.

Intensity of reflected visible wavelength light, (e.g., “reflectance”) is defined for glass side “g” or for film side “f”. Intensity from glass side reflectance, (e.g., R_gY), shows light intensity measured from the side of the glass substrate opposite the side of the coated layers. Intensity from film side reflectance, (e.g., R_fY), shows light intensity measured from the side of the glass substrate on which the coated layers are formed. Transmittance, (e.g., TY), shows light intensity measured for the transmitted light.

Color characteristics are measured and reported herein using the CIE LAB a^* , b^* coordinates and scale (i.e. the CIE a^*b^* diagram, Ill. CIE-C, 2 degree observer). In the CIE LAB color system, the “ L^* ” value indicates the lightness of the color, the “ a^* ” value indicates the position between magenta and green (more negative values indicate stronger green and more positive values indicate stronger magenta), and the “ b^* ” value indicates the position between yellow and blue (more negative values indicate stronger blue and more positive values indicate stronger yellow).

Emissivity (E) is a characteristic of both absorption and reflectance of light at given wavelengths. It can usually represented as a complement of the reflectance by the film side, (e.g., $E = 1 - R_f$). For architectural purposes, emissivity values can be important in the far range of the infrared spectrum, (e.g. about 2,500-40,000 nm). Thus the emissivity value reported here includes normal emissivity (EN), as measured in the far range of the infrared spectrum. Haze is a percentage of light that deviates from the incident beam greater than 2.5 degrees on the average.

Data are also shown for the difference between heat treated (HT) and as-coated (AC) low emissivity stacks. The value ΔE^* (and Δa^* , Δb^* , ΔY) are important in determining whether or not upon heat treatment there is matchability, or substantial matchability, of the coated panels. For purposes of example, the term Δa^* , for example, is indicative of how much color value a^* changes due to heat treatment. Also, ΔE^* is indicative of the change in reflectance and/or transmittance (including color appearance) in a coated panel after a heat treatment. ΔE^* corresponds to the CIELAB Scale L^* , a^* , b^* , and measures color properties before heat treatment (L_0^* , a_0^* , b_0^*) and color properties after heat treatment (L_1^* , a_1^* , b_1^*):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

where:

$$\Delta L^* = L_1^* - L_0^*$$

$$\Delta a^* = a_1^* - a_0^*$$

$$\Delta b^* = b_1^* - b_0^*$$

5 The color change of glass side reflection can be calculated as $R_g \Delta E^*$. The color change of light transmission can be calculated as $T \Delta E^*$, $T|\Delta a^*|$ and $T|\Delta b^*|$. The luminance change of light transmission can be calculated as $T \Delta Y$.

As can be seen from Fig. 6, the low emissivity stacks described herein can show a visible transmittance (TY%) of about 85 - 90%, a reflectance value (at glass side $R_g Y$ or film side $R_f Y$) of about 5 - 8%. As can be seen from Fig. 6, the low emissivity stacks described herein can show a low $R_f \Delta E^*$ value (i.e. the color change on the film side) when comparing the as coated (i.e. "AC") and the heat treated (i.e. "HT") data (i.e. "HT - AC"). The low emissivity stacks that include the AlZnSnO second top dielectric layer exhibit $R_f \Delta E^*$ values of less than 2.0. In contrast, the low emissivity stacks that do not include the AlZnSnO second top dielectric layer (e.g. they employ a ZnO second top dielectric layer) exhibit $R_f \Delta E^*$ values of greater than 3.4. Desirable values of $R_f \Delta E^*$ are less than 3.0. Therefore, a noticeable color change for the low emissivity stacks that do not include the AlZnSnO second top dielectric layer (e.g. they employ a ZnO optical filler layer) would be present after heat treatment.

Fig. 7 illustrates a flow chart for sputtering coated layers according to some embodiments. At least one infrared reflective stack is formed sequentially on a substrate, together with a second top dielectric layer between a first top dielectric layer and an upper protective layer. The second top dielectric layer can include an aluminum zinc tin oxide alloy (e.g. AlZnSnO). In some embodiments, some or all of the aluminum in the AlZnSnO second top dielectric layer can be replaced by one or more of lithium, sodium, magnesium, potassium, calcium, or titanium. In addition, a Ni-Nb-based alloy (e.g. NiTiNbO) can be used as a barrier layer for the silver layers.

In operation 700, a substrate is provided. The substrate can be a transparent substrate, such as a glass substrate, a polymer substrate, or other substrates discussed previously. In operation 710, a first layer is formed on the substrate. The first layer can be operable as a lower protective layer. In some embodiments, the first layer can include silicon nitride. The thickness of the first layer can be between about 10 and 30 nm.

In operation 720, one or more infrared reflective stacks are formed above the first layer. Each of the one or more infrared reflective stacks can include (from bottom to top) a bottom dielectric layer, a seed layer, an IR reflective layer, and a barrier layer. In some embodiments, the bottom dielectric layer can include AlSnO. In some embodiments, the seed layer can include ZnO. In some embodiments, the IR reflective layer can include silver. In some embodiments, the barrier layer can include NiTiNbO.

In operation 730, a sixth layer is formed above the one or more infrared reflective stacks. The sixth layer can be operable as a first top dielectric layer. The sixth layer can include AlSnO. The thickness of the sixth layer can be between 5 and 100 nm.

5 In operation 740, a seventh layer is formed above the sixth layer. The seventh layer can be operable as a second top dielectric layer. The seventh layer can include AlZnSnO. The thickness of the seventh layer can be between 3 and 20 nm. In some embodiments, some or all of the aluminum in the AlZnSnO optical filler layer can be replaced by one or more of lithium, sodium, magnesium, potassium, calcium, or titanium.

10 In operation 750, an eighth layer is formed above the seventh layer. The eighth layer can be operable as an upper protective layer. The eighth layer can include silicon nitride. The thickness of the eighth layer can be between 10 and 30 nm.

FIG. 8 is a process flowchart corresponding to a method 800 of forming an article including a silver reflective layer and a barrier layer for protecting this reflective layer from oxidation, in accordance with some embodiments. Method 800 may commence with providing a substrate during operation 802. In some embodiments, the provided substrate is a glass substrate. The substrate may include one or more previous deposited layers. For example, the substrate may include a lower protective layer and a seed layer. In some embodiments, one or more of these layers may not be present on the substrate. Various examples of these layers and substrates are described above with reference to FIG. 1.

20 Method 800 may proceed with forming a bottom dielectric layer over the substrate during operation 803. As stated above, in some embodiments, the substrate may include a lower protective layer. Thus, the bottom dielectric layer may be formed over the bottom diffusion layer and may directly interface the lower protective layer. As similarly discussed above with reference to FIG. 1, the bottom dielectric stack may include a first bottom dielectric layer and a second bottom dielectric layer. The first bottom dielectric layer may include zinc tin oxide and the second bottom dielectric layer may include tin aluminum oxide. In some embodiments, the bottom dielectric layer may be formed using a deposition technique, such as reactive sputtering. For example, the bottom dielectric layer may be formed by reactive sputtering a first bottom dielectric layer target that includes an alloy of zinc and tin, and subsequently reactive sputtering a second bottom dielectric layer target that includes an alloy of tin and aluminum.

