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(54) **SOLAR CONTROL COATINGS WITH DISCONTINUOUS METAL LAYER**

SONNENSCHUTZBESCHICHTUNGEN MIT UNTERBROCHENER METALLSCHICHT

REVÊTEMENTS ANTISOLAIRES CONTENANT UNE COUCHE MÉTALLIQUE DISCONTINUE

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention relates generally to solar control coatings and, in one particular embodiment, to a solar control coating having increased absorbance and asymmetrical reflectance.

Technical Considerations

[0002] Solar control coatings are known in the fields of architectural and automotive transparencies. These solar control coatings block or filter selected ranges of electromagnetic radiation, such as in the range of solar infrared or solar ultraviolet radiation, to reduce the amount of solar energy entering the vehicle or building. This reduction of solar energy transmittance helps reduce the load on the cooling units of the vehicle or building. In automotive applications, the transparency (such as a windshield) is typically required to have a relatively high visible light transmittance, such as greater than 70 percent, to allow passengers to see out of the vehicle. For architectural applications, the visible light transmittance can be lower. In some architectural applications, it may be desirable to have a reflective outer surface so as to decrease visibility into the building to retain as much privacy as possible, while still allowing visible light to enter the building and also allowing the workers inside the building to see out. Also, these transparencies are typically tempered or heat treated for increased safety.

[0003] For example WO 96/13379 discloses a solar control film having low visible light transmittance and low visible light reflectance comprised of two or more transparent substrates (14) each bearing a thin, transparent, discontinuous, incoherent film of metal (18) having low visible light reflectance and a degree of visible light blocking capacity, the substrates being so assembled and laminated into a composite (10) that the visible light blocking capacities of the metal films are effectively combined to provide a composite having low visible light transmittance as well as low visible light reflectance. Performance characteristics are enhanced by providing on one or more of the substrates a transparent coating (16) of high refractive index underlying the metal film. The material of high refractive index is preferably a synthetic high oxygen content oxide of bismuth, which facilitates efficient an economical production of the solar control film.

US 2004/0146645 A1 describes an article having a sealed layered edge, e.g. an automotive laminate and a multiple glazed unit including a pair of glass sheet in a fixed relationship with one another. A sputtered coating is desposited on a major surface of one of the sheets and includes at least one combination of a metal film, e.g. a silver film and a dielectric film. Discontinuities in the metal film at the marginal edges of the coated sheet provide voids in the metal film to impede or stop corrosion of the metal film. The discontinuities include (1) break lines or segments in the coating, (2) coating thickness variations provided by abrading the coating an (3) spaced discrete coating areas on the marginal edges of the coated sheet. The discontinuities may be made in the metal film using a laser, an abrasive surface, a coating mask and/or coating deletion techniques.

Japanese Patent application No. 2000180759 describes transparent laminates suitable as filter for electromagnetic radiation comprising a transparent substrate, metal thin films, each having a thickness of 1-30 nm and transparent thin films, each having a thickness of 10-150 nm, which are alternately laminated, these thin films being joined to the surface of the transparent substrate to form a transparent laminar block. At least one of the metal thin films in the transparent laminar block is not of a continuous film structure.

[0004] In one known architectural transparency, a heat strengthened glass substrate is coated with a solar control coating having an absorber material, such as a nickel-chromium alloy material (e.g., Inconel®), to absorb visible light to darken the window. This transparency also includes a relatively thick, continuous, infrared reflective metal layer to reflect solar energy, such as solar infrared energy. However, a problem with this known transparency is that the glass substrate must be cut to a desired shape and tempered before the coating is applied. If the coating is applied before the glass substrate is tempered, the resultant coating becomes hazy during the high temperature processings required for the tempering process. This haze is aesthetically undesirable.

[0005] It would be desirable to be able to apply a solar control coating onto non-tempered glass sheets and ship the glass sheets to a manufacturer who could then cut the sheets to a desired size for a particular job and then temper or heat treat the cut pieces without adversely impacting upon the aesthetic or solar control properties of the resultant transparency.

SUMMARY OF THE INVENTION

[0006] In one broad aspect of the invention, the coating of the invention is as defined in claim 1 including two or more continuous, infrared reflective metal layers in combination with a subcritical (i.e., discontinuous) metal layer. The dis-

continuous metal layer increases the visible light absorption of the coating and, in combination with dielectric layers of appropriate thickness, can also provide the coated article with asymmetrical reflectance.

[0007] A coating of the invention comprises a plurality of metallic layers alternating with a plurality of dielectric layers, with at least one of the metallic layers comprising a subcritical metallic layer having discontinuous metal regions.

[0008] A coated article according to the present invention comprises a substrate and a coating stack of the present invention over at least a portion of the substrate as defined in claim 1. The coating stack comprises a plurality of metallic layers and a plurality of dielectric layers, wherein at least one of the metallic layers comprises a subcritical metallic layer having discontinuous metallic regions.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The invention will be described with reference to the following drawing figures wherein like reference numbers identify like parts throughout.

Fig. 1 is a side view (not to scale) of an insulating glass unit (IGU) having a coating of the invention;
Fig. 2 is a side view (not to scale) of a coating incorporating features of the invention;
Fig. 3 is a side, sectional view (not to scale) of a subcritical metal layer with a primer layer;
Fig. 4 is a side view (not to scale) of another coating incorporating features of the invention;
Fig. 5 is a side view (not to scale) of a further coating incorporating features of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0010] As used herein, spatial or directional terms, such as "left", "right", "inner", "outer", "above", "below", and the like, relate to the invention as it is shown in the drawing figures. However, it is to be understood that the invention can assume various alternative orientations and, accordingly, such terms are not to be considered as limiting. Accordingly, unless indicated to the contrary, the numerical values set forth in the following specification and claims may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical value should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Further, as used herein, the terms "formed over", "deposited over", or "provided over" mean formed, deposited, or provided on but not necessarily in contact with the surface. For example, a coating layer "formed over" a substrate does not preclude the presence of one or more other coating layers or films of the same or different composition located between the formed coating layer and the substrate. As used herein, the terms "polymer" or "polymeric" include oligomers, homopolymers, copolymers, and terpolymers, e.g., polymers formed from two or more types of monomers or polymers. The terms "visible region" or "visible light" refer to electromagnetic radiation having a wavelength in the range of 380 nm to 800 nm. The terms "infrared region" or "infrared radiation" refer to electromagnetic radiation having a wavelength in the range of greater than 800 nm to 100,000 nm. The terms "ultraviolet region" or "ultraviolet radiation" mean electromagnetic energy having a wavelength in the range of 300 nm to less than 380 nm. As used herein, the term "film" refers to a coating region of a desired or selected coating composition. A "layer" can comprise one or more "films", and a "coating" or "coating stack" can comprise one or more "layers". The term "asymmetrical reflectivity" means that the visible light reflectance of the coating from one side is different than that of the coating from the opposite side. The term "critical thickness" means a thickness above which a coating material forms a continuous, uninterrupted layer and below which the coating material forms discontinuous regions or islands of the coating material rather than a continuous layer. The term "subcritical thickness" means a thickness below the critical thickness such that the coating material forms isolated, non-connected regions of the coating material. The term "islanded" means that the coating material is not a continuous layer but, rather, that the material is deposited to form isolated regions or islands.

[0011] For purposes of the following discussion, the invention will be discussed with reference to use with an architectural transparency, such as, but not limited to, an insulating glass unit (IGU). As used herein, the term "architectural transparency" refers to any transparency located on a building, such as, but not limited to, windows and sky lights. However, it is to be understood that the invention is not limited to use with such architectural transparencies but could be practiced with transparencies in any desired field, such as, but not limited to, laminated or non-laminated residential and/or commercial windows, insulating glass units, and/or transparencies for land, air, space, above water and underwater vehicles. Therefore, it is to be understood that the specifically disclosed exemplary embodiments are presented simply to explain the general concepts of the invention, and that the invention is not limited to these specific exemplary embodiments. Additionally, while a typical "transparency" can have sufficient visible light transmission such that materials can be viewed through the transparency, in the practice of the invention, the "transparency" need not be transparent to visible light but may be translucent or opaque.

[0012] A non-limiting transparency 10 incorporating features of the invention is illustrated in Fig. 1. The transparency

10 can have any desired visible light, infrared radiation, or ultraviolet radiation transmission and/or reflection. For example, the transparency 10 can have a visible light transmission of any desired amount, e.g., greater than 0% up to 100%.

[0013] The exemplary transparency 10 of Fig. 1 is in the form of a conventional insulating glass unit and includes a first ply 12 with a first major surface 14 (No. 1 surface) and an opposed second major surface 16 (No. 2 surface). In the illustrated non-limiting embodiment, the first major surface 14 faces the building exterior, i.e., is an outer major surface, and the second major surface 16 faces the interior of the building. The transparency 10 also includes a second ply 18 having an outer (first) major surface 20 (No. 3 surface) and an inner (second) major surface 22 (No. 4 surface) and spaced from the first ply 12. This numbering of the ply surfaces is in keeping with conventional practice in the fenestration art. The first and second plies 12, 18 can be connected together in any suitable manner, such as by being adhesively bonded to a conventional spacer frame 24. A gap or chamber 26 is formed between the two plies 12, 18. The chamber 26 can be filled with a selected atmosphere, such as air, or a non-reactive gas such as argon or krypton gas. A solar control coating 30 (or any of the other coatings described below) is formed over at least a portion of one of the plies 12, 18, such as, but not limited to, over at least a portion of the No. 2 surface 16 or at least a portion of the No. 3 surface 20. Although, the coating could also be on the No.1 surface or the No. 4 surface, if desired. Examples of insulating glass units are found, for example, in U.S. Patent Nos. 4,193,236; 4,464,874; 5,088,258; and 5,106,663.

[0014] In the broad practice of the invention, the plies 12, 18 of the transparency 10 can be of the same or different materials. The plies 12, 18 can include any desired material having any desired characteristics. For example, one or more of the plies 12, 18 can be transparent or translucent to visible light. By "transparent" is meant having visible light transmission of greater than 0% up to 100%. Alternatively, one or more of the plies 12, 18 can be translucent. By "translucent" is meant allowing electromagnetic energy (e.g., visible light) to pass through but diffusing this energy such that objects on the side opposite the viewer are not clearly visible. Examples of suitable materials include, but are not limited to, plastic substrates (such as acrylic polymers, such as polyacrylates; polyalkylmethacrylates, such as polymethylmethacrylates, polyethylmethacrylates, polypropylmethacrylates, and the like; polyurethanes; polycarbonates; polyalkylterephthalates, such as polyethyleneterephthalate (PET), polypropyleneterephthalates, polybutyleneterephthalates, and the like; polysiloxane-containing polymers; or copolymers of any monomers for preparing these, or any mixtures thereof); ceramic substrates; glass substrates; or mixtures or combinations of any of the above. For example, one or more of the plies 12, 18 can include conventional soda-lime-silicate glass, borosilicate glass, or leaded glass. The glass can be clear glass. By "clear glass" is meant non-tinted or non-colored glass. Alternatively, the glass can be tinted or otherwise colored glass. The glass can be annealed or heat-treated glass. As used herein, the term "heat treated" means tempered or at least partially tempered. The glass can be of any type, such as conventional float glass, and can be of any composition having any optical properties, e.g., any value of visible transmission, ultraviolet transmission, infrared transmission, and/or total solar energy transmission. By "float glass" is meant glass formed by a conventional float process in which molten glass is deposited onto a molten metal bath and controllably cooled to form a float glass ribbon. Examples of float glass processes are disclosed in U.S. Patent Nos. 4,466,562 and 4,671,155.

[0015] The first and second plies 12, 18 can each be, for example, clear float glass or can be tinted or colored glass or one ply 12, 18 can be clear glass and the other ply 12, 18 colored glass. Although not limiting to the invention, examples of glass suitable for the first ply 12 and/or second ply 18 are described in U.S. Patent Nos. 4,746,347; 4,792,536; 5,030,593; 5,030,594; 5,240,886; 5,385,872; and 5,393,593. The first and second plies 12, 18 can be of any desired dimensions, e.g., length, width, shape, or thickness. In one exemplary automotive transparency, the first and second plies can each be 1 mm to 10 mm thick, such as 1 mm to 8 mm thick, such as 2 mm to 8 mm, such as 3 mm to 7 mm, such as 5 mm to 7 mm, such as 6 mm thick. Non-limiting examples of glass that can be used for the practice of the invention include clear glass, Starphire®, Solargreen®, Solextra®, GL-20®, GL-35™, Solarbronze®, Solargray® glass, Pacifica® glass, SolarBlue® glass, and Optiblue® glass, all commercially available from PPG Industries Inc. of Pittsburgh, Pennsylvania.

[0016] The solar control coating 30 of the invention is deposited over at least a portion of at least one major surface of one of the glass plies 12, 18. In the example shown in Fig. 1, the coating 30 is formed over at least a portion of the inner surface 16 of the outboard glass ply 12. As used herein, the term "solar control coating" refers to a coating comprised of one or more layers or films that affect the solar properties of the coated article, such as, but not limited to, the amount of solar radiation, for example, visible, infrared, or ultraviolet radiation, reflected from, absorbed by, or passing through the coated article; shading coefficient; emissivity, etc. The solar control coating 30 can block, absorb, or filter selected portions of the solar spectrum, such as, but not limited to, the IR, UV, and/or visible spectrums.

[0017] The solar control coating 30 can be deposited by any conventional method, such as, but not limited to, conventional chemical vapor deposition (CVD) and/or physical vapor deposition (PVD) methods. Examples of CVD processes include spray pyrolysis. Examples of PVD processes include electron beam evaporation and vacuum sputtering (such as magnetron sputter vapor deposition (MSVD)). Other coating methods could also be used, such as, but not limited to, sol-gel deposition. In one non-limiting embodiment, the coating 30 can be deposited by MSVD. Examples of MSVD coating devices and methods will be well understood by one of ordinary skill in the art and are described, for example, in U.S. Patent Nos. 4,379,040; 4,861,669; 4,898,789; 4,898,790; 4,900,633; 4,920,006; 4,938,857; 5,328,768; and

5,492,750.

