Innovation, Sciences et Développement économique Canada
Office de la Propriété Intellectuelle du Canada

Innovation, Science and Economic Development Canada
Canadian Intellectual Property Office

CA 3238671 A1 2023/08/24

(21) **3 238 671**

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) **A1**

(86) **Date de dépôt PCT/PCT Filing Date:** 2023/02/16
(87) **Date publication PCT/PCT Publication Date:** 2023/08/24
(85) **Entrée phase nationale/National Entry:** 2024/05/21
(86) **N° demande PCT/PCT Application No.:** IB 2023/051396
(87) **N° publication PCT/PCT Publication No.:** 2023/156927
(30) **Priorité/Priority:** 2022/02/17 (US17/674,082)

(51) **Cl.Int./Int.Cl.** ***C03C 17/34*** (2006.01)

(71) **Demandeurs/Applicants:**
GUARDIAN GLASS, LLC, US;
GUARDIAN EUROPE S.A.R.L., LU

(72) **Inventeurs/Inventors:**
MULLER, JENS-PETER, LU;
VERNHES, RICHARD, LU;
SZIRBIK, ISTVAN, LU;
HEGEDUS, NIKOLETT, LU;
CHU, ALLEN, US;
BUTZ, JOCHEN, LU

(74) **Agent:** CPST INTELLECTUAL PROPERTY INC.

(54) **Titre : ARTICLE REVETU POUVANT ETRE TRAITE THERMIQUEMENT COMPORTANT UN OU PLUSIEURS REVETEMENT(S) ANTIREFLET SUR UN SUBSTRAT**
(54) **Title: HEAT TREATABLE COATED ARTICLE HAVING ANTIREFLECTIVE COATING(S) ON SUBSTRATE**

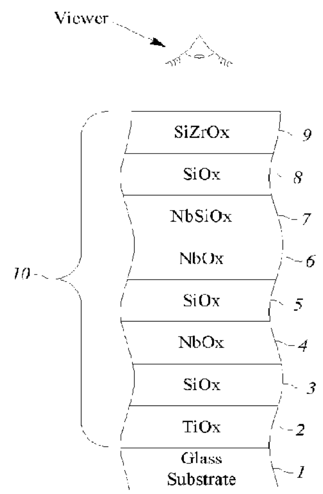

FIG. 1

(57) **Abrégé/Abstract:**
A coated article including a first antireflective (AR) coating supported by a glass substrate, wherein the first coating can include, moving away from the glass substrate: a dielectric first high index layer; a dielectric first low index layer; a dielectric second high index layer; a dielectric second low index layer; a dielectric third high index layer; a dielectric first medium index layer; a dielectric third low index layer; and an overcoat layer; wherein the first coating contains no IR reflecting layer based on silver and/or gold; wherein, from the perspective of a viewer of the coated article, the first coating can be configured so that the coated article has a film side reflective ΔE* value of no greater than 3.0 upon heat treatment of at least about 580 degrees C. The ΔE* value(s) can be measured either with a substantially symmetrical/similar AR coating on the other side of the same glass substrate, or absent any AR coating on the other side of the glass substrate.

Date Submitted: 2024/05/21

CA App. No.: 3238671

Abstract:

A coated article including a first antireflective (AR) coating supported by a glass substrate, wherein the first coating can include, moving away from the glass substrate: a dielectric first high index layer; a dielectric first low index layer; a dielectric second high index layer; a dielectric second low index layer; a dielectric third high index layer; a dielectric first medium index layer; a dielectric third low index layer; and an overcoat layer; wherein the first coating contains no IR reflecting layer based on silver and/or gold; wherein, from the perspective of a viewer of the coated article, the first coating can be configured so that the coated article has a film side reflective E* value of no greater than 3.0 upon heat treatment of at least about 580 degrees C. The E* value(s) can be measured either with a substantially symmetrical/similar AR coating on the other side of the same glass substrate, or absent any AR coating on the other side of the glass substrate.

HEAT TREATABLE COATED ARTICLE HAVING ANTIREFLECTIVE COATING(S) ON SUBSTRATE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority from U.S. Application No. 17/674,082, filed on February 17, 2022, the contents of which are incorporated herein in its entirety.