Method 800 may proceed with forming a seed layer over the bottom dielectric stack during operation 804. As similarly discussed above with reference to FIG. 1, a seed layer may include one of various combinations of metals or metal oxides. Moreover, the seed layer may be formed using any suitable deposition technique, such as reactive sputtering.

35 Method 800 may proceed with forming a reflective layer over the substrate during operation 805 or, more specifically, over one or more layers previously formed on the provided substrate, such as the seed layer formed during operation 804. This operation may involve

sputtering silver in a non-reactive environment. The silver layer may be deposited in an argon environment at a pressure of 2 millitorr. The resulting deposition rate may be about 2.9 Angstroms per second. The target to substrate spacing may be about 240 millimeters. The thickness of the reflective layer may be between about 50 Angstroms and 200 Angstroms.

- 5 Method 800 may proceed with forming a barrier layer over the reflective layer during operation 806. As noted above, the reflective layer may be formed from an alloy including one or more of nickel, chromium, titanium, niobium, and aluminum that is formed by co-sputtering these metals in a non-reactive environment. In some embodiments, the barrier layer is deposited in the same processing chamber as the reflective layer without breaking the vacuum in the chamber.
- 10 Overall, the reflective layer needs to be protected from oxygen prior to deposition of the barrier layer. In some embodiments, a partially fabricated article may be maintained in an oxygen-free environment after forming the reflective layer and prior to forming the barrier layer.

- Operation 806 may use a single sputtering target that includes all metals. Alternatively, multiple targets, each including one or more metals, may be used. When a target includes
- 15 multiple metals, these metals may be in a form of an alloy arranged into a unified body or may be present as separate components of the target. The composition of metals in the one or more targets may correspond to the desired composition of the barrier layer. For example, a target including 5-10% by weight of nickel, 25-30% by weight of chromium, 30-35% by weight of titanium, and 30-35% by weight of aluminum may be used. In some embodiments, one target
- 20 may include nickel and chromium (e.g., having a 4:1 weight ratio of nickel to chromium) and another target may include titanium and aluminum (e.g., having a 1:1 weight ratio). The power level used on the titanium- aluminum target may double of that used for the nickel-chromium level, e.g., 200W and 100W respectively for 3-inch targets positioned about 12 inches away from the substrate resulting in a 2-4 Angstroms per minute deposition rate.

- 25 Method 800 may then proceed with forming a top dielectric stack over the barrier layer during operation 808. In some embodiments, the top dielectric stack may directly interface the barrier layer and a subsequently formed layer, such as a top diffusion layer. As similarly discussed above with reference to FIG. 1, the top dielectric stack may include a first top dielectric layer and a second top dielectric layer. The first top dielectric layer may include tin aluminum
- 30 oxide and the second top dielectric layer may include zinc oxide or aluminum zinc tin oxide. In some embodiments, the top dielectric stack may be formed using a deposition technique, such as reactive sputtering. For example, the top dielectric stack may be formed by reactive sputtering a first top dielectric layer target that includes an alloy of tin and aluminum, and subsequently reactive sputtering a second top dielectric layer target.

- 35 If another reflective layer needs to be deposited on the substrate, operations 804-808 may be repeated as indicated by decision block 810.

FIG. 9 is a graph illustrating the results of a spectral analysis of one or more dielectric stacks with and without the application of a heat treatment, implemented in accordance with some embodiments. As shown in FIG. 9, the reflection spectrums that resulted for dielectric stacks exhibited almost no change in transmittance and reflectance characteristics when a heat treatment was used during the manufacturing process. For example, line 902 represents a transmissivity of an as-coated low emissivity window that has not received a heat treatment. Similarly, line 904 represents a glass-side reflection and line 906 represents a film-side reflection of an as-coated window. Line 908 represents a transmissivity of a low emissivity window that has received a heat treatment. Similarly line 910 represents a glass-side reflection and line 912 represents a film-side reflection of heat treated window. As is shown in FIG. 9 and by lines 902 - 912, the transmissivity, glass-side reflection, and film-side reflection for both as-coated and heat treated windows are very similar, and the application of the heat treatment does not substantially affect the transmittance and reflectance of low emissivity windows including dielectric stacks as disclosed herein.

FIG. 10 is an example of a score card identifying one or more optical properties of a dielectric layer stack, implemented in accordance with some embodiments. Among other properties, FIG. 10 describes color characteristics of low emissivity windows including dielectric layer stacks as disclosed herein. The color characteristics were measured and reported using the CIE LAB a^* , b^* coordinates and scale. In the CIE LAB color system, the “ L^* ” value indicates the lightness of the color, the “ a^* ” value indicates the position between magenta and green (more negative values indicate stronger green and more positive values indicate stronger magenta), and the “ b^* ” value indicates the position between yellow and blue (more negative values indicate stronger blue and more positive values indicate stronger yellow).

Data are shown for as-coated stacks and heat treated stacks. As can be seen from FIG. 10, the low emissivity stacks described herein exhibit a high visible transmittance (TY%) of about 85 - 90%. Moreover, FIG. 10 indicates that the a^* and b^* values for each of the as-coated windows and the heat treated windows are very similar and do not substantially change once a heat-treatment has been applied. Accordingly, there is very little difference between a color of the glass-side reflection and film-side reflection of the as-coated panels and the heat treated panels. FIG. 10 further illustrates how the low emissivity stacks described herein exhibit a low $R_g\Delta E$ value, which may be an overall metric of change in glass side color characteristics of the low emissivity windows calculated based on changes in L^* , a^* , and b^* values. The low $R_g\Delta E$ value calculated based on a comparison of as-coated and heat treated L^* , a^* , and b^* values indicates that the low emissivity panels disclosed herein exhibit a low change in color of glass-side reflection, thus making them suitable for either manufacturing process.

Although the foregoing examples have been described in some detail for purposes of clarity of understanding, the invention is not limited to the details provided. There are many

alternative ways of implementing the invention. The disclosed examples are illustrative and not restrictive.