Islanded Metal Layer

[0018] An exemplary non-limiting solar control coating 30 of the invention is shown in Fig. 2. This exemplary coating 30 includes a base layer or first dielectric layer 40 deposited over at least a portion of a major surface of a substrate (e.g., the No. 2 surface 16 of the first ply 12). The first dielectric layer 40 can be a single layer or can comprise more than one film of metal oxides, oxides of metal alloys, nitrides, oxynitrides, or mixtures thereof. The first dielectric layer 40 can be transparent to visible light. Suitable metal oxides for the first dielectric layer 40 include oxides of hafnium, zirconium, niobium, zinc, bismuth, lead, indium, tin, and mixtures thereof. These metal oxides can have small amounts of other materials, such as manganese in bismuth oxide, tin in indium oxide, etc. Additionally, oxides of metal alloys or metal mixtures can be used, such as oxides containing zinc and tin (e.g., zinc stannate, defined below), oxides of indium-tin alloys, silicon nitrides, silicon aluminum nitrides, or aluminum nitrides. Further, doped metal oxides, such as antimony or indium doped tin oxides or nickel or boron doped silicon oxides, can be used. The first dielectric layer 40 can be a substantially single phase film, such as a metal alloy oxide film, e.g., zinc stannate, or can be a mixture of phases composed of zinc and tin oxides or can be composed of a plurality of films.

[0019] For example, the first dielectric layer 40 (whether a single film or multiple film layer) can have a thickness in the range of 10 nm (100 Å) to 60 nm (600 A), such as 20 nm (200 Å) to 50 nm (500 A), such as 25 nm (250 Å) to 35 nm (350 A), such as 25 nm (250 Å) to 31 nm (310 A), such as 28 nm (280 A) to 31 nm (310 A), such as 30 nm (300 Å) to 33 nm (330 Å), such as 31 nm (310 A) to 33 nm (330 A).

[0020] The first dielectric layer 40 can comprise a multi-film structure having a first film 42, e.g., a metal alloy oxide film, deposited over at least a portion of a substrate (such as the inner major surface 16 of the first ply 12) and a second film 44, e.g., a metal oxide or oxide mixture film, deposited over the first metal alloy oxide film 42. In one non-limiting embodiment, the first film 42 can be a zinc/tin alloy oxide. By "zinc/tin alloy oxide" is meant both true alloys and also mixtures of the oxides. The zinc/tin alloy oxide can be that obtained from magnetron sputtering vacuum deposition from a cathode of zinc and tin. One non-limiting cathode can comprise zinc and tin in proportions of 5 wt.% to 95 wt.% zinc and 95 wt.% to 5 wt.% tin, such as 10 wt.% to 90 wt.% zinc and 90 wt.% to 10 wt.% tin. However, other ratios of zinc to tin could also be used. One suitable metal alloy oxide that can be present in the first film 42 is zinc stannate. By "zinc stannate" is meant a composition of $Zn_XSn_{1-X}O_{2-X}$ (Formula 1) where "x" varies in the range of greater than 0 to less than 1. For instance, "x" can be greater than 0 and can be any fraction or decimal between greater than 0 to less than 1. For example, where x = 2/3, Formula 1 is $Zn_{2/3}Sn_{1/3}O_{4/3}$, which is more commonly described as "Zn_2SnO_4". A zinc stannate-containing film has one or more of the forms of Formula 1 in a predominant amount in the film.

[0021] The second film 44 can be a metal oxide film, such as zinc oxide. The zinc oxide film can be deposited from a zinc cathode that includes other materials to improve the sputtering characteristics of the cathode. For example, the zinc cathode can include a small amount (e.g., up to 10 wt.%, such as up to 5 wt.%) of tin to improve sputtering. In which case, the resultant zinc oxide film would include a small percentage of tin oxide, e.g., up to 10 wt.% tin oxide, e.g., up to 5 wt.% tin oxide. A coating layer deposited from a zinc cathode having up to 10 wt.% tin (added to enhance the conductivity of the cathode) is referred to herein as "a zinc oxide film" even though a small amount of tin may be present. The small amount of tin in the cathode (e.g., less than or equal to 10 wt.%, such as less than or equal to 5 wt.%) is believed to form tin oxide in the predominantly zinc oxide second film 44.

[0022] For example, the first film 42 can be zinc stannate and the second film 44 can be zinc oxide (for example, 90 wt.% zinc oxide and 10 wt.% tin oxide). For example, the first film 42 can comprise zinc stannate having a thickness in the range of 5 nm (50 Å) to 60 nm (600 Å), such as 5 nm (50 Å) to 50 nm (500 A), such as 7.5 nm (75 A) to 35 nm (350 Å), such as 10 nm (100 A) to 25 nm (250 Å), such as 15 nm (150 Å) to 25 nm (250 A), such as 19.5 nm (195 A) to 25 nm (250 A), such as 20 nm (200 A) to 25 nm (250 A), such as 20 nm (200 A) to 22 nm (220 A).

[0023] The second film 44 can comprise zinc oxide having a thickness in the range of 5 nm (50 Å) to 20 nm (200 A), such as 7.5 nm (75 A) to 20 nm (200 A), such as 10 nm (100 A) to 15 nm (150 A), such as 10 nm (100 A) to 11 nm (110 Å).

[0024] A first heat and/or radiation reflective metallic layer 46 is deposited over the first dielectric layer 40. The first reflective layer 46 can include a reflective metal, such as, but not limited to, metallic gold, copper, palladium, aluminum, silver, or mixtures, alloys, or combinations thereof. In one embodiment, the first reflective layer 46 comprises a metallic silver layer having a thickness in the range of 5 nm (50 Å) to 30 nm (300 Å), e.g., 5 nm (50 A) to 25 nm (250 A), e.g., 5 nm (50 A) to 20 nm (200 A), such as 7 nm (70 A) to 20 nm (200 A), such as 10 nm (100 Å) to 20 nm (200 A), such as 12.5 nm (125 Å) to 20 nm (200Å), such as 15 nm (150 A) to 18.5 nm (185 Å). The first metallic layer 46 is a continuous layer. By "continuous layer" is meant that the coating forms a continuous film of the material and not isolated coating regions.

[0025] A first primer layer 48 is located over the first reflective layer 46. The first primer layer 48 can be a single film or a multiple film layer. The first primer layer 48 can include an oxygen-capturing material that can be sacrificial during the deposition process to prevent degradation or oxidation of the first reflective layer 46 during the sputtering process

or subsequent heating processes. The first primer layer 48 can also absorb at least a portion of electromagnetic radiation, such as visible light, passing through the coating 30. Examples of materials useful for the first primer layer 48 include titanium, silicon, silicon dioxide, silicon nitride, silicon oxynitride, nickel-chrome alloys (such as Inconel), zirconium, aluminum, alloys of silicon and aluminum, alloys containing cobalt and chromium (e.g., Stellite®), and mixtures thereof. For example, the first primer layer 48 can be titanium and can have a thickness in the range of 0.5 nm (5 Å) to 5 nm (50 A), e.g., 1 nm (10 A) to 4 nm (40 Å), e.g., 2 nm (20 A) to 4 nm (40 Å), e.g., 2 nm (20 Å) to 3.5 nm (35 A).

[0026] A second dielectric layer 50 is located over the first primer layer 48). The second dielectric layer 50 can comprise one or more metal oxide or metal alloy oxide-containing films, such as those described above with respect to the first dielectric layer 40. For example, the second dielectric layer 50 can include a first metal oxide film 52, e.g., a zinc oxide film, deposited over the first primer film 48 and a second metal alloy oxide film 54, e.g., a zinc stannate (Zn_2SnO_4 film, deposited over the first zinc oxide film 52. An optional third metal oxide film 56, e.g., another zinc oxide layer, can be deposited over the zinc stannate layer.

[0027] The second dielectric layer 50 can have a total thickness (e.g., the combined thicknesses of the layers) is in the range of 5 nm (50 A) to 100 nm (1000 Å), e.g., 5 nm (50 A) to 50 nm (500 A), e.g., 10 nm (100 A) to 37 nm (370 A), e.g., 10 nm (100 A) to 30 nm (300 Å), e.g., 10 nm (100 A) to 20 nm (200 Å), e.g., 15 nm (150 Å) to 20 nm (200 A), e.g., 18 nm (180 Å) to 19 nm (190 Å).

[0028] For example, for a multi-film layer, the zinc oxide film 52 (and optional second zinc oxide film 56, if present) can have a thickness in the range of 1 nm (10 Å) to 20 nm (200 A), e.g., 5 nm (50 Å) to 20 nm (200 A), e.g., 6 nm (60 A) to 15 nm (150 A), e.g., 7 nm (70 Å) to 8.5 nm (85 A). The metal alloy oxide layer (zinc stannate) 54 can have a thickness in the range of 5 nm (50 Å) to 80 nm (800 A), e.g., 5 nm (50 A) to 50 nm (500 A), e.g., 10 nm (100 A) to 30 nm (300 A), e.g., 11 nm (110 Å) to 23.5 nm (235 Å), e.g., 11 nm (110 Å) to 12 nm (120 Å).

[0029] A subcritical thickness (discontinuous) second metallic layer 58 is located over the second dielectric layer 50 (e.g., over the second zinc oxide film 56, if present, or over the zinc stannate film 54 if not). The metallic material, such as, but not limited to, metallic gold, copper, palladium, aluminum, silver, or mixtures, alloys, or combinations thereof, is applied at a subcritical thickness such that isolated regions or islands of the material are formed rather than a continuous layer of the material. For silver, it has been determined that the critical thickness is less than 5 nm (50 Å), such as less than 4 nm (40 A), such as less than 3 nm (30 Å), such as less than 2.5 nm (25 A). For silver, the transition between a continuous layer and a subcritical layer occurs in the range of 2.5 nm (25 A) to 5 nm (50 Å). It is estimated that copper, gold, and palladium would exhibit similar subcritical behavior in this range. The second metallic layer 58 can include any one or more of the materials described above with respect to the first reflective layer 46 but these materials are not present as a continuous film. In one non-limiting embodiment, the second layer 58 comprises islanded silver with the islands having an effective thickness in the range of 0.1 nm (1 Å) to 7 nm (70 A), e.g., 1 nm (10 Å) to 4 nm (40 A), e.g., 1 nm (10Å) to 3.5 nm (35 A), e.g., 1 nm (10 Å) to 3 nm (30 A), e.g., 1.5 nm (15 A) to 3 nm (30 Å), e.g., 2 nm (20 A) to 3 nm (30 A), e.g., 2.5 nm (25 A) to 3 nm (30 Å). The subcritical metallic layer 58 absorbs electromagnetic radiation according to the Plasmon Resonance Theory. This absorption depends at least partly on the boundary conditions at the interface of the metallic islands. The subcritical metallic layer 58 is not an infrared reflecting layer, like the first metallic layer 46. The subcritical silver layer 58 is not a continuous layer. It is estimated that for silver, the metallic islands or balls of silver metal deposited below the subcritical thickness can have a height of about 2 nm to 7 nm, such as 5 nm to 7 nm. It is estimated that if the subcritical silver layer could be spread out uniformly, it would have a thickness of about 1.1 nm. It is estimated that optically, the discontinuous metal layer behaves as an effective layer thickness of 2.6 nm. Depositing the discontinuous metallic layer over zinc stannate rather than zinc oxide appears to increase the visible light absorbance of the coating, e.g., of the discontinuous metallic layer.

[0030] A second primer layer 60 can be deposited over the second metallic layer 58. The second primer layer 60 can be as described above with respect to the first primer layer 48. In one example, the second primer layer can be a nickel-chromium alloy (such as Inconel) having a thickness in the range of 0.5 nm (5 Å) to 5 nm (50 A), e.g., 1 nm (10 A) to 2.5 nm (25 Å), e.g., 1.5 nm (15 A) to 2.5 nm (25 A), e.g., 1.5 nm (15 A) to 2.2 nm (22 Å). Since the absorbance of the subcritical material depends at least partly on the boundary conditions, different primers (e.g., having different refractive indices) can provide the coating with different absorbance spectra and, hence, with different colors.

[0031] A third dielectric layer 62 is deposited over the second metallic layer 58 (e.g., over the second primer film 60). The third dielectric layer 62 can also include one or more metal oxide or metal alloy oxide-containing layers, such as discussed above with respect to the first and second dielectric layers 40, 50. In one example, the third dielectric layer 62 is a multi-film layer similar to the second dielectric layer 50. For example, the third dielectric layer 62 can include a first metal oxide layer 64, e.g., a zinc oxide layer, a second metal alloy oxide-containing layer 66, e.g., a zinc stannate layer deposited over the zinc oxide layer 64, and an optional third metal oxide layer 68, e.g., another zinc oxide layer, deposited over the zinc stannate layer 66. In one example, both of the zinc oxide layers 64, 68 are present and each has a thickness in the range of 5 nm (50 Å) to 20 nm (200 A), such as 7.5 nm (75 A) to 15 nm (150 A), such as 8 nm (80 A) to 15 nm (150 A), such as 9.5 nm (95 Å) to 12 nm (120 Å). The metal alloy oxide layer 66 can have a thickness in the range of 10 nm (100 Å) to 80 nm (800 Å), e.g., 20 nm (200 A) to 70 nm (700 Å), e.g., 30 nm (300 A) to 60 nm (600

A), e.g., 38 nm (380 A) to 50 nm (500 A), e.g., 38 nm (380 A) to 45 nm (450 Å).