FIELD

[0002] The present disclosure relates to a coated article including coating(s) on a substrate (e.g., glass substrate). Such coated article can have improved antireflective properties upon heat treatment.

BACKGROUND

[0003] This presently disclosed subject matter relates to a coated article including an antireflective (AR) coating(s) on a substrate (e.g., glass substrate). The coating can be designed to reduce color change of the overall coated article, from the perspective of a viewer, upon heat treatment (e.g., thermal tempering), and/or to improve other optical characteristic(s) such as one or more of: providing substantially neutral coloration, reducing color variability and/or thermal stability, reducing haze, providing lower visible reflection, and/or reducing effects of aging (e.g., reflectance more stable over time, as coated (AC) and/or as heat treated (HT)). One or more such coating(s) can be provided on a given substrate, such as a single such AR coating on a single side of a glass substrate, or a pair of such AR coatings on opposite sides of a glass substrate. Such coated articles can be used in the context of monolithic windows, storefront windows, museum glass showcases, picture frame glass, retail display case windows, tabletops, insulating glass (IG) window units, laminated windows, and/or other suitable applications.

[0004] Coated articles having AR coatings are known in the art. Such coated articles are often subjected to heat treatment such as thermal tempering. Unfortunately, such coated articles have substantially different appearances with respect to color before and after heat treatment, respectively (high reflective ΔE^* values). In other words, the heat treatment causes significant change in reflective coloration of the coated article. This is undesirable because non-heat-treated and heat-treated coated articles will have significantly different appearances from the perspective of a viewer.

[0005] It has been found to be particularly difficult to design a given AR coating to have a low reflective ΔE* value. In other words, it has been found that it is difficult to design AR coatings to have low reflective color shift upon heat treatment such as thermal tempering.

[0006] U.S. Patent No. 11,112,538 (incorporated herein by reference in its entirety) discloses an antireflective (AR) coating on a glass substrate, where the coating can include the following layers moving from the glass substrate outwardly:

Layer	Example Range (Å)	Preferred (Å)	Most Preferred (Å)
Glass			
titanium oxide:	40-200 Å	60-120 Å	80-105 Å
silicon oxide:	100-800 Å	200-600 Å	340-420 Å
niobium oxide:	200-2000 Å	700-1400 Å	900-1200 Å
niobium silicon oxide:	50-900 Å	100-800 Å	200-300 Å
silicon oxide:	200-1000 Å	560-700 Å	590-650 Å
Zirconium silicon oxide:	30-400 Å	40-200 Å	50-150 Å

[0007] Unfortunately, it has been found that the above AR coating from Table 11 of U.S. Patent No. 11,112,538 can be disadvantageous at least with respect to realizing one or more of: (i) undesirably large haze values upon heat treatment, (ii) substantially different appearances with respect to color before and after heat treatment, respectively (high reflective ΔE* values), if an AR coating is provided on only one side of the glass substrate, (iii) needing asymmetrical/different AR coatings on opposite sides of the same glass substrate to achieve desirable ΔE* value(s), since the color shift generated by the coating on the front side for example is needed to compensate for the color shift of the coating on the back side (i.e., low color shift is not possible for situations where an AR coating is provided on only one side of the glass substrate), and/or (iii) undesirably large reflectance changes upon aging.

[0008] Thus, it would be desirable to provide a coated article which improves upon one or more of the above characteristics (i), (ii), and/or (iii).

SUMMARY

[0009] The presently disclosed subject matter provides for a coated article including a first antireflective (AR) coating supported by a glass substrate, wherein the first coating comprises, moving away from the glass substrate: a dielectric first high index layer; a dielectric first low index layer; a dielectric second high index layer; a dielectric second low index layer; a dielectric third high index layer; a dielectric first medium index layer; a dielectric third low index layer; and an overcoat layer; wherein the first coating contains no IR reflecting layer based on silver and/or gold; wherein, from the perspective of a viewer of the coated article, the first coating is configured so that the coated article has a film side reflective ΔE* value of no greater than 3.0 upon heat treatment of at least about 580 degrees C.