What is claimed is:

1. A film stack comprising:
a transparent substrate;
a first layer formed above the substrate, the first layer comprising silicon nitride;
5 a second layer formed above the first layer, the second layer comprising aluminum-tin-oxide;
a third layer formed above the second layer, the third layer comprising zinc oxide;
a fourth layer formed above the third layer, the fourth layer comprising silver;
a fifth layer formed above the fourth layer, the fifth layer comprising nickel-titanium-
10 niobium-oxide;
a sixth layer formed above the fifth layer, the sixth layer comprising aluminum-tin-oxide;
a seventh layer formed above the sixth layer, the seventh layer comprising X-zinc-tin-oxide, wherein X is at least one of aluminum, lithium, sodium, magnesium, potassium, calcium, or titanium;
15 an eighth layer formed above the seventh layer, the eighth layer comprising silicon nitride.
2. The film stack of claim 1 wherein the first and second layers are operable as dielectric layers.
- 20 3. The film stack of claim 1 wherein the third layer promotes a preferred crystallographic orientation of the fourth layer.
4. The film stack of claim 1 wherein the fifth layer is operable as a barrier layer.
- 25 5. The film stack of claim 1 wherein an absorbance in the visible range defined by $[A = 100 - TT - R_f]$ is less than 8%.
6. The film stack of claim 1 wherein a difference in the reflectance on the film side defined
30 by $[HT - AC(R_f \Delta E^*)]$ after a heat treatment of 650C for 8 minutes is less than 3.
7. The film stack of claim 1 wherein a difference in the reflectance on the glass side defined
by $[HT - AC(R_g \Delta E^*)]$ after a heat treatment of 650C for 8 minutes is less than 2.
- 35 8. A method of forming a film stack, the method comprising:
providing a transparent substrate;

- forming a first layer above the substrate, the first layer comprising silicon nitride;
forming a second layer above the first layer, the second layer comprising aluminum-tin-oxide;
forming a third layer above the second layer, the third layer comprising zinc oxide;
5 forming a fourth layer above the third layer, the fourth layer comprising silver;
forming a fifth layer above the fourth layer, the fifth layer comprising nickel-titanium-niobium-oxide;
forming a sixth layer above the fifth layer, the sixth layer comprising aluminum-tin-oxide;
10 forming a seventh layer above the sixth layer, the seventh layer comprising X-zinc-tin-oxide, wherein X is at least one of aluminum, lithium, sodium, magnesium, potassium, calcium, or titanium;
forming an eighth layer above the seventh layer, the eighth layer comprising silicon nitride.
- 15 9. The method of claim 8 further comprising heating the film stack after the forming of the eighth layer.
10. The method of claim 8 wherein the first through eighth layers are formed using a physical
20 vapor deposition (PVD) technique.
11. A low emissivity panel comprising:
a substrate;
a bottom dielectric stack formed over the substrate;
25 a seed layer formed over the bottom dielectric stack such that the bottom dielectric stack is formed between the seed layer and the substrate;
a reflective layer formed over the seed layer such that the seed layer is formed between the reflective layer and the bottom dielectric stack;
a barrier layer formed over the reflective layer such that the reflective layer is formed
30 between the barrier layer and the seed layer; and
a top dielectric stack formed over the barrier layer such that the barrier layer is formed between the top dielectric stack and the reflective layer,
the bottom dielectric stack comprising a first bottom dielectric layer and a second bottom dielectric layer,
35 the first bottom dielectric layer comprising zinc tin oxide,
the second bottom dielectric layer comprising tin aluminum oxide,

the top dielectric stack comprising a first top dielectric layer and a second top dielectric layer,

the first top dielectric layer comprising tin aluminum oxide,

the second top dielectric layer comprising zinc oxide.

5

12. The low emissivity panel of claim 11, wherein the top dielectric stack and the bottom dielectric stack each have a thickness of between about 5 nm and 30 nm.
13. The low emissivity panel of claim 11, wherein a glass-side reflection of the low
10 emissivity panel changes by less than 3% in response to an application of a heat treatment to the low emissivity panel.
14. The low emissivity panel of claim 11, wherein a color of a glass side reflection of the low
15 emissivity panel changes by less than 3% in response to an application of the heat treatment to the low emissivity panel.
15. The low emissivity panel of claim 11, wherein an atomic ratio of aluminum to tin in the first top dielectric layer is between about 0.3 and 0.65.
- 20 16. The low emissivity panel of claim 11, wherein the second top dielectric layer includes no metals other than zinc.
17. The low emissivity panel of claim 11, wherein the first bottom dielectric layer is formed between the second bottom dielectric layer and the substrate.
- 25 18. The low emissivity panel of claim 11, wherein an atomic ratio of aluminum to tin in the second bottom dielectric layer is between about 0.3 and 0.65.
19. The low emissivity panel of claim 11, wherein an atomic ratio of zinc to tin in the first
30 bottom dielectric layer is between about 1.8 and 2.2.
20. The low emissivity panel of claim 11 further comprising a bottom diffusion layer formed between the substrate and the bottom dielectric stack.