[0032] In one example, the total thickness of the third dielectric layer 62 (e.g., the combined thicknesses of the zinc oxide and zinc stannate layers) is in the range of 20 nm (200 Å) to 100 nm (1000 A), e.g., 40 nm (400 A) to 90 nm (900 A), e.g., 50 nm (500 Å) to 90 nm (900 A), e.g., 65 nm (650 Å) to 80 nm (800 A), e.g., 69 nm (690 A) to 72 nm (720 Å).

[0033] A third heat and/or radiation reflective metallic layer 70 is deposited over the third dielectric layer 62. The third reflective layer 70 can be of any of the materials discussed above with respect to the first reflective layer. In one non-limiting example, the third reflective layer 70 includes silver and has a thickness in the range of 2.5 nm (25 Å) to 30 nm (300 A), e.g., 5 nm (50 Å) to 30 nm (300 Å), e.g., 5 nm (50 A) to 20 nm (200 Å), such as 7 nm (70 Å) to 15.1 nm (151 A), such as 10 nm (100 Å) to 15 nm (150 A), such as 13.7 nm (137 A) to 15 nm (150 A). The third metallic layer is a continuous layer.

[0034] A third primer layer 72 is located over the third reflective layer 70. The third primer layer 72 can be as described above with respect to the first or second primer layers. In one non-limiting example, the third primer layer is titanium and has a thickness in the range of 0.5 nm (5 Å) to 5 nm (50 A), e.g., 1 nm (10 Å) to 3.3 nm (33 A), e.g., 2 nm (20 A) to 3 nm (30 A).

[0035] A fourth dielectric layer 74 is located over the third primer layer 72. The fourth dielectric layer 74 can be comprised of one or more metal oxide or metal alloy oxide-containing layers, such as those discussed above with respect to the first, second, or third dielectric layers 40, 50, 62. In one non-limiting example, the fourth dielectric layer 74 is a multi-film layer having a first metal oxide layer 76, e.g., a zinc oxide layer, deposited over the third primer film 72, and a second metal alloy oxide layer 78, e.g., a zinc stannate layer, deposited over the zinc oxide layer 76. In one non-limiting embodiment, the zinc oxide layer 76 can have a thickness in the range of 2.5 nm (25 Å) to 20 nm (200 Å), such as 5 nm (50 Å) to 15 nm (150 A), such as 6 nm (60 A) to 10 nm (100 A), such as 8 nm (80 Å) to 9 nm (90 Å). The zinc stannate layer 78 can have a thickness in the range of 2.5 nm (25 Å) to 50 nm (500 A), e.g., 5 nm (50 A) to 50 nm (500 Å), e.g., 10 nm (100 Å) to 40 nm (400 A), e.g., 15 nm (150 Å) to 30 nm (300 Å), e.g., 15 nm (150 Å) to 20 nm (200 Å), e.g., 17 nm (170 Å) to 19 nm (190 Å).

[0036] In one non-limiting example, the total thickness of the fourth dielectric layer 74 (e.g., the combined thicknesses of the zinc oxide and zinc stannate layers) is in the range of 10 nm (100 A) to 80 nm (800 Å), e.g., 20 nm (200 A) to 60 nm (600 A), e.g., 25 nm (250 A) to 40 nm (400 A), e.g., 25 nm (250 A) to 27 nm (270 Å).

[0037] An overcoat 80 can be located over the fourth dielectric layer 74. The overcoat 80 can help protect the underlying coating layers from mechanical and chemical attack. The overcoat 80 can be, for example, a metal oxide or metal nitride layer. For example, the overcoat 80 can be titania having a thickness in the range of 1 nm (10 Å) to 10 nm (100 A), such as 2 nm (20 Å) to 8 nm (80 A), such as 3 nm (30 A) to 5 nm (50 A), such as 3 nm (30 A) to 4.5 nm (45 A). Other materials useful for the overcoat include other oxides, such as silica, alumina, or a mixture of silica and alumina.

[0038] In one non-limiting embodiment, the transparency 10 of the invention has a percent reflectance (%R) of visible light from the No. 1 surface in the range of 5% to 50%, such as 20% to 40%, such as 25% to 30%. The transparency 10 has a visible light transmittance of greater than 20%, such as greater than 30%, such as greater than 40%. The transparency has a solar heat gain coefficient (SHGC) of less than 0.3, such as less than 0.27, such as less than 0.25.

[0039] Unlike prior articles, the ply coated with the coating 30 can be tempered or heat treated without adversely impacting upon the performance characteristics of the article or producing haze. Also, the article of the invention has a neutral or moderate reflected color, such as blue or blue-green, in both reflection and transmission.

[0040] The lack of haze upon heating is believed due to the islanded structure of the discontinuous intermediate metallic layer. A side view of a subcritical metallic layer 90 having discontinuous coating regions 91 formed on a dielectric layer 92 and covered by a primer layer 94 is shown in Fig 3. The subcritical metal thickness causes the metal material to form discontinuous regions or islands of metal or metal oxide on the dielectric layer 92. When the primer layer is applied over the subcritical metal layer, the material of the primer layer covers the islands and can also extend into the gaps between adjacent islands of the subcritical metal and contact the underlying layer 92.

[0041] The coating 30 of the invention provides various advantages over known coatings. For example, the subcritical metallic layer increases the visible light absorbance of the coating, making the coated article darker. The combination of the subcritical metallic layer with selected thicknesses of the dielectric layers can provide the coated article with an asymmetrical reflectance. The color of the article can be tuned in transmission by changing the primer(s) used in the coating. Also, the coating of the invention is able to be heat treated without introducing haze.

[0042] While the above example included two continuous metal layers and one discontinuous metal layer, it is to be understood that this is just one non-limiting example. In the broad practice of the invention, the coating of the invention could include multiple continuous metallic layers and multiple discontinuous metallic layers. For example, a coated article could include a single subcritical metallic layer located between two dielectric layers. Or, the coating could include 3 or more metallic layers, such as 4 or more metallic layers, such as 5 or more metallic layers, such as 6 or more metallic layers, with at least one of the metallic layers being a subcritical metallic layer.

Titanium Primer

[0043] Another exemplary coating 130 of the invention is shown in Fig. 4. This exemplary coating 130 includes a base layer or first dielectric layer 140 deposited over at least a portion of a major surface of a substrate (e.g., the No. 2 surface 16 of the first ply 12). The first dielectric layer 140 can be similar to the first dielectric layer 40 described above. The first dielectric layer 140 can be a single layer or can comprise more than one film of metal oxides, oxides of metal alloys, nitrides, oxynitrides, or mixtures thereof. The first dielectric layer 140 can be transparent to visible light. Suitable metal oxides for the first dielectric layer 140 include oxides of hafnium, zirconium, niobium, zinc, bismuth, lead, indium, tin, and mixtures thereof. These metal oxides can have small amounts of other materials, such as manganese in bismuth oxide, tin in indium oxide, etc. Additionally, oxides of metal alloys or metal mixtures can be used, such as oxides containing zinc and tin (e.g., zinc stannate, defined below), oxides of indium-tin alloys, silicon nitrides, silicon aluminum nitrides, or aluminum nitrides. Further, doped metal oxides, such as antimony or indium doped tin oxides or nickel or boron doped silicon oxides, can be used. The first dielectric layer 140 can be a substantially single phase film, such as a metal alloy oxide film, e.g., zinc stannate, or can be a mixture of phases composed of zinc and tin oxides or can be composed of a plurality of films.

[0044] For example, the first dielectric layer 140 (whether a single film or multiple film layer) can have a thickness in the range of 10 nm (100 Å) to 60 nm (600 A), such as 10 nm (100 Å) to 50 nm (500 A), such as 10 nm (100 Å) to 35 nm (350 A), such as 15 nm (150 A) to 30 nm (300 A), such as 20 nm (200 Å) to 25 nm (250 Å), such as 21 nm (210 A) to 22 nm (220 Å).

[0045] The first dielectric layer 140 can comprise a multi-film structure having a first film 142, e.g., a metal alloy oxide film, deposited over at least a portion of a substrate (such as the inner major surface 16 of the first ply 12) and a second film 144, e.g., a metal oxide or oxide mixture film, deposited over the first metal alloy oxide film 142. In one non-limiting embodiment, the first film 142 can be zinc stannate.

[0046] For example, the first film 142 can be zinc stannate and the second film 144 can be zinc oxide (for example, 90 wt.% zinc oxide and 10 wt.% tin oxide). For example, the first film 142 can comprise zinc stannate having a thickness in the range of 5 nm (50 Å) to 60 nm (600 A), such as 5 nm (50 A) to 50 nm (500 A), such as 7.5 nm (75 Å) to 35 nm (350 A), such as 10 nm (100 A) to 25 nm (250 A), such as 10 nm (100 A) to 20 nm (200 A), such as 10 nm (100 A) to 15 nm (150 A), such as 14 nm (140 A) to 15 nm (150 A).

[0047] The second film 144 can comprise zinc oxide having a thickness in the range of 5 nm (50 Å) to 20 nm (200 A), such as 5 nm (50 A) to 15 nm (150 A), such as 7 nm (70 A) to 10 nm (100 A).

[0048] A first heat and/or radiation reflective metallic layer 146 is deposited over the first dielectric layer 140. The first reflective layer 146 can include a reflective metal, such as, but not limited to, metallic gold, copper, palladium, silver, or mixtures, alloys, or combinations thereof. In one embodiment, the first reflective layer 46 comprises a metallic silver layer having a thickness in the range of 2.5 nm (25 Å) to 30 nm (300 A), e.g., 5 nm (50 A) to 30 nm (300 A), e.g., 5 nm (50 Å) to 25 nm (250 Å), e.g., 5 nm (50 Å) to 20 nm (200 A), such as 7 nm (70 A) to 20 nm (200 A), such as 10 nm (100 A) to 20 nm (200 A), such as 12 nm (120 A) to 18 nm (180 Å).

[0049] A first primer layer 148 is located over the first reflective layer 146. The first primer layer 148 can be a single film or a multiple film layer. The first primer layer 148 can include an oxygen-capturing material that can be sacrificial during the deposition process to prevent degradation or oxidation of the first reflective layer 146 during the sputtering process or subsequent heating processes. The first primer layer 148 can also absorb at least a portion of electromagnetic radiation, such as visible light, passing through the coating 130. Examples of materials useful for the first primer layer 148 include titanium, Inconel, Stellite®, and mixtures thereof. For example, the first primer layer 148 can have a thickness in the range of 0.5 nm (5 Å) to 5 nm (50 Å), e.g., 1 nm (10 A) to 4 nm (40 A), e.g., 2 nm (20 Å) to 4 nm (40 A), e.g., 2 nm (20 Å) to 3 nm (30 A). In one example, the first primer 148 is titanium.

[0050] A second dielectric layer 150 is located over the first primer layer 48. The second dielectric layer 150 can comprise one or more metal oxide or metal alloy oxide-containing films, such as those described above with respect to the first dielectric layer 140. For example, the second dielectric layer 150 can include a first metal oxide film 152, e.g., a zinc oxide film, deposited over the first primer film 148 and a second metal alloy oxide film 154, e.g., a zinc stannate (Zn_2SnO_4) film, deposited over the first zinc oxide film 152. An optional third metal oxide film 156, e.g., another zinc oxide layer, can be deposited over the zinc stannate layer.

[0051] The second dielectric layer 150 can have a total thickness (e.g., the combined thicknesses of the layers if more than one layer is present) is in the range of 5 nm (50 A) to 100 nm (1000 A), e.g., 5 nm (50 A) to 50 nm (500 A), e.g., 10 nm (100 Å) to 40 nm (400 A), e.g., 20 nm (200 Å) to 40 nm (400 A), e.g., 30 nm (300 A) to 40 nm (400 A), e.g., 35. nm (350 A) to 40 nm (400 Å), e.g., 35 nm (350 A) to 37 nm (370 Å).

[0052] For example, for a multi-film layer, the zinc oxide film 152 (and optional second zinc oxide film 156, if present) can have a thickness in the range of 10 nm (10 Å) to 20 nm (200 A), e.g., 5 nm (50 Å) to 20 nm (200 A), e.g., 5 nm (50 A) to 15 nm (150 A), e.g., 5 nm (50 A) to 8.5 nm (85 A). The metal alloy oxide layer (zinc stannate) 54 can have a thickness in the range of 5 nm (50 Å) to 80 nm (800 A), e.g., 5 nm (50 A) to 50 nm (500 A), e.g., 10 nm (100 Å) to 30

nm (300 Å), e.g., 27 nm (270 Å) to 30, nm (300 A).

[0053] A subcritical (discontinuous) metallic layer 158 is located over the second dielectric layer 150 (e.g., over the second zinc oxide film 156, if present, or over the zinc stannate film 154 if not). The second metallic layer 158 can include any one or more of the metallic materials described above with respect to the first reflective layer 146. In one non-limiting embodiment, the second metallic layer 158 comprises islanded silver with the islands having an effective thickness in the range of 0.1 nm (1 Å) to 5 nm (50 A), e.g., 1 nm (10 A) to 4 nm (40 A), e.g., 1 nm (10 Å) to 3.5 nm (35 A), e.g., 1 nm (10 Å) to 3 nm (30 A), e.g., 1.5 nm (15 Å) to 3 nm (30 Å), e.g., 2 nm (20 Å) to 3 nm (30 A), e.g., 2.5 nm (25 Å) to 3 nm (30 A).

[0054] A second primer layer 160 can be deposited over the second metallic layer 158. The second primer layer 160 can be as described above with respect to the first primer layer 148. For example, the second primer layer can be titanium having a thickness in the range of 0.5 nm (5 Å) to 5 nm (50 Å), e.g., 1 nm (10 A) to 3.5 nm (35 Å), e.g., 1.5 nm (15 Å) to 3.5 nm (35 Å), e.g., 2 nm (20 Å) to 3 nm (30 A).