[0010] In certain embodiments, the third high index layer is located between and directly contacting the second low index layer and the first medium index layer. In certain embodiments, the first coating is configured so that the coated article has a film side reflective ΔE* value of no greater than 2.5. In certain embodiments, the first coating is configured so that the coated article has a film side reflective ΔE* value of no greater than 2.0.

[0011] In certain embodiments, the first coating is configured so that the coated article has a glass side reflective ΔE* value of no greater than 2.5. In certain embodiments, the first coating is configured so that the coated article has a glass side reflective ΔE* value of no greater than 2.0.

[0012] In certain embodiments, the first coating on the glass substrate has a visible reflectance of no greater than 5%. In certain embodiments, first coating on the glass substrate has a visible reflectance of no greater than 1%.

[0013] In certain embodiments, the coated article has a visible transmission of at least 70%. In certain embodiments, the coated article has a visible transmission of at least 90%.

[0014] In certain embodiments, the AR coating is provided on only one side of the glass substrate, so that no AR coating is provided on the side of the glass substrate opposite said AR coating.

[0015] In certain embodiments, all layers of the first coating are transparent dielectric layers.

[0016] In certain embodiments, the coated article is heat treated, and has a haze value no greater than 0.50.

[0017] In certain embodiments, the coated article is thermally tempered.

[0018] In certain embodiments, the first coating is configured so that the coated article has film side reflective a* value of from -4 to 0, and a film side reflective b* value of from -10 to -5, before and/or after any optional heat treatment. In certain embodiments, the first coating is configured so that the coated article has film side reflective a* value of from -3 to -1, and a film side reflective b* value of from -9 to -6, before and/or after any optional heat treatment.

[0019] In certain embodiments, the first, second, and third high index layers each have a refractive index (n) of at least 2.15, and the first, second, and third low index layers each have a refractive index (n) of no greater than 1.7.

[0020] In certain embodiments, the dielectric second low index layer comprises an oxide of silicon.

[0021] In certain embodiments, the dielectric third high index layer comprises an oxide of niobium.

[0022] In certain embodiments, the first, second, and third low index layers each comprise an oxide of silicon.

[0023] In certain embodiments, the first high index layer comprises an oxide of titanium.

[0024] In certain embodiments, the second and third high index layers each comprise an oxide of niobium.

[0025] In certain embodiments, the medium index layer comprises an oxide of silicon and an oxide of niobium.

[0026] In certain embodiments, the overcoat layer comprises oxide of Zr and Si.

[0027] In certain embodiments, the first low index layer of the first coating is at least twice as thick as the second low index layer of the first coating.

[0028] In certain embodiments, the third low index layer of the first coating is at least twice as thick as the second low index layer of the first coating.

[0029] In certain embodiments, the second and third high index layers are substantially the same thickness, plus/minus 15%.

[0030] In certain embodiments, a second coating on is a side of the glass substrate opposite the first coating, wherein the second coating comprises, moving away from the glass substrate: a dielectric first high index layer; a dielectric first low index layer; a dielectric second high index layer; a dielectric second low index layer comprising an oxide of silicon; a dielectric third high index layer comprising an oxide of niobium; a dielectric first medium index layer, wherein the third high index layer comprising the oxide of niobium is located between and directly contacting the second low index layer comprising the oxide of silicon and the first medium index layer; a dielectric third low index layer; and an overcoat layer.

[0031] The presently disclosed subject matter also provides for a coated article including a first antireflective (AR) coating supported by a glass substrate, wherein the first coating comprises, moving away from the glass substrate: a dielectric first high index layer; a dielectric first low index layer; a dielectric second high index layer; a dielectric second low index layer comprising an oxide of silicon; a dielectric third high index layer an oxide of niobium; a dielectric first medium index layer, wherein the third high index layer is located between and directly contacting the second low index layer and the first medium index layer; a dielectric third low index layer; and an overcoat layer; wherein the first coating contains no IR reflecting layer based on silver and/or gold; wherein, from the perspective of a viewer of the coated article, the first coating is configured so that the coated article has a film side reflective ΔE* value of no greater than 3.0 upon heat treatment of at least about 580 degrees C.