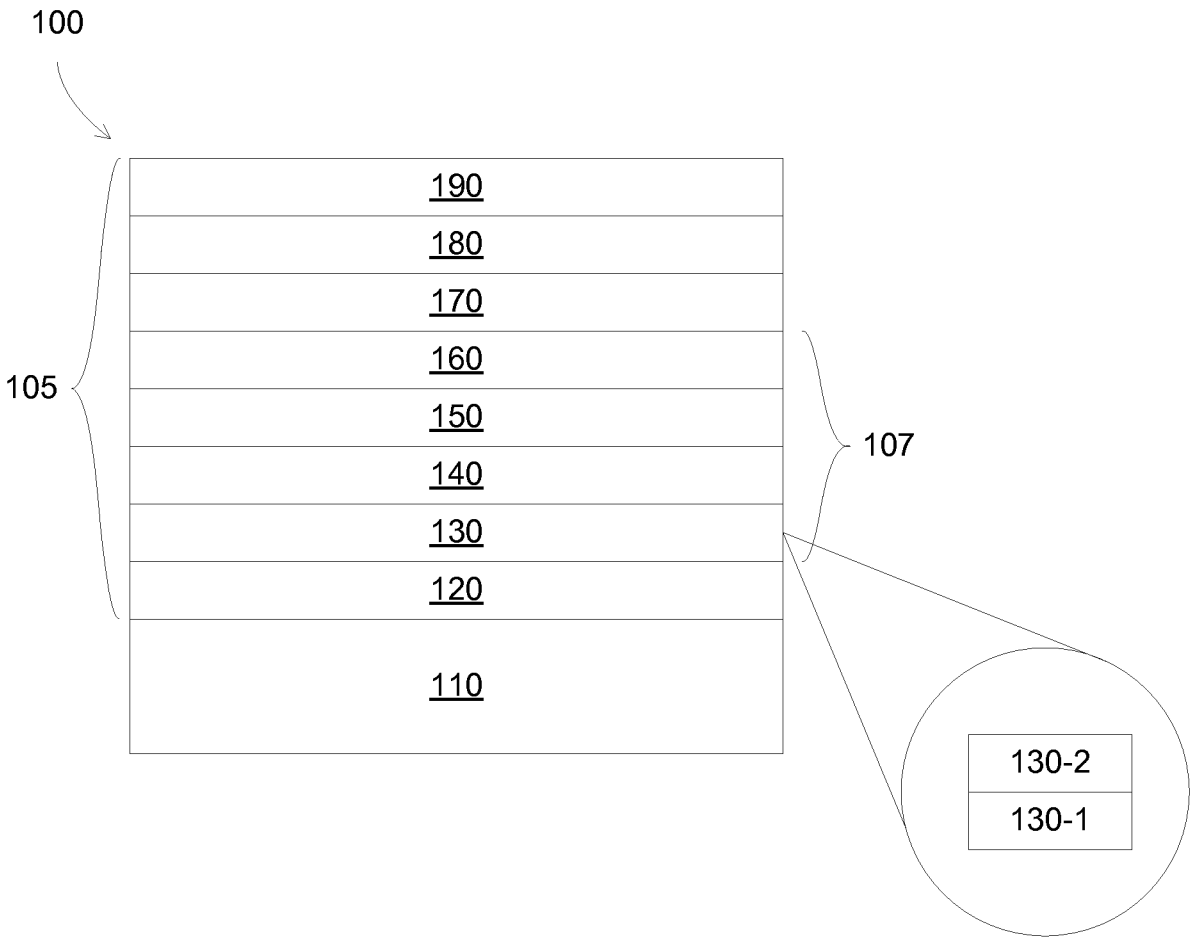


Fig. 1

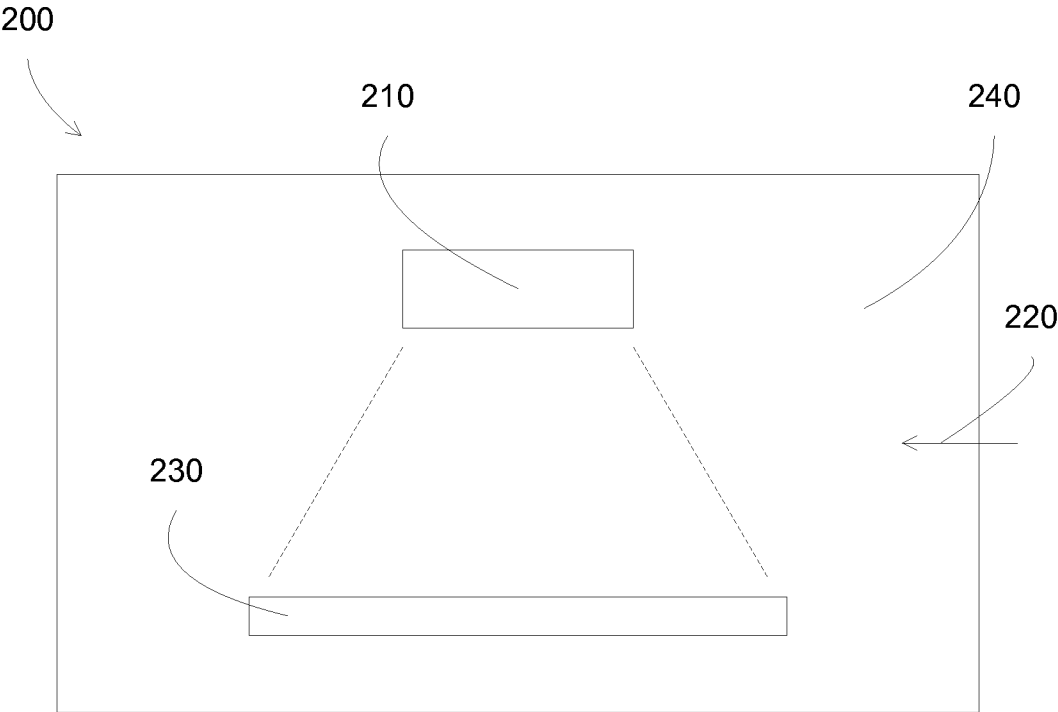


Fig. 2A

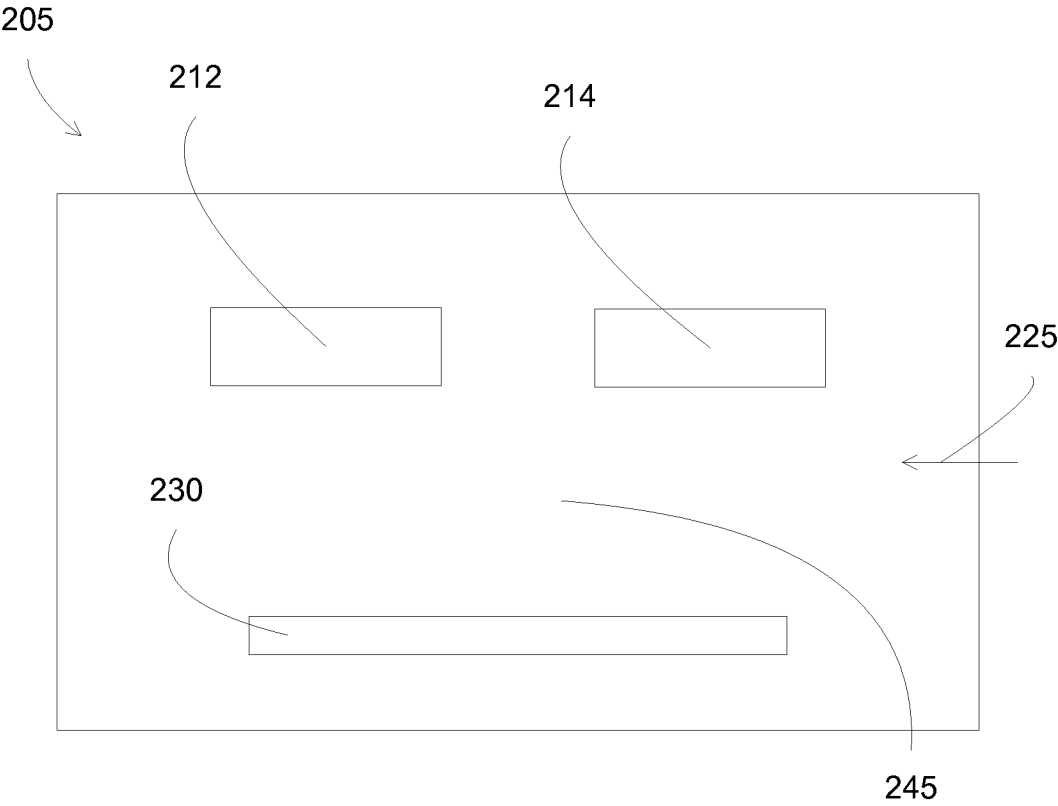


Fig. 2B

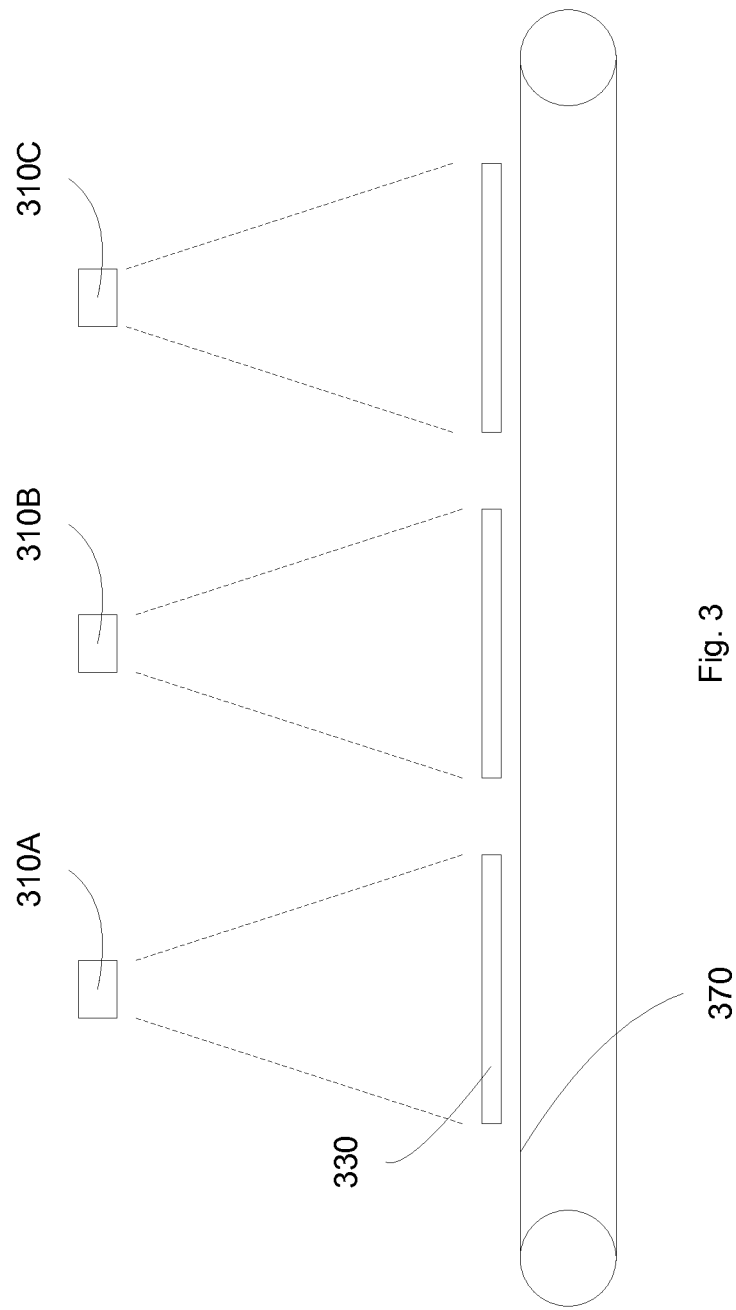


Fig. 3

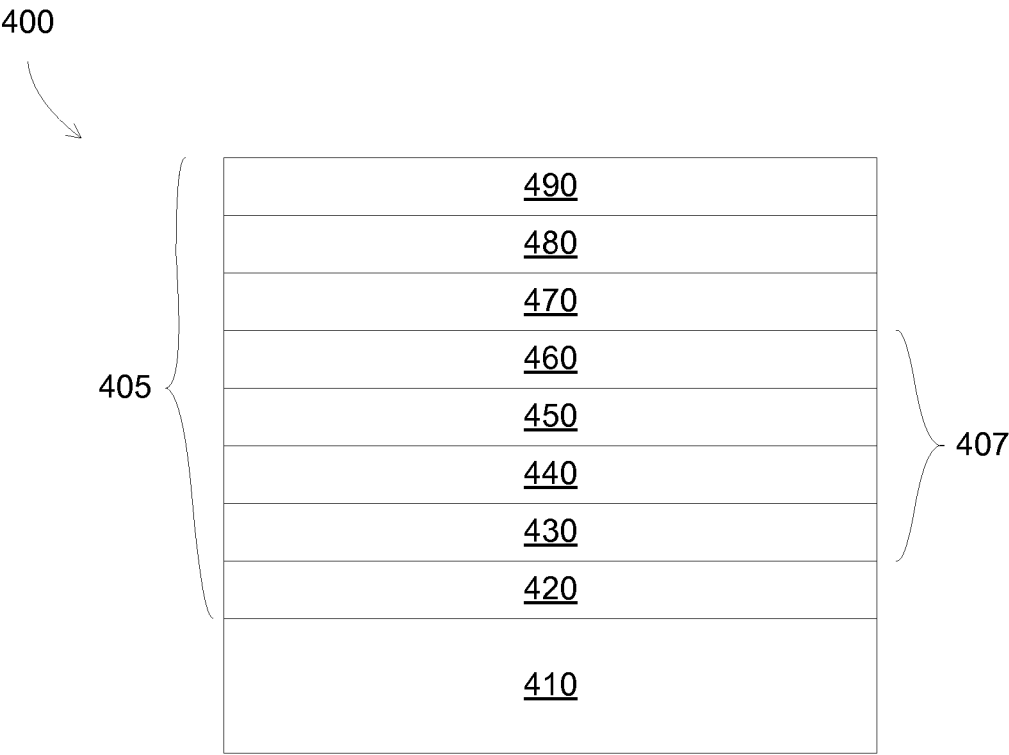


Fig. 4

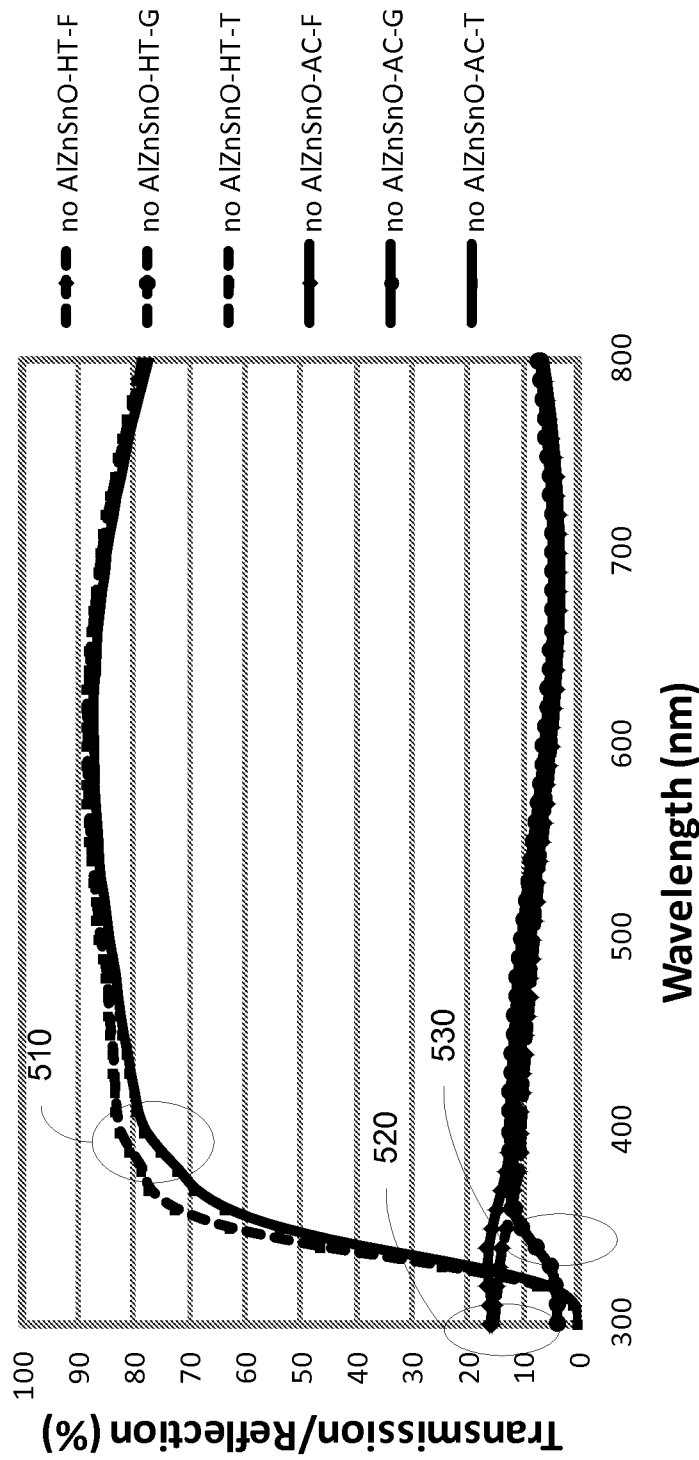


Fig. 5A

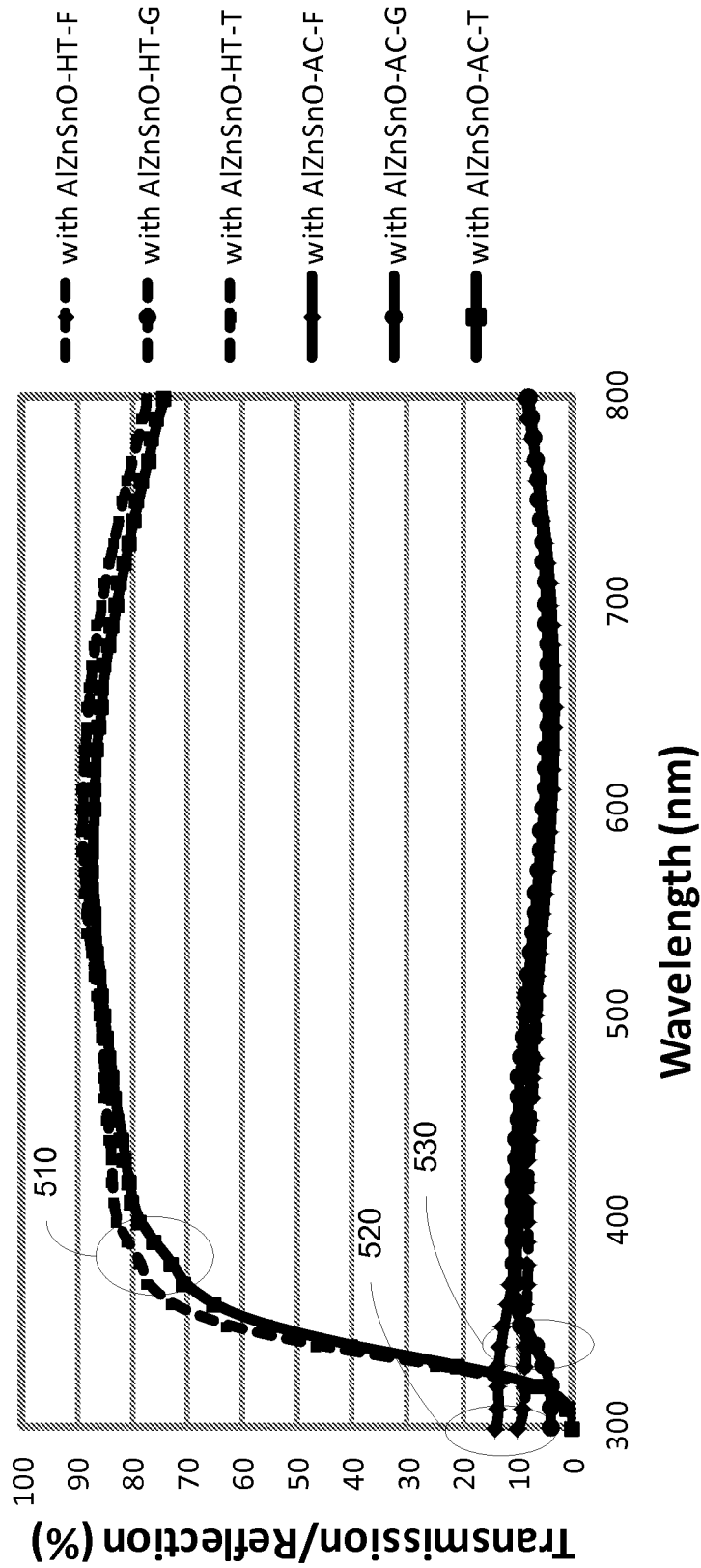


Fig. 5B

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			AlZnSnO	no	no	with	with