[0055] A third dielectric layer 162 is deposited over the second reflective layer 158 (e.g., over the second primer layer 160). The third dielectric layer 162 can also include one or more metal oxide or metal alloy oxide-containing layers, such as discussed above with respect to the first and second dielectric layers 140, 150. In one example, the third dielectric layer 162 is a multi-film layer similar to the second dielectric layer 150. For example, the third dielectric layer 162 can include a first metal oxide layer 164, e.g., a zinc oxide layer, a second metal alloy oxide-containing layer 166, e.g., a zinc stannate layer deposited over the zinc oxide layer 164, and an optional third metal oxide layer 168, e.g., another zinc oxide layer, deposited over the zinc stannate layer 166. In one example, both of the zinc oxide layers 164, 168 are present and each has a thicknesses in the range of 5 nm (50 Å) to 20 nm (200 Å), such as 7.5 nm (75 A) to 15 nm (150 A), such as 8 nm (80 A) to 15 nm (150 Å), such as 9.5 nm (95 A) to 10 nm (100 Å). The metal alloy oxide layer 166 can have a thickness in the range of 10 nm (100 Å) to 80 nm (800 A), e.g., 20 nm (200 A) to 70 nm (700 A), e.g., 30 nm (300 A) to 60 nm (600 A), e.g., 50 nm (500 Å) to 60 nm (600 A), e.g., 56 nm (560 Å) to 60 nm (600 Å).

[0056] In one example, the total thickness of the third dielectric layer 162 (e.g., the combined thicknesses of the zinc oxide and zinc stannate layers) is in the range of 20 nm (200 A) to 100 nm (1000 A), e.g., 40 nm (400 A) to 90 nm (900 A), e.g., 50 nm (500 A) to 90 nm (900 A), e.g., 65 nm (650 Å) to 80 nm (800 Å), e.g., 69 nm (690 Å) to 76 nm (760 Å).

[0057] A third heat and/or radiation reflective metallic layer 170 is deposited over the third dielectric layer 162. The third reflective layer 170 can be of any of the materials discussed above with respect to the first and second reflective layers. In one non-limiting example, the third reflective layer 170 includes silver and has a thickness in the range of 2.5 nm (25 Å) to 30 nm (300 A), e.g., 5 nm (50 Å) to 30 nm (300 A), e.g., 5 nm (50 Å) to 20 nm (200 A), such as 7 nm (70 Å) to 20 nm (200 Å), such as 10 nm (100 Å) to 20 nm (200 A), such as 17 nm (170 Å) to 20 nm (200 Å).

[0058] A third primer layer 172 is located over the third reflective layer 170. The third primer layer 172 can be as described above with respect to the first or second primer layers. In one non-limiting example, the third primer layer is titanium and has a thickness in the range of 0.5 nm (5 Å) to 5 nm (50 Å), e.g., 1 nm (10 Å) to 3 nm (30 A), e.g., 2 nm (20 A) to 3 nm (30 Å).

[0059] A fourth dielectric layer 174 is located over the third primer film 172). The fourth dielectric layer 174 can be comprised of one or more metal oxide or metal alloy oxide-containing layers, such as those discussed above with respect to the first, second, or third dielectric layers 140, 150, 162. In one non-limiting example, the fourth dielectric layer 174 is a multi-film layer having a first metal oxide layer 176, e.g., a zinc oxide layer, deposited over the third primer film 172, and a second metal alloy oxide layer 178, e.g., a zinc stannate layer, deposited over the zinc oxide layer 176. In one non-limiting embodiment, the zinc oxide layer 176 can have a thickness in the range of 2.5 nm (25 Å) to 20 nm (200 A), such as 5 nm (50 A) to 15 nm (150 Å), such as 6 nm (60 A) to 10 nm (100 Å), such as 7 nm (70 A) to 9 nm (90 Å). The zinc stannate layer 178 can have a thickness in the range of 2.5 nm (25 Å) to 50 nm (500 A), e.g., 5 nm (50 A) to 50 nm (500 A), e.g., 10 nm (100 Å) to 40 nm (400 Å), e.g., 15 nm (150 Å) to 30 nm (300 Å), e.g., 15 nm (150 Å) to 20 nm (200 A), e.g., 17 nm (170 Å) to 20 nm (200 Å).

[0060] In one non-limiting example, the total thickness of the fourth dielectric layer 174 (e.g., the combined thicknesses of the zinc oxide and zinc stannate layers) is in the range of 10 nm (100 A) to 80 nm (800 A), e.g., 20 nm (200 A) to 60 nm (600 Å), e.g., 25 nm (250 Å) to 40 nm (400 A), e.g., 25 nm (250 Å) to 27 nm (270 A).

[0061] An overcoat 180 can be located over the fourth dielectric layer 174. The overcoat 180 can help protect the underlying coating layers from mechanical and chemical attack. The overcoat 180 can be, for example, a metal oxide or metal nitride layer. For example, the overcoat 180 can be titania having a thickness in the range of 1 nm (10 Å) to 10 nm (100 A), such as 2 nm (20 Å) to 8 nm (80 Å), such as 3 nm (30 Å) to 5 nm (50 Å), such as 3 nm (30 A) to 4 nm (40 Å).

Capsule

[0062] Another exemplary non-limiting coating 230 of the invention is shown in Fig. 5. This exemplary coating 230 includes a base layer or first dielectric layer 240 deposited over at least a portion of a major surface of a substrate (e.g., the No. 2 surface 16 of the first ply 12). The first dielectric layer 240 can be a single layer or can comprise more than one film of metal oxides, oxides of metal alloys, nitrides, oxynitrides, or mixtures thereof. The first dielectric layer 240

can be transparent to visible light. Suitable metal oxides for the first dielectric layer 240 include oxides of hafnium, zirconium, niobium, zinc, bismuth, lead, indium, tin, and mixtures thereof. These metal oxides can have small amounts of other materials, such as manganese in bismuth oxide, tin in indium oxide, etc. Additionally, oxides of metal alloys or metal mixtures can be used, such as oxides containing zinc and tin (e.g., zinc stannate, defined below), oxides of indium-tin alloys, silicon nitrides, silicon aluminum nitrides, or aluminum nitrides. Further, doped metal oxides, such as antimony or indium doped tin oxides or nickel or boron doped silicon oxides, can be used. The first dielectric layer 240 can be a substantially single phase film, such as a metal alloy oxide film, e.g., zinc stannate, or can be a mixture of phases composed of zinc and tin oxides or can be composed of a plurality of films.

[0063] For example, the first dielectric layer 240 (whether a single film or multiple film layer) can have a thickness in the range of 10 nm (100 Å) to 60 nm (600 Å), such as 20 nm (200 A) to 50 nm (500 Å), such as 25 nm (250 Å) to 35 nm (350 Å), such as 25 nm (250 A) to 31 nm (310 A), such as 28 nm (280 A) to 31 nm (310 Å), such as 29 nm (290 A) to 30 nm (300 A).

[0064] The first dielectric layer 240 can comprise a multi-film structure having a first film 242, e.g., a metal alloy oxide film, deposited over at least a portion of a substrate (such as the inner major surface 16 of the first ply 12) and a second film 244, e.g., a metal oxide or oxide mixture film, deposited over the first metal alloy oxide film 242. In one non-limiting embodiment, the first film 242 can be zinc stannate.

[0065] For example, the first film 242 can be zinc stannate and the second film 244 can be zinc oxide (for example, 90 wt.% zinc oxide and 10 wt.% tin oxide). For example, the first film 242 can comprise zinc stannate having a thickness in the range of 5 nm (50 Å) to 60 nm (600 A), such as 5 nm (50 A) to 50 nm (500 A), such as 7.5 nm (75 A) to 35 nm (350 A), such as 10 nm (100 A) to 25 nm (250 Å), such as 15 nm (150 A) to 25 nm (250 A), such as 20 nm (200 Å) to 25 nm (250 Å), such as 20 nm (200 A) to 24 nm (240 Å).

[0066] The second film 244 can comprise zinc oxide having a thickness in the range of 5 nm (50 Å) to 20 nm (200 A), such as 5 nm (50 A) to 17.5 nm (175 A), such as 5 nm (50 A) to 15 nm (150 A), such as 5 nm (50 Å) to 10 nm (100 Å).

[0067] A first heat and/or radiation reflective metallic layer 246 is deposited over the first dielectric layer 240. The first reflective layer 246 can include a reflective metal, such as, but not limited to, metallic gold, copper, palladium, silver, or mixtures, alloys, or combinations thereof. In one embodiment, the first reflective layer 246 comprises a metallic silver layer having a thickness in the range of 5 nm (50 Å) to 30 nm (300 A), e.g., 5 nm (50 A) to 25 nm (250 A), e.g., 5 nm (50 Å) to 20 nm (200 A), such as 7 nm (70 A) to 20 nm (200 Å), such as 10 nm (100 A) to 20 nm (200 A), such as 14 nm (140 A) to 18 nm (180 Å).

[0068] A first primer layer 248 is located over the first reflective layer 246. The first primer layer 248 can be a single film or a multiple film layer. The first primer layer 248 can include an oxygen-capturing material that can be sacrificial during the deposition process to prevent degradation or oxidation of the first reflective layer 246 during the sputtering process or subsequent heating processes. The first primer layer 248 can also absorb at least a portion of electromagnetic radiation, such as visible light, passing through the coating 230. Examples of materials useful for the first primer layer 248 include titanium, Inconel, Stellite®, and mixtures thereof. For example, the first primer layer 248 can have a thickness in the range of 0.5 nm (5 Å) to 5 nm (50 A), e.g., 1 nm (10 A) to 4 nm (40 A), e.g., 1.5 nm (15 A) to 3 nm (30 A), e.g., 1.6 nm(16 A) to 3 nm (30 A).

[0069] A second dielectric layer 250 is located over the first primer layer 248. The second dielectric layer 250 comprises one or more metal oxide or metal alloy oxide-containing films, described above with respect to the first dielectric layer 240. For example, the second dielectric layer 250 can include a first metal oxide film 252, e.g., a zinc oxide film, deposited over the first primer film 248 and a second metal alloy oxide film 254, e.g., a zinc stannate (Zn_2SnO_4 film, deposited over the first zinc oxide film 252. An optional third metal oxide film 256, e.g., another zinc oxide layer, can be deposited over the zinc stannate layer.

[0070] The second dielectric layer 250 can have a total thickness (e.g., the combined thicknesses of the layers) in the range of 5 nm (50 A) to 100 nm (1000 A), e.g., 5 nm (50 A) to 50 nm (500 A), e.g., 10 nm (100 A) to 37 nm (370 A), e.g., 10 nm (100 A) to 30 nm (300 Å), e.g., 10 nm (100 A) to 25 nm (250 Å), e.g., 20 nm (200 Å) to 23 nm (230 A).

[0071] For example, for a multi-film layer, the zinc oxide film 252 (and optional third zinc oxide film 256, if present) can have a thickness in the range of 1 nm (10 Å) to 20 nm (200 Å) , e.g., 5 nm (50 A) to 20 nm (200 Å), e.g., 6 nm (60 A) to 15 nm (150 A), e.g., 7.5 nm (75 A) to 8.5 nm (85 Å). The metal alloy oxide layer (zinc stannate) 254 can have a thickness in the range of 5 nm (50 Å) to 80 nm (800 A), e.g., 5 nm (50 A) to 50 nm (500 A), e.g., 10 nm (100 A) to 20 nm (200 A), e.g., 15.5 nm(155 Å) to 20 nm (200 A).

[0072] An absorbing layer 257 is located over the second dielectric layer 250 (e.g., over the third zinc oxide film 256, if present, or over the zinc stannate film 254 if not). The absorbing layer 257 is a multilayer structure having a first absorbing layer 259, a metallic layer 261, and a second absorbing layer 263. The first and second absorbing layers 259, 263 can be the same or different materials. Material suitable for the absorbing layers includes metal or silicon oxide or nitrides. For example, the first and second absorbing layers 259, 265 can be silicon nitride. The first absorbing layer 259 can have a thickness in the range of 1 nm (10 Å) to 20 nm (200 A), e.g., 5 nm (50 A) to 20 nm (200 Å), e.g., 6 nm (60 A) to 15 nm (150 A), e.g., 8 nm (80 A) to 9 nm (90 Å). The second absorbing layer 263 can also be silicon nitride and

can have a thickness in the range of 1 nm (10 Å) to 20 nm (200 Å), e.g., 5 nm (50 A) to 20 nm (200 A), e.g., 6 nm (60 Å) to 15 nm (150 Å), e.g., 7.5 nm (75 A) to 10 nm (100 Å).

[0073] The metallic layer 261 is a subcritical thickness layer as described above. In one example, the metallic layer 261 is a cobalt-chromium alloy (such as Stellite®) and has a thickness in the range of 0.1 nm (1 Å) to 5 nm (50 Å), e.g., 1 nm (10 Å) to 4 nm (40 Å), e.g., 1 nm (10 A) to 3.5 nm (35 Å), e.g., 1 nm (10 Å) to 3 nm (30 Å), e.g., 1.5 nm (15 Å) to 3 nm (30 A), e.g., 2 nm (20 A) to 3 nm (30 Å), e.g., 2.5 nm (25 A) to 3 nm (30 A).