[0032] The presently disclosed subject matter also provides for a coated article including first and second antireflective (AR) coatings supported by a glass substrate, wherein the first and second AR coatings are provided on opposite sides of the glass substrate and each comprises, moving away from the glass substrate: a dielectric first high index layer; a dielectric first low index layer; a dielectric second high index layer; a dielectric second low index layer comprising an oxide of silicon; a dielectric third high index layer comprising an oxide of niobium; a dielectric first medium index layer, wherein the third high index layer comprising the oxide of niobium is located between and directly contacting the second low index layer comprising the oxide of silicon and the first medium index layer; a dielectric third low index layer; and an overcoat layer; wherein the first and second coatings contains no IR reflecting layer based on silver and/or gold; wherein, from the perspective of a viewer of the coated article, the first and second AR coatings are configured so that the coated article has a film side reflective ΔE* value of no greater than 3.0 upon heat treatment of at least about 580 degrees C.

[0033] The presently disclosed subject matter also provides a method of making a transparent coated glass product having a coated article comprising a first coating on a glass substrate wherein the first coating comprises from the glass substrate moving outwardly: a dielectric first high index layer; a dielectric first low index layer; a dielectric second high index layer; a dielectric second low index layer comprising an oxide of silicon; a dielectric third high index layer comprising an oxide of niobium; a dielectric first medium index layer, wherein the third high index layer comprising the oxide of niobium is located between and directly contacting the second low index layer comprising the oxide of silicon and the first medium index layer; a dielectric third low index layer; and an overcoat layer; wherein the first coating contains no IR reflecting layer based on silver and/or gold; and heat treating the coated article at a temperature of at least 580 degrees C so that the heat treating causes, from the perspective of a viewer of the coated article, the coated article to realize a film side reflective ΔE^* value of no greater than 3.0 due to the heat treating.

[0034] The foregoing has outlined broadly the features and technical advantages of the present application in order that the detailed description that follows may be better understood.

[0035] Additional features and advantages of the application will be described hereinafter which form the subject of the claims of the application. It should be appreciated by those skilled in the art that the conception and specific embodiment disclosed can be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present application. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the application as set forth in the appended claims. The novel features which are believed to be characteristic of the application, both as to its organization and method of operation, together with further objects and advantages will be better understood from the following description.

DRAWINGS

[0036] Fig. 1 is a cross sectional view of a monolithic coated article (heat treated or not heat treated) according to an example embodiment of the disclosed subject matter.

[0037] Fig. 2 is a cross sectional view of a monolithic coated article (heat treated or not heat treated) according to another example embodiment of this presently disclosed subject matter.

DETAILED DESCRIPTION

[0038] Reference now will be made in detail to embodiments, one or more examples of which are illustrated in the drawings. Each example is provided by way of explanation of the embodiments, not limitation of the present disclosure. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made to the embodiments without departing from the scope or spirit of the present disclosure. For instance, features illustrated or described as part of one embodiment can be used with another embodiment to yield a still further embodiment. Thus, it is intended that aspects of the present disclosure cover such modifications and variations.

[0039] For clarity and not by way of limitation, this detailed description is divided into the following sub-portions:

6.1. Definitions; and

6.2. Coatings.

6.1. Definitions

[0040] It is to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to limit the scope of the presently disclosed subject matter.

[0041] As used in the specification and the appended claims, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a compound” includes mixtures of compounds.

[0042] The term “about” or “approximately” means within an acceptable error range for the particular value as determined by one of ordinary skill in the art, which will depend in part on how the value is measured or determined, i.e., the limitations of the measurement system.

[0043] As used herein, the terms “comprises,” “comprising,” or any other variation thereof, are intended to cover a non-exclusive inclusion, such that a process, method, article, or apparatus that comprises a list of elements does not include only those elements but can include other elements not expressly listed or inherent to such process, method, article, or apparatus.

[0044] In the detailed description herein, references to “embodiment,” “an embodiment,” “example embodiment,” “in various embodiments,” etc., indicate that the embodiment(s) described can include a particular feature, structure, or characteristic, but every embodiment might not necessarily include the particular feature, structure, or characteristic. Moreover, such phrases are not necessarily referring to the same embodiment. Further, when a particular feature, structure, or characteristic is described in connection with an embodiment, it is submitted that it is within the knowledge of one skilled in the art to affect such feature, structure, or characteristic in connection with other embodiments whether or not explicitly described. After reading the description, it will be apparent to one skilled in the relevant art(s) how to implement the disclosure in alternative embodiments.