			Target	AC	HT	AC	HT
Monolithic Optics (III 'C', 2 deg obs)	T	Y (%)	(86, 89)	86.29	87.85	86.15	87.47
		L*		94.44	95.1	94.38	94.94
		a*	(-2.8, 0.2)	-1.03	-0.31	-0.64	-0.42
		b*	(-0.2, 3.8)	2.75	2.44	3.17	2.43
	Rg	Y (%)	(6.2, 7.2)	6.75	6.52	8.01	7.43
		L*		31.24	30.7	34.01	32.78
		a*	(-3.5, -0.5)	-2.31	-2.7	-3.59	-3.11
		b*	(-9.7, -5.7)	-11.14	-10.86	-11.16	-11.31
	Rf	Y (%)	(4.5, 5.5)	5.09	5.22	6.53	6.18
		L*		26.98	27.34	30.71	29.87
		a*	(-2.7, 0.3)	-1.56	-2.48	-3.11	-3.13
		b*	(-10.3, -6.3)	-12.55	-9.22	-12.35	-10.78
	A[vis] (100-TT-Rf)		(6.5, 8.5)	8.62	6.93	7.32	6.35
Rs (ohms/sq)			(5.5, 6.5)		5.70		
Normal Emissivity (EN)			(0.06, 0.08)	0.073	0.067	0.070	0.054
Haze (%)			< 0.6		0.51		0.57
HT - AC	Rf ΔE*		< 3	3.47		1.78	
	Rg ΔE*		< 3	0.72		1.33	
	T ΔE*		< 3	1.02		0.95	
	T Δb*		< 1	0.31		0.74	
	T ΔY% (HT > AC)		(0, 3)	1.56		1.32	