[0074] A third dielectric layer 262 is deposited over the absorbing layer 257. The third dielectric layer 262 includes one or more metal oxide or metal alloy oxide-containing layers, as discussed above with respect to the first and second dielectric layers 240, 250. In one example, the third dielectric layer 262 is a multi-film layer similar to the second dielectric layer 250. For example, the third dielectric layer 262 can include an optional first metal oxide layer 264, e.g., a zinc oxide layer, a second metal alloy oxide-containing layer 266, e.g., a zinc stannate layer deposited over the zinc oxide layer 264 (if present), and an optional third metal oxide layer 268, e.g., another zinc oxide layer, deposited over the zinc stannate (second) layer 266. In one example, the first zinc oxide layer 264 (if present) and the third zinc oxide layer 268 can each have a thickness in the range of 5 nm (50 Å) to 20 nm (200 A), such as 7.5 nm (75 A) to 15 nm (150 Å), such as 8 nm (80 A) to 15 nm (150 Å), such as 9.5 nm (95 A) to 10.5 nm (105 A). The metal alloy oxide layer (second) 266 can have a thickness in the range of 10 nm (100 Å) to 80 nm (800 A), e.g., 20 nm (200 Å) to 70 nm (700 A), e.g., 30 nm (300 Å) to 60 nm (600 A), e.g., 38 nm (380 A) to 50 nm (500 A), e.g., 42 nm (420 A) to 45 nm (450 Å).

[0075] In one example, the total thickness of the third dielectric layer 262 (e.g., the combined thicknesses of the zinc oxide and zinc stannate layers) is in the range of 20 nm (200 Å) to 100 nm (1000 A), e.g., 40 nm (400 A) to 90 nm (900 Å), e.g., 50 nm (500 A) to 90 nm (900 Å), e.g., 50 nm (500 A) to 60 nm (600 A), e.g., 52.5 nm (525 A) to 55 nm (550 A).

[0076] A third heat and/or radiation reflective metallic layer 270 is deposited over the third dielectric layer 262. The third reflective layer 270 can be of any of the materials discussed above with respect to the first and second reflective layers. In one non-limiting example, the third reflective layer 270 includes silver and has a thickness in the range of 5 nm (50 Å) to 30 nm (300 A), e.g., 5 nm (50 A) to 20 nm (200 A), such as 7 nm (70 Å) to 15 nm (150 A), such as 10 nm (100 Å) to 15 nm (150 A), such as 12.8 nm(128 Å) to 15 nm (150 Å).

[0077] A third primer layer 272 is located over the third reflective layer 270. The third primer layer 272 can be as described above with respect to the first or second primer layers. In one non-limiting example, the third primer layer is titanium and has a thickness in the range of 0.5 nm (5 Å) to 5 nm (50 A), e.g., 1 nm (10 A) to 3 nm (30 Å), e.g., 1.7 nm(17 A) to 3 nm (30 Å).

[0078] A fourth dielectric layer 274 is located over the third primer layer 272). The fourth dielectric layer 274 comprises of one or more metal oxide or metal alloy oxide-containing layers discussed above with respect to the first, second, or third dielectric layers 240, 250, 262. In one non-limiting example, the fourth dielectric layer 274 is a multi-film layer having a first metal oxide layer 276, e.g., a zinc oxide layer, deposited over the third primer film 272, and a second metal alloy oxide layer 278, e.g., a zinc stannate layer, deposited over the zinc oxide layer 276. In one non-limiting embodiment, the zinc oxide layer 276 can have a thickness in the range of 2.5 nm (25 Å) to 20 nm (200 Å), such as 5 nm (50 A) to 15 nm (150 A), such as 6 nm (60 Å) to 10 nm (100 A), such as 6 nm (60 A) to 7 nm (70 Å). The zinc stannate layer 78 can have a thickness in the range of 2.5 nm (25 Å) to 50 nm (500 Å), e.g., 5 nm (50 A) to 50 nm (500 A), e.g., 10 nm (100 A) to 40 nm (400 A), e.g., 15 nm (150 A) to 30 nm (300 Å), e.g., 15 nm (150 Å) to 20 nm (200 Å), e.g., 18 nm (180 Å) to 19 nm (190 Å).

[0079] In one non-limiting example, the total thickness of the fourth dielectric layer 274 (e.g., the combined thickness of the zinc oxide and zinc stannate layers) is in the range of 10 nm (100 A) to 80 nm (800 Å), e.g., 20 nm (200 A) to 60 nm (600 A), e.g., 25 nm (250 A) to 40 nm (400 A), e.g., 25 nm (250 A) to 27 nm (270 Å).

[0080] An overcoat 280 can be located over the fourth dielectric layer 274. The overcoat 280 can help protect the underlying coating layers from mechanical and chemical attack. The overcoat 280 can be, for example, a metal oxide or metal nitride layer. For example, the overcoat 280 can be titania having a thickness in the range of 1 nm (10 Å) to 10 nm (100 A), such as 2 nm (20 A) to 8 nm (80 Å), such as 3 nm (30 Å) to 5 nm (50 Å), such as 3 nm (30 A) to 4 nm (40 A).

Small Band Gap Semiconductor Materials As Absorber Layer

[0081] In some applications, it may be desirable to modify particular transmitted color without affecting the solar control performance of the coating. One way to do this would be by the use of integrating a semiconductor material into a solar control coating that has a band gap edge in the visible region of the electromagnetic spectrum. As will be appreciated by one skilled in the art, at the edge of a semiconductor band gap, shorter wave length radiation is absorbed by the semiconductor material while longer wavelength energy is transmitted through the material. That is, the material is transparent to radiation above the edge of the band gap. By selecting a material having a band gap edge in the visible region, one can select the wavelength of electromagnetic radiation that is absorbed or passes through the semiconductor material. By using semiconductor materials with small band gaps, such as but not limited to, germanium or germanium-based alloys, the absorption edge can be placed near the long-wavelength side of the visible spectrum. In this way, the

optical transmission can be reduced without absorbing near or far infrared radiation, minimizing unnecessary heating of the glass into absorption. This semiconductor material can be placed within a conventional solar control coating, such as between two silver layers, above a silver layer, below a silver layer, or anywhere else within the stack.

[0082] The following Examples illustrate various embodiments of the invention. However, it is to be understood that the invention is not limited to these specific embodiments.

EXAMPLES

[0083] In the following Examples, "Rf" refers to the film side reflectance, "Rg" refers to the glass side reflectance, "T" refers to the transmittance through the article, "Rg60" refers to the glass side reflectance at a 60 degree angle, "Rx" refers to the exterior reflectance of a standard IGU from the No. 1 surface, "Rint" refers to the reflectance of the IGU from the inside (No. 4) surface, "VLT" refers to the visible light transmittance, and "SHGC" refers to the solar heat gain coefficient. A "standard IGU" has an outer ply of 6 mm thick glass, an inner ply of 6 mm glass, a 0.5 inch (1.27 cm) gap filled with air, with the coating on the No. 2 surface. "S.C." means "subcritical" thickness (that is, the layer was not a continuous layer but was deposited to form discontinuous coating regions.)

[0084] In the following examples, "heat treated" means that the coated substrate was heated in a box furnace to a temperature of 1,185°F to simulate tempering and then air cooled to room temperature before the optical characteristics were measured.

[0085] The color coordinates a*, b*, and L* are those of the conventional CIE (1931) and CIELAB systems that will be understood by one of ordinary skill in the art.

[0086] In order to model the response of the subcritical layer structure to electromagnetic radiation so that the optical properties of the entire stack can be optimized and controlled, the subcritical layer can be modeled as two idealized layers. These idealized layers have uniform optical properties (i.e., index of refraction (n) and extinction co-efficient (k)) through their thickness, as do the other layers in the stack. Thus, the thicknesses referred to in the examples are the thicknesses of these idealized layers and are meaningful in the context of calculating the optical response of a given coating stack containing these layers.

[0087] Also, the thickness values associated with the "subcritical" layers in the following Examples are "effective thickness" calculated based on a reference coating speed that is slower than the actual coating speed of the commercial coater. For example, a silver layer is applied onto a substrate at the same coating rate as a commercial coater but at a reduced line speed (reference coating speed) compared to the commercial coater. The thickness of the coating deposited at the reference coating speed is measured and then the "effective thickness" for a coating deposited at the same coating rate but at the faster line speed of the commercial coater is extrapolated. For example, if a particular coating rate provides a silver coating of 25 nm (250 A) at reference coating speed that is one-tenth the line speed of the commercial coater, then the "effective thickness" of the silver layer at the same coating rate but at the commercial coater line speed (i.e., ten time faster than the reference coating run) is extrapolated to be 2.5 nm (25 A) (i.e., one tenth the thickness). However, as will be appreciated, the silver layer at this effective thickness (below the subcritical thickness) would not be a continuous layer but rather would be a discontinuous layer having discontinuous regions of silver material.

EXAMPLE 1

[0088] A coating was deposited by a conventional MSVD coater (commercially available from Applied Materials) on a 6 mm piece of clear glass. The coated glass had the following structure:

titania	4 nm (40 Å)
zinc stannate	19 nm (190 Å)
zinc oxide (90/10)	8 nm (80 Å)
titanium	3 nm (30 Å)
silver	15 nm (150 Å)
zinc oxide	12 nm (120 Å)
zinc stannate	45 nm (450 Å)
zinc oxide	12 nm (120 Å)
Inconel	2.2 nm (22 Å)
S.C. silver	2.5 nm (25 Å)
zinc stannate	11 nm (110 Å)
zinc oxide	7 nm (70 Å)
titanium	3 nm (30 Å)

(continued)

silver	18 nm (180 Å)
zinc oxide	11 nm (110 Å)
zinc stannate	20 nm (200 Å)
clear glass	6 mm

[0089] This coated glass was heat treated as described above and had the optical characteristics shown in Table 1 below. The article was incorporated into a standard IGU as the outer ply (the inner ply was uncoated 6 mm clear glass) and had the optical characteristics set forth in Table 2 below.

EXAMPLE 2

[0090] A coating was deposited by a conventional Airco MSVD coater on a 6 mm piece of Starphire® glass. The coated glass had the following structure:

titania	4 nm (40 Å)
zinc stannate	17 nm (170 Å)
zinc oxide (90/10)	8 nm (80 Å)
titanium	2 nm(20 Å)
silver	15 nm (150 Å)
zinc oxide	12 nm (120 Å)
zinc stannate	48 nm (480 A)
zinc oxide	12 nm (120 Å)
Inconel	2.2 nm (22 Å)
S.C. silver	2.5 nm (25 Å)
zinc stannate	11 nm (110 A)
zinc oxide	7 nm (70 Å)
titanium	2 nm (20 Å)
silver	18 nm (180 Å)
zinc oxide	11 nm (110 Å)
zinc stannate	22 nm (220 Å)
Starphire® glass	6 mm

[0091] This coated glass was heat treated as described above and had the optical characteristics shown in Table 1 below. The article was incorporated into a standard IGU as the outer ply (the inner ply was uncoated 6 mm Starphire® glass) and had the optical characteristics set forth in Table 2 below.

EXAMPLE 3

[0092] A coating was deposited by a conventional Airco MSVD coater on a 6 mm piece of Optiblue® glass. The coated glass had the following structure:

titania	4 nm (40 Å)
zinc stannate	17 nm (170 Å)
zinc oxide (90/10)	8 nm (80 Å)
titanium	2 nm (20 Å)
silver	15 nm (150 Å)
zinc oxide	12 nm (120 Å)
zinc stannate	48 nm (480 Å)
zinc oxide	12 nm (120 Å)
Inconel	2.2 nm (22 Å)
S.C. silver	2.5 nm (25 Å)
zinc stannate	11 nm (110 Å)

(continued)

zinc oxide	7 nm (70 Å)
titanium	2 nm (20 Å)
silver	18 nm (180 Å)
zinc oxide	11 nm (110 Å)
zinc stannate	22 nm (220 Å)
Optiblue® glass	6 mm

[0093] This coated glass was heat treated as described above and had the optical characteristics shown in Table 1 below. The article was incorporated into a standard IGU as the outer ply (the inner ply was uncoated 6 mm Starphire® glass) and had the optical characteristics set forth in Table 2 below.

EXAMPLE 4

[0094] A coating was deposited by a conventional Airco MSVD coater on a 6 mm piece of clear glass. The coated glass had the following structure:

titania	4 nm (40 Å)
zinc stannate	20 nm (200 Å)
zinc oxide (90/10)	7 nm (70 Å)
titanium	3 nm (30 Å)
silver	17 nm (170 Å)
zinc oxide	10 nm (100 Å)
zinc stannate	56 nm (560 Å)
zinc oxide	10 nm (100 Å)
titanium	3 nm (30 Å)
S.C. silver	2.5 nm (25 Å)
Zinc oxide	5 nm (50 Å)
zinc stannate	27 nm (270 Å)
zinc oxide	5 nm (50 Å)
titanium	3 nm (30 Å)
silver	12 nm (120 Å)
zinc oxide	7 nm (70 Å)
zinc stannate	14 nm (140 Å)
clear glass	6 mm

[0095] This coated glass was heat treated as described above and had the optical characteristics shown in Table 1 below. The article was incorporated into a standard IGU as the outer ply (the inner ply was uncoated 6 mm clear glass) and had the optical characteristics set forth in Table 2 below.

EXAMPLE 5

[0096] A coating was deposited by a conventional Airco MSVD coater on a 6 mm piece of clear glass. The coated glass had the following structure:

titania	4 nm (40 Å)
zinc stannate	17 nm (170 Å)
zinc oxide (90/10)	8 nm (80 Å)
titanium	3 nm (30 Å)
silver	13.7 nm (137 Å)
zinc oxide	9.5 nm (95 Å)
zinc stannate	38 nm (380 Å)
zinc oxide	9.5 nm (95 Å)

(continued)

Inconel	1.5 nm (15 Å)
S.C. silver	3 nm (30 Å)
zinc stannate	23.5 nm (235 Å)
zinc oxide	8.5 nm (85 Å)
titanium	3 nm (30 Å)
silver	12.5 nm (125 Å)
zinc oxide	10 nm (100 Å)
zinc stannate	20 nm (200 Å)
clear glass	6 mm

[0097] This coated glass was heat treated as described above and had the optical characteristics shown in Table 1 below. The article was incorporated into a standard IGU as the outer ply (the inner ply was uncoated 6 mm clear glass) and had the optical characteristics set forth in Table 2 below.