[0045] It is noted that the terms “oxide” and “nitride” as used herein include various stoichiometries. For example, the term silicon oxide includes stoichiometric SiO_2, as well as non-stoichiometric silicon oxide. As another example, the term titanium oxide includes stoichiometric TiO_2, as well as non-stoichiometric titanium oxide.

[0046] Various embodiments of the presently disclosed subject matter will now be described in more detail below.

6.2. Coatings

[0047] Example embodiments of this disclosed subject matter relate to a coated article including a glass substrate 1, where a coating 10 is provided on the glass substrate 1. One antireflective (AR) coating 10, or a pair of AR coatings 10, 20, can be provided on the glass substrate 1. Other coatings can also be provided, such as low-E coating(s). In certain example embodiments, the coating 10 (and/or 20) can be designed to reduce color change of the overall coated article upon heat treatment (HT), from the perspective of a viewer at least at a normal viewing angle, so as to realize low reflective ΔE^* value(s) upon HT (e.g., thermal tempering). The coating 10 (and/or 20) can be configured so that the coated article realizes one or more of: improved thermal stability so as to realize low reflective ΔE^* value(s) of no greater than 3.0 (more preferably no greater than 2.5, even more preferably no greater than 2.0, and most preferably no greater than about 1.5) upon HT, reduced haze values upon HT, substantially neutral coloration to a viewer, reduced color variability, low visible reflection, and/or reduced effects of aging (e.g., low reflectance changes upon aging, and/or visible reflectance more stable over time as coated (AC) and/or as heat treated (HT)). One or more such coating(s) can be provided on a given substrate, such as a single such AR coating 10 on a single side of a glass substrate 1 as shown in Fig. 1, or a pair of such AR coatings 10, 20 on opposite sides of a glass substrate 1 as shown in Fig. 2. Such coated articles (e.g., see Figs. 1 and 2) can be used in the context of monolithic windows, storefront windows, museum glass showcases, picture frame glass, retail display case windows, tabletops, insulating glass (IG) window units, laminated windows, and/or other suitable applications. The coating(s) can be provided directly, or indirectly, on the glass substrate. The coating(s) can be antireflective (AR) coatings in certain example embodiments. From the perspective of the viewer, visible color change due to HT (e.g., thermal tempering) can be reduced or minimized, so that non-heat-treated versions and heat treated versions of the coated article appear similar to the viewer.

[0048] In certain example embodiments, it has surprisingly and unexpectedly been found that modifying the above-identified coating from Table 11 of U.S. Patent No. 11,112,538, by adding a low index layer (e.g., silicon oxide based, such as SiO_2 based) 5 and an adjacent high index layer (e.g., niobium oxide based, such as NbO_x based) 6, to the middle of the layer stack of, results in one or more of: improved haze values, improved thermal stability upon heat treatment (HT) (i.e., lower reflective ΔE^* value(s)), substantially neutral coloration to a viewer, reduced color variability, low visible reflection, and/or reduced effects of aging (e.g., low reflectance changes upon aging, and/or visible reflectance more stable over time as coated (AC) and/or as heat treated (HT)). The same applies to corresponding layers 5' and 6' of coating 20. In certain example embodiments, the layer stack of the coating (10 and/or 20) can include two co-sputtered layers 7, 7', 9, 9' for improved durability. The center low index layer (e.g, SiO_x) 5, 5' has been found with NbO_x 6, 6' to reduce haze, and to reduce color shift upon HT so as to provide improved thermal stability and thus lower reflective ΔE^* value(s). The TiO_x undercoat 2, 2' can be provided for added thermal stability. SiO_x 3, 5, 8 provides for a dense microstructure, leading to lower aging effects.