Fig. 6

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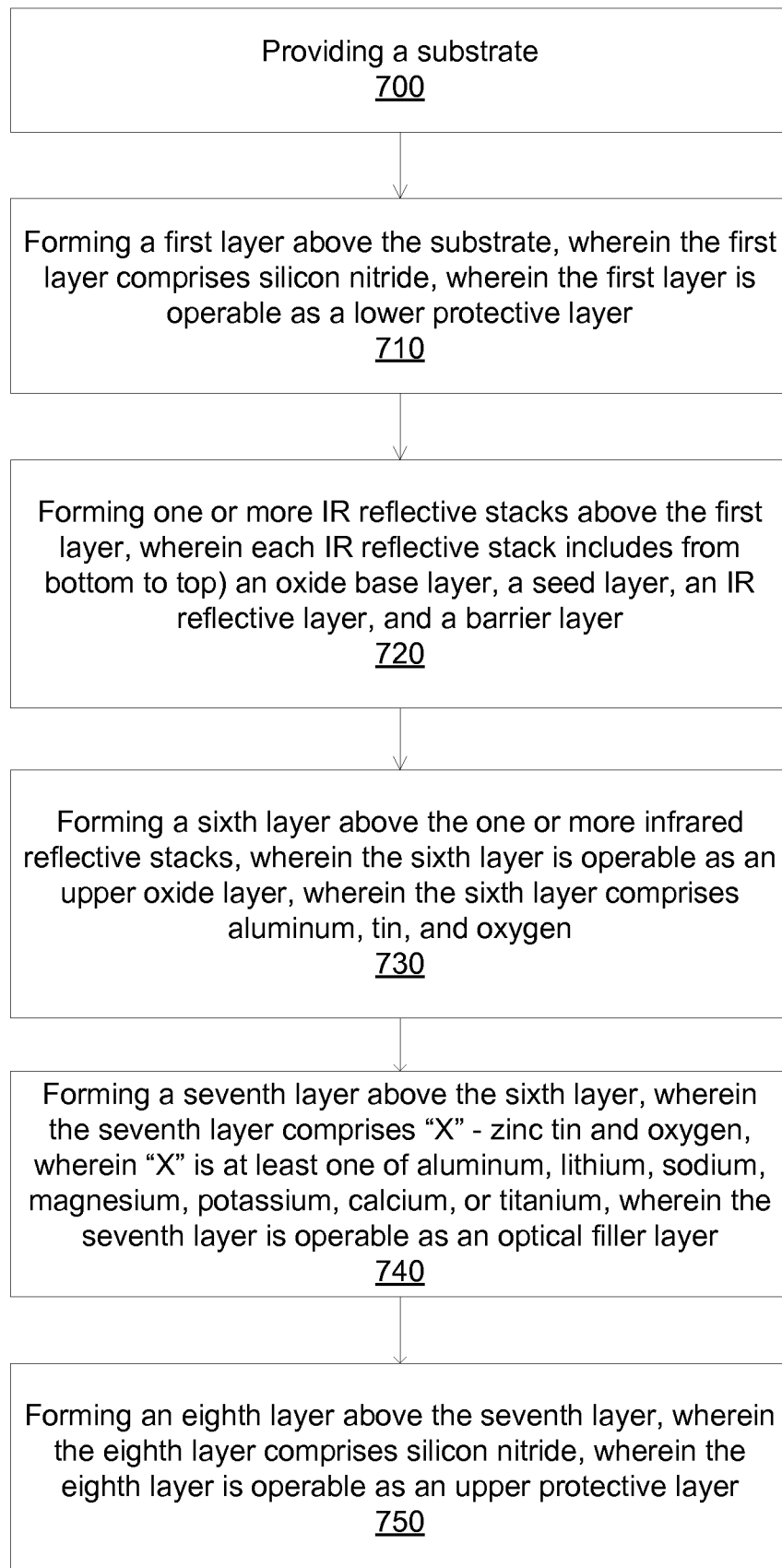


Fig. 7

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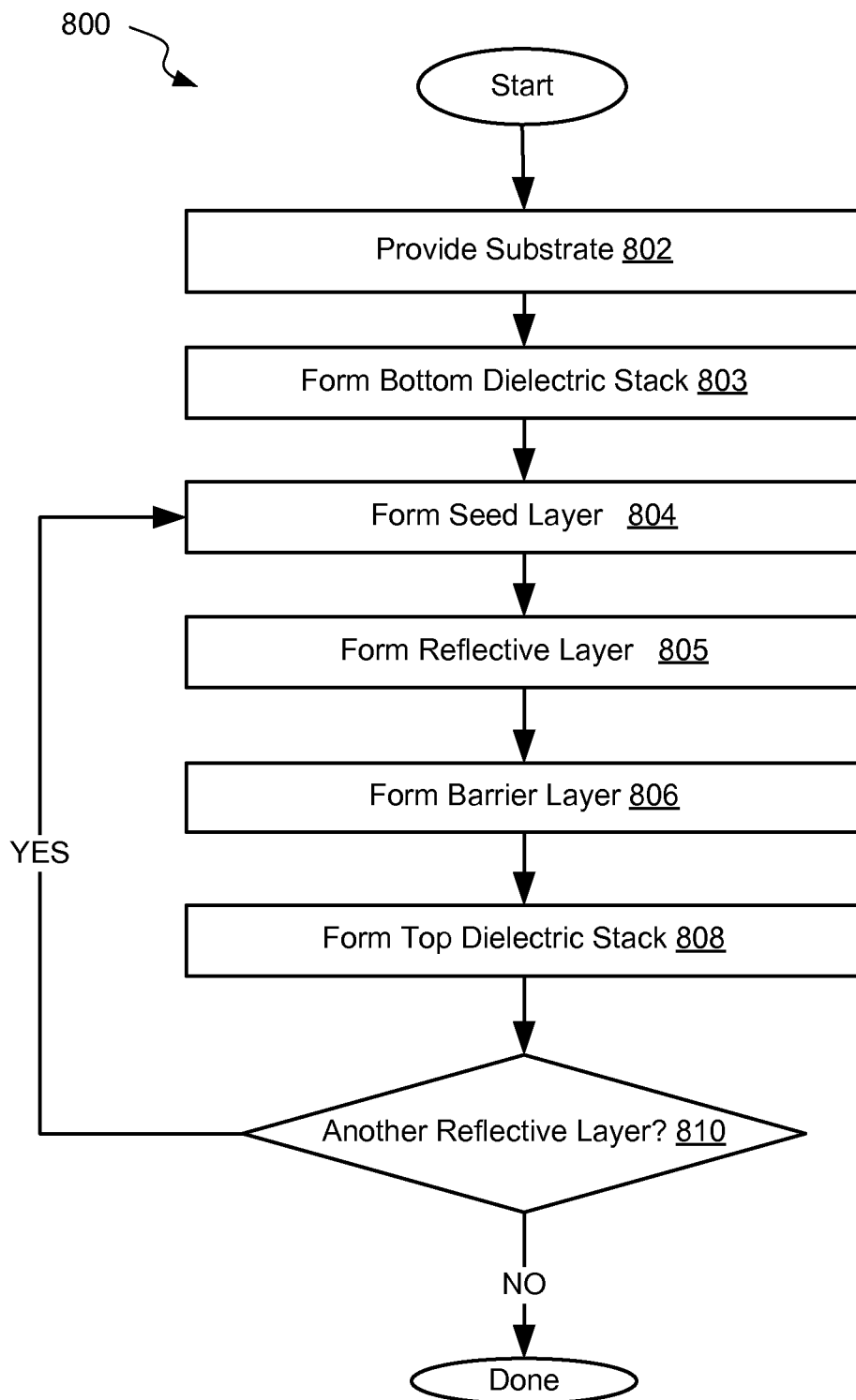