EXAMPLE 6 (not according to the present invention)

[0098] A coating was deposited by a conventional Airco MSVD coater on a 6 mm piece of clear glass. The coated glass had the following structure:

titania	4 nm (40 Å)
zinc stannate	32 nm (320 Å)
zinc oxide (90/10)	15 nm (150 Å)
titanium	1.5 nm (15 Å)
Inconel	1.5 nm (15 Å)
silver	17 nm (170 Å)
zinc oxide	7.5 nm (75 Å)
zinc stannate	50 nm (500 Å)
zinc oxide	7.5 nm (75 Å)
titanium	1.5 nm (15 Å)
Inconel	0.5 nm (5 Å)
silver	7.3 nm(73 Å)
zinc oxide	8.5 nm (85 Å)
zinc stannate	35.5 nm(355 A)
clear glass	6 mm

[0099] This coated glass was not heat treated and had the optical characteristics shown in Table 1 below. The article was incorporated into a standard IGU as the outer ply (the inner ply was uncoated 6 mm clear glass) and had the optical characteristics set forth in Table 2 below.

EXAMPLE 7 (not according to the invention)

[0100] A coating was deposited by a conventional Airco MSVD coater on a 6 mm piece of clear glass. The coated glass had the following structure:

titania	4 nm (40 Å)
zinc stannate	19 nm (190 Å)
zinc oxide (90/10)	6 nm (60 Å)
titanium	1.7 nm(17 Å)
silver	12.8 nm(128 Å)
zinc oxide	10.5 nm (105 Å)
zinc stannate	42 nm (420 Å)
zinc oxide	12 nm (120 Å)

(continued)

silicon nitride	10 nm (100 Å)
Stellite®	3 nm (30 Å)
silicon nitride	8 nm (80 Å)
zinc stannate	15.5 nm(155 Å)
zinc oxide	7.5 nm (75 Å)
titanium	1.6 nm(16 Å)
silver	14 nm (140 Å)
zinc oxide	5 nm (50 Å)
zinc stannate	24 nm (240 Å)
clear glass	6 mm

clear glass 6 mm

[0101] This coated glass was not heat treated and the had optical characteristics shown in Table 1 below. The article was incorporated into a standard IGU as the outer ply (the inner ply was uncoated 6 mm clear glass) and had the optical characteristics set forth in Table 2 below.

EXAMPLE 8 (not according to the invention)

[0102] A coating was deposited by a conventional Airco MSVD coater on a 6 mm piece of clear glass. The coated glass had the following structure:

titania	4 nm (40 Å)
zinc stannate	18 nm (180 Å)
zinc oxide (90/10)	7 nm (70 Å)
titanium	3 nm (30 Å)
silver	12.8 nm(128 Å)
zinc oxide	10.5 nm (105 Å)
zinc stannate	42 nm (420 Å)
zinc oxide	12 nm (120 Å)
silicon nitride	10 nm (100 Å)
Stellite®	3 nm (30 Å)
silicon nitride	8 nm (80 Å)
zinc stannate	15.5 nm(155 Å)
zinc oxide	7.5 nm (75 Å)
titanium	3 nm (30 Å)
silver	14 nm (140 Å)
zinc oxide	5 nm (50 Å)
zinc stannate	24 nm (240 Å)
clear glass	6 mm

[0103] This coated glass was heat treated as described above and had the optical characteristics shown in Table 1 below. The article was incorporated into a standard IGU as the outer ply (the inner ply was uncoated 6 mm clear glass) and had the optical characteristics set forth in Table 2 below.

EXAMPLE 9

[0104] A coating was deposited by a conventional Airco MSVD coater on a 6 mm piece of clear glass. The coated glass had the following structure:

titania	4,3 nm (43 Å)
zinc stannate	19.6 nm(196 Å)
zinc oxide (90/10)	8.1 nm(81 Å)

(continued)

titanium	3.3 nm (33 Å)
silver	15.1 nm (151 Å)
zinc oxide	12 nm (120 Å)
zinc stannate	44.8 nm(448 Å)
zinc oxide	12 nm (120 Å)
Inconel	2.2 nm (22 Å)
S.C. silver	2.6 nm(26 Å)
zinc stannate	11.6 nm(116 Å)
zinc oxide	7 nm (70 Å)
titanium	3.5 nm (35 Å)
silver	18.2 nm(182 Å)
zinc oxide	11 nm (110 Å)
zinc stannate	19.8 nm(198 Å)
clear glass	6 mm

TABLE 1

Example No.	RfL*	Rfa*	Rfb*	RgL*	Rga*	Rgb*	TL*	Ta*	Tb*	Rg60L*	Rg60a*	Rg60b*
1	31.4	-3.15	-22.31	61.58	-0.86	-0.54	73.97	-4.61	-3.32	63.10	-7.10	-1.30
2	34.6	6.2	19.3	62.6	1.0	-0.9	75.2	4.0	2.2	NA	NA	NA
3	31.6	-5.1	-20.7	49.6	0.2	-6.9	65.4	-3.8	-7.3	NA	NA	NA
4	44.5	-0.5	-9.7	58.6	-3.2	0.4	76.3	-6.3	-6.0	NA	NA	NA
5	30.4	-6.7	-9.5	44	-1.7	-3.5	84.9	-3.0	0.9	NA	NA	NA
6	57.53	-1.65	-3.83	58.19	-1.69	2.07	72.23	-3.46	-3.57	NA	NA	NA
7	31.0	-1.8	-12.1	58.1	-1.3	1.7	73.0	-5.7	-0.7	NA	NA	NA
8	33.2	-1.3	-12.1	61.5	-2.2	2.2	72.2	-4.5	-1.4	NA	NA	NA

TABLE 2

Example No.	RxL*	Rxa*	Rxb*	RintL*	Rinta*	Rintb*	TL*	Ta*	Tb*	Rx	Rint	VLT	SHGC
1	63.07	-1.16	-0.87	44.02	-2.57	-13	70.75	-5.81	-3.53	32	14	42	0.232
2	64.2	0.4	-1.0	45.8	-3.9	-12.2	72.6	-4.1	-2.3	33	15	44	0.234
3	50.8	0.8	-8.2	43.6	-2.6	-13.2	62.4	-5.3	-7.1	19	13	31	0.2
4	60.7	-3.6	-0.5	51.8	-1.9	-6.9	73.4	-7.5	-5.6	29	20	45	0.27
5	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
6	60.0	-2.2	1.4	61.1	-3.6	-2.7	69.8	-4.5	-3.5	28	29	40	0.240
7	59.4	-1.2	1.0	43.6	-1.5	-7.6	69.7	-6.8	-0.7	28	14	40	0.23
8	62.5	-1.8	1.4	44.6	-1.1	-8.2	69.1	-5.7	-0.9	31	14	39	0.23

Claims

1. A coated article, comprising:

a substrate; and
a coating over at least a portion of the substrate, the coating comprising:

- a first dielectric layer deposited over at least a portion of the substrate;

wherein the first dielectric layer comprises one or more film(s) of oxides of metal alloys, nitrides, oxynitrides, metal oxides of hafnium, zirconium, niobium, zinc, bismuth, lead, indium, tin or mixtures thereof;

- a first heat and/or radiation reflective continuous metallic layer deposited over the first dielectric layer;
- a first primer layer, located over the first reflective layer,
- a second dielectric layer located over the first primer layer;

wherein the second dielectric layer comprises oxides of metallic alloys, oxides of hafnium, zirconium, niobium, zinc, bismuth, lead, indium, tin or mixtures thereof;

- a second discontinuous metallic layer, forming isolated, non-connected regions, located over the second dielectric layer;

wherein, when the metal is silver, the thickness of the layer forming isolated, non-connected regions is less than 50 Å;
optionally, a second primer layer, deposited over the second metallic layer,

- a third dielectric layer deposited over the second metallic layer, or optionally over the second primer layer

wherein the third dielectric layer comprises oxides of metal alloys, oxides of hafnium, zirconium, niobium, zinc, bismuth, lead, indium, tin or mixtures thereof;

- a third heat and /or radiation reflective continuous metallic layer deposited over the third dielectric layer;
- a third primer layer located over the third reflective layer;
- a fourth dielectric layer located over the third primer layer;

wherein the fourth dielectric layer comprises oxides of metal alloys, oxides of hafnium, zirconium, niobium, zinc, bismuth, lead, indium, tin or mixtures thereof;

2. The article of claim 1, wherein the continuous metallic layer comprises the same metal as the discontinuous metallic layer forming isolated, non-connected regions, and
wherein the metal comprises metallic gold, copper, palladium, aluminum, silver, or mixtures, alloys, or combinations thereof.

3. The article of claim 1, wherein the first metallic layer comprises metallic silver and the metallic layer, forming isolated, non-connected regions, comprises discontinuous silver regions.

4. The article according to claim 1 having a second primer layer deposited over the second metallic layer, wherein the second primer layer comprises a material selected from titanium, silicon, silicon dioxide, silicon nitride, silicon oxynitride, zirconium, aluminum, alloys of silicon and aluminum, alloys of nickel and chromium, alloys containing cobalt and chromium or a mixture thereof, the second primer layer preferably comprising a nickel-chromium alloy.

5. The coated article of claim 1, wherein the substrate is a glass substrate.

6. The article according to claim 1, further comprising a protective overcoat located over the fourth dielectric layer.

7. The article according to claim 6, wherein the protective overcoat is made of titania.

8. The article according to claim 1, wherein the first dielectric layer comprises a zinc oxide layer deposited over a zinc stannate layer.

9. The article according to claim 1, wherein the first primer layer comprises a material selected from titanium, silicon, silicon dioxide, silicon nitride, silicon oxynitride, zirconium, aluminum, alloys of silicon and aluminum, alloys of nickel and chromium, alloys containing cobalt and chromium or a mixture thereof, the first primer layer preferably being made of titanium.

10. The article according to claim 1, wherein the second dielectric layer comprises a zinc stannate layer deposited over a zinc oxide layer.

11. The article according to claim 1, wherein the third dielectric layer comprises a zinc stannate layer deposited over a zinc oxide layer, and optionally another zinc oxide layer deposited over the zinc stannate layer.

12. The article according to claim 1, wherein the third continuous metallic layer comprises silver.

13. The article according to claim 1, wherein the third primer layer comprises a material selected from titanium, silicon, silicon dioxide, silicon nitride, silicon oxynitride, zirconium, aluminum, alloys of silicon and aluminum, alloys of nickel and chromium, alloys containing cobalt and chromium or a mixture thereof, the third primer layer preferably being made of titanium.

14. The article according to claim 1, wherein the fourth dielectric layer comprises a zinc stannate layer deposited over a zinc oxide layer.

Patentansprüche

1. Ein beschichteter Gegenstand umfassend:

ein Substrat; und
eine Beschichtung über wenigstens einem Teil des Substrats, wobei die Beschichtung umfasst:

- eine erste dielektrische Schicht, aufgebracht über wenigstens einem Teil des Substrats;

wobei die erste dielektrische Schicht einen oder mehrere Film(e) von Oxiden von Metalllegierungen, Nitriden, Oxynitriden, Metalloxiden von Hafnium, Zirkonium, Niob, Zink, Bismuth, Blei, Indium, Zinn oder Mischungen derselben umfasst;

- eine erste wärme- und/oder strahlungsreflektierende kontinuierliche metallische Schicht, abgeschieden über der ersten dielektrischen Schicht;
- eine erste Primerschicht, angeordnet über der ersten reflektierenden Schicht,
- eine zweite dielektrische Schicht, angeordnet über der ersten Primerschicht;

wobei die zweite dielektrische Schicht Oxide von metallischen Legierungen, Oxide von Hafnium, Zirkonium, Niob, Zink, Bismuth, Blei, Indium, Zinn oder Mischungen derselben umfasst;

- eine zweite diskontinuierliche metallische Schicht, die isolierte, nicht miteinander verbundene Regionen bildet, angeordnet über der zweiten dielektrischen Schicht;

wobei, wenn das Metall Silber ist, die Schichtdicke der Schicht, die isolierte, nicht miteinander verbundene Regionen bildet, weniger als 50 Å ist;

- wahlweise eine zweite Primerschicht, aufgebracht über der zweiten metallischen Schicht,
- eine dritte dielektrische Schicht, aufgebracht über der zweiten metallischen Schicht oder wahlweise über der zweiten Primerschicht,

wobei die dritte dielektrische Schicht Oxide von Metalllegierungen, Oxide von Hafnium, Zirkonium, Niob, Zink, Bismuth, Blei, Indium, Zinn oder Mischungen derselben umfasst;

- eine dritte wärme- und/oder strahlungsreflektierende kontinuierliche metallische Schicht, aufgebracht über der dritten dielektrischen Schicht;
- eine dritte Primerschicht, angeordnet über der dritten reflektierenden Schicht;
- eine vierte dielektrische Schicht, angeordnet über der dritten Primerschicht;

wobei die vierte dielektrische Schicht Oxide von Metalllegierungen, Oxide von Hafnium, Zirkonium, Niob, Zink, Bismuth, Blei, Indium, Zinn oder Mischungen derselben umfasst.

2. Der Gegenstand gemäß Anspruch 1, wobei die kontinuierliche metallische Schicht das gleiche Metall wie die diskontinuierliche metallische Schicht, welche isolierte, nicht miteinander verbundene Regionen bildet, umfasst und wobei das Metall metallisches Gold, Kupfer, Palladium, Aluminium, Silber oder Mischungen, Legierungen oder Kombination derselben umfasst.

3. Der Gegenstand gemäß Anspruch 1, wobei die erste metallische Schicht metallisches Silber umfasst und die metallische Schicht, die isolierte, nicht miteinander verbundene Regionen bildet, diskontinuierliche Silberregionen umfasst.