[0049] The coatings 10 and 20 can be provided directly, or indirectly, on the glass substrate 1. The coatings 10 and 20 are designed to reduce color change of the overall coated article, from the perspective of a viewer, upon heat treatment (e.g., thermal tempering). The coatings 10 and 20 can be antireflective (AR) coatings in certain example embodiments. Contrary to U.S. Patent No. 11,112,538 where two different coatings need to be applied on both/opposite sides of the glass substrate, certain example embodiments of this case provide for a coated article that can achieve desirably low ΔE^* value(s) either by (a) using an AR coating (e.g., 10) on only one side of the glass substrate 1 as shown in Fig. 1, and/or (b) using essentially the same layer stack design for both sides of the glass as shown in Fig. 2 to achieve low color shift due to HT (e.g., thermal tempering). From the perspective of the viewer, visible color change due to HT can be reduced or minimized, so that non-heat-treated versions and heat treated versions of the coated article appear similar to the viewer. In certain example embodiments, the first and/or second coatings 10 and 20 are designed so that the coated article realizes substantially neutral color, from the perspective of a viewer, both before and after HT. The first and second coatings 10 and 20 can have the same, or different, layer stacks in different embodiments of this disclosed subject matter.

[0050] Typical AR coatings themselves mostly have non-neutral reflective coloration such as blue, purple or pink coloration, and thus cannot themselves achieve reflective neutral coloration. Moreover, the non-neutral coloration of typical AR coatings becomes worse after HT such as thermal tempering. Thus, example embodiments of this disclosed subject matter relate to an anti-reflective coating article which can achieve reflective neutral visible coloration, both before and after heat treatment such as thermal tempering, which is advantageous for the reasons discussed herein.

[0051] Coated articles can optionally be "heat treated" (HT) in certain example embodiments of this disclosed subject matter, and are preferably designed to be heat treatable. The terms "heat treatment", "heat treated" and "heat treating" as used herein mean heating the article to a temperature sufficient to achieve thermal tempering, heat bending, and/or heat strengthening of the glass inclusive article. This definition includes, for example, heating a coated article in an oven or furnace at a temperature of least about 580 degrees C, more preferably at least about 600 degrees C, for a sufficient period to allow tempering, bending, and/or heat strengthening. In certain instances, the HT can be for at least about 4 or 5 minutes. The coated article may or may not be heat treated in different embodiments of this disclosed subject matter.

[0052] The value ΔE* is known in the art, and is important in determining whether or not upon heat treatment (HT) there is matchability, or substantial matchability, in the context of this disclosed subject matter. Color herein is described by reference to the a*, b* values. For purposes of example, the term Δa* is simply indicative of how much color value a* changes due to heat treatment. The term ΔE* is well understood in the art and is reported, along with various techniques for determining it, in ASTM 2244-93 as well as being reported in Hunter et. al., *The Measurement of Appearance*, 2nd Ed. Cptr. 9, page 162 et seq. [John Wiley & Sons, 1987]. As used in the art, ΔE* (and ΔE) is a way of adequately expressing the change (or lack thereof) in reflectance and/or transmittance (and thus color appearance, as well) in an article after or due to HT. ΔE can be calculated by the "ab" technique, or by the Hunter technique (designated by employing a subscript "H"). ΔE* corresponds to the CIE LAB Scale L*, a*, b*. For example, as reported in Hunter et. al. referenced above, the rectangular coordinate/scale technique (CIE LAB 1976) known as the L*, a*, b* scale can be used, wherein:

L* is (CIE 1976) lightness units
a* is (CIE 1976) red-green units
b* is (CIE 1976) yellow-blue units

and the distance ΔE* between L^*_o a^*_o b^*_o and L^*_1 a^*_1 b^*_1 is:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (1)$$

where:

$$\Delta L^* = L^*_1 - L^*_o \quad (2)$$

$$\Delta a^* = a^*_1 - a^*_o \quad (3)$$

$$\Delta b^* = b^*_1 - b^*_o \quad (4)$$

where the subscript "o" represents the coating (coated article) before heat treatment and the subscript "1" represents the coating (coated article) after heat treatment; and the numbers employed (e.g., a*, b*, L*) are those calculated by the aforesaid (CIE LAB 1976) L*, a*, b* coordinate technique. In a similar manner, ΔE can be calculated using equation (1) by replacing a*, b*, L* with Hunter Lab values a_h, b_h, L_h.