FIG. 8

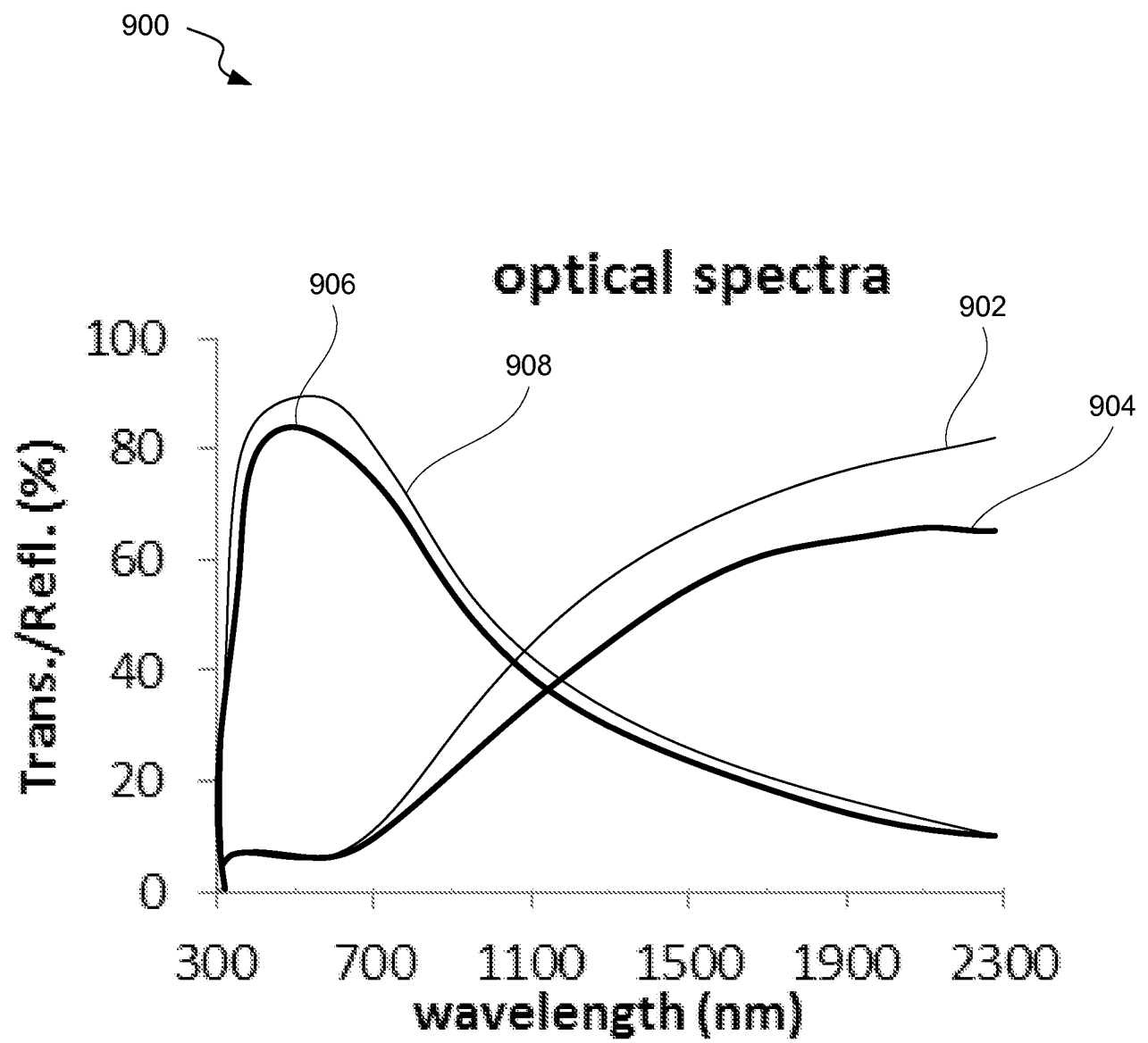


FIG. 9

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			B-10-02	B-10-02
			AC	HT
Monolith ic Optics (III 'C', 2 deg obs)	T	Y (%)	83.18	88.44
		L*	93.09	95.34
		a*	-1.71	-1.64
		b*	0.03	1.48
	Rg	Y (%)	5.78	5.36
		L*	28.86	27.74
		a*	3.93	3.87
		b*	-2.73	-3.54
	Rf	Y (%)	7.63	5.71
		L*	33.2	28.67
		a*	3.31	2.87
		b*	-1.84	-2.15
Normal Emissivity (EN)			0.077	0.061
HT - AC	Rg ΔE^*		1.38	
	T ΔE^*		2.68	
	T $ \Delta b^* $		1.45	
NFRC 2001	Tsol		52.5	55.8
	SHGC(3)		60.9	63.9
Thermal	LSG(3)		1.24	1.26

FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US14/26382

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C03C 17/36; C23C 14/06; B32B 17/06 (2014.01)

USPC - 204/192.1; 428/426, 428

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)

IPC(8): C03C 17/36; C23C 14/06, 14/00; B32B 17/06, 15/04, 5/00; E06B 3/66 (2014.01)

USPC: 204/192.1; 428/426, 428, 432, 701

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)

MicroPatent (US-G, US-A, EP-A, EP-B, WO, JP-bib, DE-C,B, DE-A, DE-T, DE-U, GB-A, FR-A); Google Patent; Google; Google Scholar; ProQuest; film stack, low emissivity, silicon nitride, aluminum, tin, zinc, nickel, titanium, niobium, oxide, silver, substrate, dielectric, seed layer, reflectance, absorbance

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2012/0225316 A1 (IMRAN, M et al.) 06 September 2012; figure 1; paragraphs [0008], [0013], [0044]-[0045], [0101], [0104]	1-4, 8-12, 15-20
Y	US 2009/0136765 A1 (MASCHWITZ, P et al.) 28 May 2009; paragraphs [0019], [0052], [0067], [0069], [0079]-[0086], [0128]-[0130], [0159]-[0165]	1-4, 8-12, 15-20
Y	US 2012/0148863 A1 (KLEINHEMPEL, R et al.) 14 June 2012; figure 3; paragraphs [0008], [0020]-[0023], [0034]	1-4, 8-12, 15-20
Y	US 2007/0224357 A1 (BUHAY, H et al.) 27 September 2007; paragraph [0036]	19
Y	US 2004/0101694 A1 (LINGLE, PJ et al.) 27 May 2004; paragraphs [0026]-[0027], [0042]-[0056], [0060]-[0061]	20
A	US 2007/0009747 A1 (MEDWICK, PA et al.) 11 January 2007; paragraphs [0052]-[0056]	1-20
A	US 2007/0206263 A1 (NEUMAN, GA et al.) 06 September 2007; entire document	1-20
P,Y	US 2013/0189526 A1 (HASSAN, MFA et al.) 25 July 2013; entire document	1-20

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

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"&" document member of the same patent family

Date of the actual completion of the international search

17 June 2014 (17.06.2014)

Date of mailing of the international search report

08 JUL 2014

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