4. Der Gegenstand gemäß Anspruch 1, welcher eine zweite Primerschicht, aufgebracht über der zweiten metallischen Schicht umfasst, wobei die zweite Primerschicht ein Material ausgewählt aus Titan, Silicium, Siliciumdioxid, Siliciumnitrid, Siliciumoxynitrid, Zirkonium, Aluminium, Legierungen von Silicium und Aluminium, Legierungen von Nickel und Chrom, Legierungen enthaltend Kobalt und Chrom oder eine Mischung derselben umfasst, wobei die zweite Primerschicht vorzugsweise eine Nickel-Chrom-Legierung umfasst.

5. Der beschichtete Gegenstand gemäß Anspruch 1, wobei das Substrat ein Glassubstrat ist.

6. Der Gegenstand gemäß Anspruch 1 umfassend des Weiteren einen schützenden Überzug, angeordnet über der vierten dielektrischen Schicht.

7. Der Gegenstand gemäß Anspruch 6, wobei der schützende Überzug aus Titandioxid hergestellt ist.

8. Der Gegenstand gemäß Anspruch 1, wobei die erste dielektrische Schicht eine Zinkoxidschicht, aufgebracht über einer Zinkstannatschicht, umfasst.

9. Der Gegenstand gemäß Anspruch 1, wobei die erste Primerschicht ein Material ausgewählt aus Titan, Silicium, Siliciumdioxid, Siliciumnitrid, Siliciumoxynitrid, Zirkonium, Aluminium, Legierungen von Silicium und Aluminium, Legierungen von Nickel und Chrom, Legierungen enthaltend Kobalt und Chrom oder eine Mischung derselben umfasst, wobei die erste Primerschicht vorzugsweise aus Titan hergestellt ist.

10. Der Gegenstand gemäß Anspruch 1, wobei die zweite dielektrische Schicht eine Zinkstannatschicht, aufgebracht über einer Zinkoxidschicht, umfasst.

11. Der Gegenstand gemäß Anspruch 1, wobei die dritte dielektrische Schicht eine Zinkstannatschicht, aufgebracht über einer Zinkoxidschicht und wahlweise eine weitere Zinkoxidschicht, aufgebracht über der Zinkstannatschicht, umfasst.

12. Der Gegenstand gemäß Anspruch 1, wobei die dritte kontinuierliche metallische Schicht Silber umfasst.

13. Der Gegenstand gemäß Anspruch 1, wobei die dritte Primerschicht ein Material ausgewählt aus Titan, Silicium, Siliciumdioxid, Siliciumnitritd, Siliciumoxynitrid, Zirkonium, Aluminium, Legierungen von Silicium und Aluminium, Legierungen von Nickel und Chrom, Legierungen enthaltend Kobalt und Chrom oder eine Mischung derselben umfasst, wobei die dritte Primerschicht vorzugsweise aus Titan hergestellt ist.

14. Der Gegenstand gemäß Anspruch 1, wobei die vierte dielektrische Schicht eine Zinkstannatschicht, aufgebracht über einer Zinkoxidschicht, umfasst.

Revendications

1. Article à revêtement, comportant :

un substrat ; et
un revêtement par-dessus au moins une partie du substrat, le revêtement comprenant :

- une première couche de diélectrique déposée sur au moins une partie du substrat ;
la première couche de diélectrique comprenant un ou plusieurs film(s) d'oxydes d'alliages métalliques, des nitrures, des oxynitrures, des oxydes métalliques d'hafnium, de zirconium, de niobium, de zinc, de bismuth,

de plomb, d'indium, d'étain ou des mélanges de ceux-ci ;
- une première couche métallique continue réfléchissant la chaleur et/ou les rayonnements, déposée par-dessus la première couche de diélectrique ;
- une première couche d'apprêt, superposée à la première couche réfléchissante,
- une deuxième couche de diélectrique superposée à la première couche d'apprêt ;
la deuxième couche de diélectrique comprenant des oxydes d'alliages métalliques, des oxydes d'hafnium, de zirconium, de niobium, de zinc, de bismuth, de plomb, d'indium, d'étain ou des mélanges de ceux-ci ;
- une deuxième couche métallique discontinue, formant des régions isolées, non reliées, superposée à la deuxième couche de diélectrique ;
si le métal est de l'argent, l'épaisseur de la couche formant des régions isolées, non reliées étant inférieure à 50 Å ;
éventuellement, une deuxième couche d'apprêt déposée par-dessus la deuxième couche métallique,
- une troisième couche de diélectrique déposée par-dessus la deuxième couche métallique, ou éventuellement par-dessus la deuxième couche d'apprêt,
la troisième couche de diélectrique comprenant des oxydes d'alliages métalliques, des oxydes d'hafnium, de zirconium, de niobium, de zinc, de bismuth, de plomb, d'indium, d'étain ou des mélanges de ceux-ci ;
- une troisième couche métallique continue réfléchissant la chaleur et/ou les rayonnements, déposée par-dessus la troisième couche de diélectrique ;
- une troisième couche d'apprêt superposée à la troisième couche réfléchissante ;
- une quatrième couche de diélectrique déposée par-dessus la troisième couche métallique,
la quatrième couche de diélectrique comprenant des oxydes d'alliages métalliques, des oxydes d'hafnium, de zirconium, de niobium, de zinc, de bismuth, de plomb, d'indium, d'étain ou des mélanges de ceux-ci ;

2. Article selon la revendication 1, dans lequel la couche métallique continue comprend le même métal que la couche métallique discontinue formant des régions isolées, non reliées, et
dans lequel le métal comprend, à l'état de métal, de l'or, du cuivre, du palladium, de l'aluminium, de l'argent ou des mélanges, des alliages ou des combinaisons de ceux-ci.

3. Article selon la revendication 1, dans lequel la première couche métallique comprend de l'argent à l'état de métal et la couche métallique discontinue formant des régions isolées, non reliées, comprend des régions discontinues en argent.

4. Article selon la revendication 1, ayant une deuxième couche d'apprêt déposée par-dessus la deuxième couche métallique, la deuxième couche d'apprêt comprenant une matière choisie parmi le titane, le silicium, le dioxyde de silicium, le nitrure de silicium, l'oxynitrure de silicium, le zirconium, l'aluminium, des alliages de silicium et d'aluminium, des alliages de nickel et de chrome, des alliages contenant du cobalt et du chrome ou un mélange de ceux-ci, la deuxième couche d'apprêt comprenant de préférence un alliage nickel-chrome.

5. Article à revêtement selon la revendication 1, dans lequel le substrat est un substrat en verre.

6. Article selon la revendication 1, comportant en outre une couche supplémentaire protectrice superposée à la quatrième couche de diélectrique.

7. Article selon la revendication 6, dans lequel la couche supplémentaire protectrice est en oxyde de titane.

8. Article selon la revendication 1, dans lequel la première couche de diélectrique comprend une couche d'oxyde de zinc déposée par-dessus une couche de stannate de zinc.

9. Article selon la revendication 1, dans lequel la première couche d'apprêt comprend une matière choisie parmi le titane, le silicium, le dioxyde de silicium, le nitrure de silicium, l'oxynitrure de silicium, le zirconium, l'aluminium, des alliages de silicium et d'aluminium, des alliages de nickel et de chrome, des alliages contenant du cobalt et du chrome ou un mélange de ceux-ci, la première couche d'apprêt étant de préférence en titane.

10. Article selon la revendication 1, dans lequel la deuxième couche de diélectrique comprend une couche de stannate de zinc déposée par-dessus une couche d'oxyde de zinc.

11. Article selon la revendication 1, dans lequel la troisième couche de diélectrique comprend une couche de stannate de zinc déposée par-dessus une couche d'oxyde de zinc, et éventuellement une autre couche d'oxyde de zinc

déposée par-dessus la couche de stannate de zinc.

12. Article selon la revendication 1, dans lequel la troisième couche métallique continue comprend de l'argent.

13. Article selon la revendication 1, dans lequel la troisième couche d'apprêt comprend une matière choisie parmi le titane, le silicium, le dioxyde de silicium, le nitrure de silicium, l'oxynitrure de silicium, le zirconium, l'aluminium, des alliages de silicium et d'aluminium, des alliages de nickel et de chrome, des alliages contenant du cobalt et du chrome ou un mélange de ceux-ci, la troisième couche d'apprêt étant de préférence en titane.

14. Article selon la revendication 1, dans lequel la quatrième couche de diélectrique comprend une couche de stannate de zinc déposée par-dessus une couche d'oxyde de zinc.

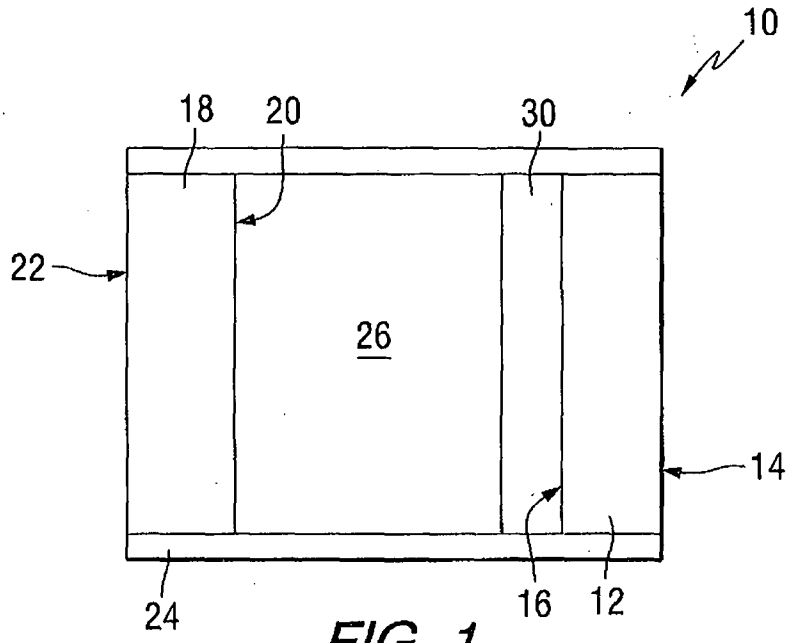

FIG. 1

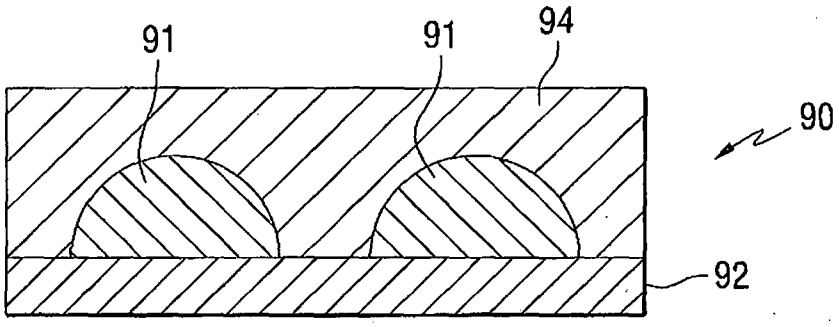

FIG. 3

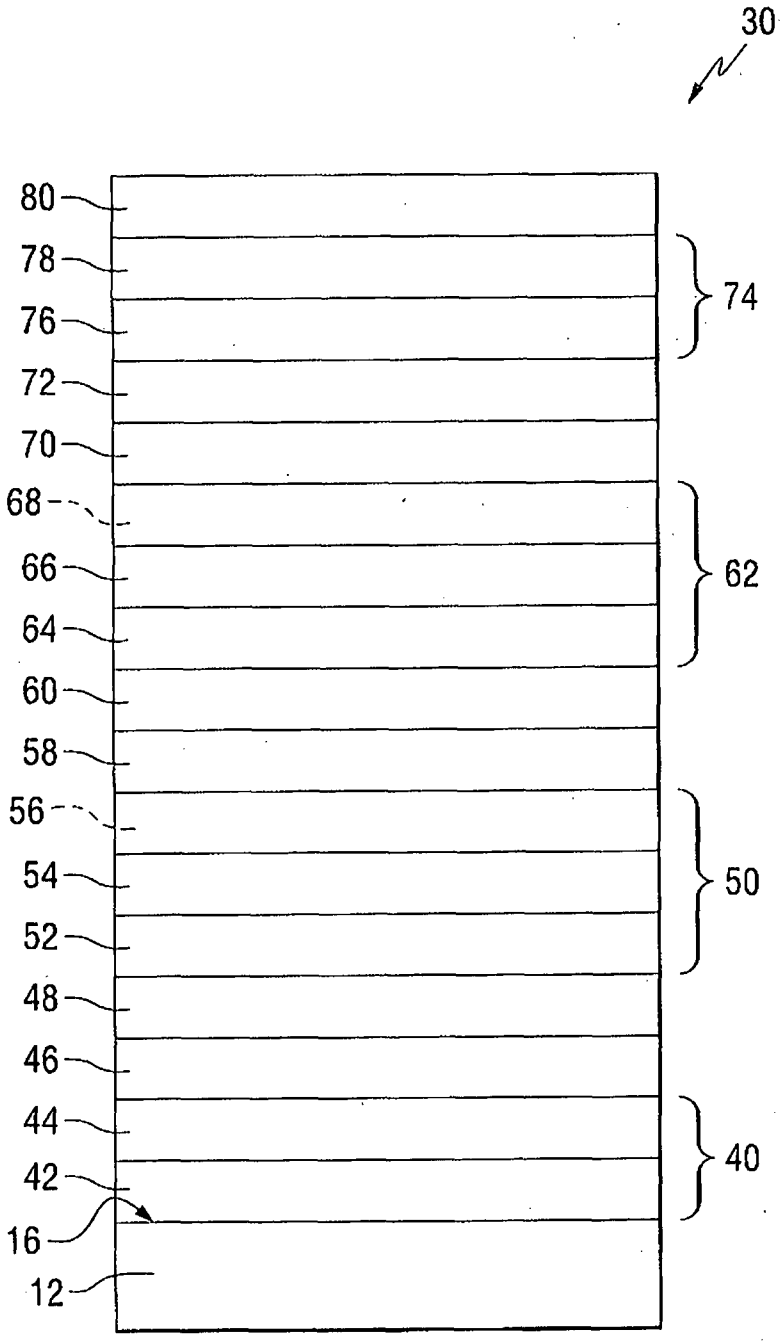

FIG. 2

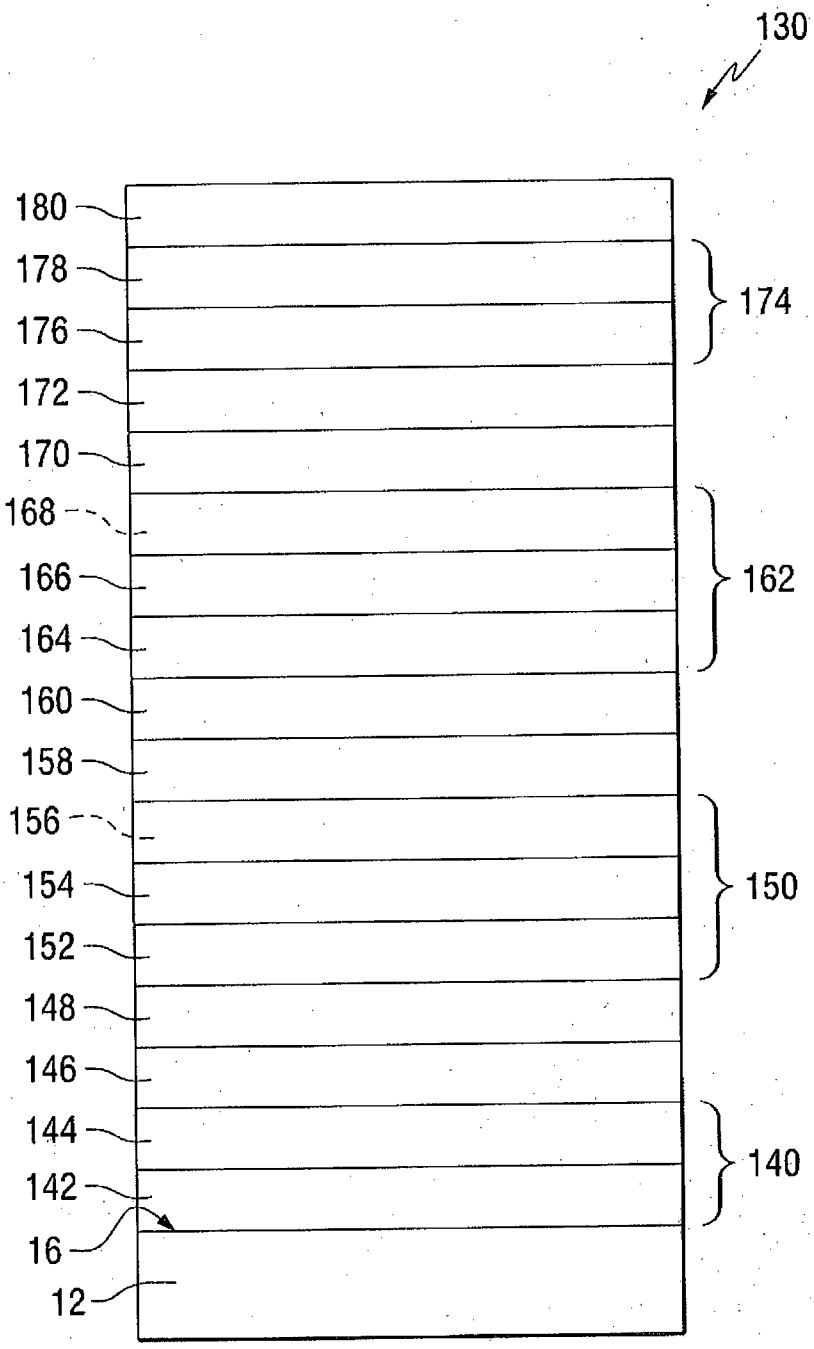
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FIG. 4

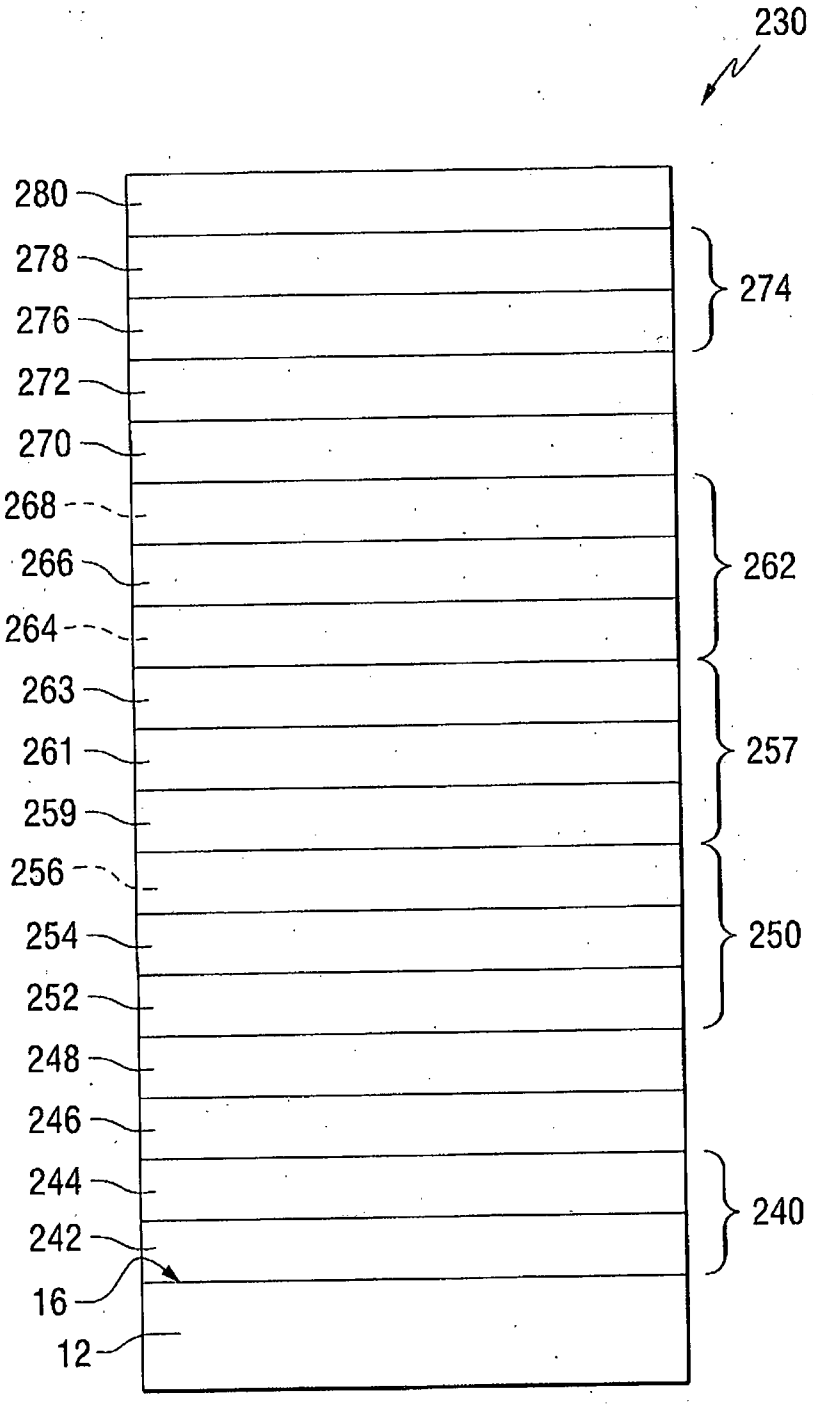
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FIG. 5

REFERENCES CITED IN THE DESCRIPTION

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NAPVÉDŐ BEVONATOK NEMÖSSZEFÜGGŐ FÉMRÉTEGGEL

Szabadalmi igénypontok

1. Bevonattal ellátott cikk, amely tartalmaz

hordozót; és

a hordozó legalább egy részén bevonatot, amely bevonat tartalmaz

- a hordozó legalább egy részére leválasztott első dielektrikumréteget;

ahol az első dielektrikumréteg a fémötvözet-oxidok, nitridek, oxinitridek, valamint a hafnium, cirkónium, nióbium, cink, bizmut, ólom, indium, ón és ezek keverékeinek fémoxidjai alkotta csoportból választott anyag képezte legalább egy réteget tartalmaz;

- az első dielektrikumrétegre leválasztott összefüggő első hő- és/vagy sugárzás-visszaverő fémréteget;

- az első visszaverő rétegen elhelyezett első alapozóréteget;

- az első alapozórétegen elhelyezett második dielektrikumréteget;

ahol a második dielektrikumréteg fémötvözet-oxidokat, valamint hafnium, cirkónium, nióbium, cink, bizmut, ólom, indium, ón és ezek keverékeinek oxidjait tartalmazza;

- a második dielektrikumrétegen elhelyezett, elszigetelt nemkapcsolódó tartományokat képező nemösszefüggő második fémréteget;

ahol abban az esetben, amikor a fémet ezüst képezi, az elszigetelt nemkapcsolódó tartományokat képező réteg vastagsága 50 Å-nél kisebb;

adott esetben második alapozóréteget, amely a második fémrétegre van leválasztva,

- a második fémrétegre vagy adott esetben a második alapozórétegre leválasztott harmadik dielektrikumréteget;

ahol a harmadik dielektrikumréteg fémötvözet-oxidokat, valamint hafnium, cirkónium, nióbium, cink, bizmut, ólom, indium, ón és ezek keverékeinek oxidjait tartalmazza;

- a harmadik dielektrikumrétegre leválasztott összefüggő harmadik hő- és/vagy sugárzás-visszaverő fémréteget;

- a harmadik visszaverő rétegen elhelyezett harmadik alapozóréteget;

- a harmadik alapozórétegen elhelyezett negyedik dielektrikumréteget;

ahol a negyedik dielektrikumréteg fémötvözet-oxidokat, valamint hafnium, cirkónium, nióbium, cink, bizmut, ólom, indium, ón és ezek keverékeinek oxidjait tartalmazza.

2. Az 1. igénypont szerinti cikk, ahol az összefüggő fémréteg az elszigetelt nemkapcsolódó tartományokat képező nemösszefüggő fémréteggel megegyező fémet tartalmaz, továbbá

ahol a fém fémes aranyat, rezet, palládiumot, alumíniumot, ezüstöt vagy ezek keverékeit, ötvözeteit vagy vegyülékeit tartalmazza.

3. Az 1. igénypont szerinti cikk, ahol az első fémréteg fémes ezüstöt tartalmaz, továbbá az elszigetelt nemkapcsolódó tartományokat képező fémréteg nemösszefüggő ezüst tartományokat tartalmaz.

4. Az 1. igénypont szerinti cikk, amely a második fémrétegre leválasztott második alapozóréteget tartalmaz, ahol a második alapozóréteg a titán, szilícium, szilícium-dioxid, szilícium-nitrid, szilícium-oxinitrid, cirkónium, alumínium, szilícium- és alumíniumötvözetek, nikkel- és krómötvözetek, kobalt- és krómtartalmú ötvözetek, valamint ezek keverékei alkotta csoportból választott anyagot tartalmaz, a második alapozóréteg előnyösen nikkel-króm ötvözetet tartalmaz.

5. Az 1. igénypont szerinti cikk, ahol a hordozót üveg hordozó képezi.

6. Az 1. igénypont szerinti cikk, amely a negyedik dielektrikumrétegen elhelyezett védő bevonatot tartalmaz.

7. A 6. igénypont szerinti cikk, ahol a védő bevonat titán-dioxidból van.

8. Az 1. igénypont szerinti cikk, ahol az első dielektrikumréteg cink-sztannát rétegre leválasztott cink-oxid réteget tartalmaz.

9. Az 1. igénypont szerinti cikk, ahol az első alapozóréteg a titán, szilícium, szilícium-dioxid, szilícium-nitrid, szilícium-oxinitrid, cirkónium, alumínium, szilícium- és alumíniumötvözetek, nikkel- és krómötvözetek, kobalt- és krómtartalmú ötvözetek, valamint ezek keverékei alkotta csoportból választott anyagot tartalmaz, az első alapozóréteg előnyösen titánból van.

10. Az 1. igénypont szerinti cikk, ahol a második dielektrikumréteg cink-oxid rétegre leválasztott cink-sztannát réteget tartalmaz.

11. Az 1. igénypont szerinti cikk, ahol a harmadik dielektrikumréteg cink-oxid rétegre leválasztott cink-sztannát réteget és, adott esetben, a cink-sztannát rétegre leválasztott további cink-oxid réteget tartalmaz.

12. Az 1. igénypont szerinti cikk, ahol az összefüggő harmadik fémréteg ezüstöt tartalmaz.

13. Az 1. igénypont szerinti cikk, ahol a harmadik alapozóréteg a titán, szilícium, szilícium-dioxid, szilícium-nitrid, szilícium-oxinitrid, cirkónium, alumínium, szilícium- és alumíniumötvözetek, nikkel- és krómötvözetek, kobalt- és krómtartalmú ötvözetek, valamint ezek keverékei alkotta csoportból választott anyagot tartalmaz, a harmadik alapozóréteg előnyösen titánból van.

14. Az 1. igénypont szerinti cikk, ahol a negyedik dielektrikumréteg cink-oxid rétegre leválasztott cink-sztannát réteget tartalmaz.