[0053] Figure 1 is a cross sectional view of a coated article according to an example embodiment of this disclosed subject matter. Glass substrate 1 (e.g., clear, green, bronze, grey, blue, or blue-green glass for instance) can be from about 1.0 to 12.0 mm thick, more preferably from about 4-8 mm thick, with an example glass substrate thickness being about 6 mm thick. All layers shown in Fig. 1 (and Fig. 2) are transparent dielectric layers, and all can be deposited via sputter-deposition or any other suitable technique. Multi-layer AR coatings offer broad antireflection regions in the spectrum, and can for example be based on AR principles of quarter-half-quarter, where moving outwardly from the glass the coatings can each include a quarter wave medium index layer, a half wave high index layer, a quarter wave low index layer, and then air. Moreover, a thin hydrophobic layer can be provided over the AR coating(s) in certain example instances, and/or one could add a thin layer between high and low index layers to improve interfacial adhesion in certain example embodiments. A single AR coating 10 is provided in the Fig. 1 embodiment. In the Fig. 1 embodiment, a low-E coating (not shown) can be provided on the side of the glass substrate 1 opposite coating 10, and such a coated article can be used in monolithic or IG window unit applications for example. Example low-E coatings are described, for purposes of example, in U.S. Patent No. 11,236,014, 11,168,023, and 10,882,997, the disclosures of which are hereby incorporated herein by reference in their entireties. Instead of a low-E coating on the side of the glass substrate 1 opposite AR coating 10, another substantially the same AR coating can be provided in a symmetrical manner as shown by AR coating 20 in Fig 2.

[0054] In the Fig. 2 embodiment, antireflective (AR) coating 10 is provided on one side of glass substrate 1, and another AR coating 20 is provided on the other side of glass substrate 1. The coatings 10 and 20 can be the same, or similar, in certain example embodiments. In the Fig. 2 embodiment, the materials of the respective layers of coatings 10 and 20 can be of the same materials, but layer thicknesses between the two coatings can vary. In certain example embodiments, coatings 10 and 20 do not contain any infrared (IR) reflecting layer based on silver or gold. AR coating 10 includes sputter-deposited layers 2, 3, 4, 5, 6, 7, 8, and 9 whereas AR coating 20 includes corresponding sputter-deposited layers 2', 3', 4', 5', 6', 7', 8', and 9'. Corresponding layers in coatings 10/20 can be of like material and/or like thickness.

[0055] Referring to Figs. 1-2, layers 2, 2', 4, 4', 6 and 6' are high index layers having a refractive index (n) of at least about 2.15, more preferably of at least about 2.20, and most preferably of at least about 2.25. High index layers 2, 2', 4, 4', 6 and 6' can each be of or including high index transparent dielectric material such as titanium oxide (e.g., TiO_x, where x is from 1.5 to 2.0, more preferably from 1.8 to 2.0, with an example being TiO_2) or niobium oxide (e.g., NbO_x where x is from 1.4 to 2.1, more preferably from 1.5 to 2.0, with examples being Nb_2O_5 and NbO_2). Note that all refractive index (n) values discussed herein are at a wavelength of 550 nm. Layers 3, 3', 5, 5', 8, and 8' are low index layers having a refractive index (n) of less than about 1.8, more preferably less than about 1.7, and most preferably less than about 1.6. Low index layers 3, 3', 5, 5', 8, and 8' can each be of or including low index transparent dielectric material such as silicon oxide (e.g., SiO_2) or any other suitable low index material. The silicon oxide (e.g., SiO_2) of any of layers 3, 3', 5 and/or 5' can be doped with other materials such as aluminum (Al) and/or nitrogen (N) in certain example embodiments of this disclosed subject matter. For example and without limitation, any of layers 3, 3', 5, 5', 8, and/or 8' can be of or including silicon oxide (e.g., SiO_2) and can include from about 0-8% (more preferably from 1-5%) Al and/or from about 0-10% (more preferably from about 1-5%) N. Likewise, the titanium oxide and/or niobium oxide of the high index layers 2, 2', 4, 4', 6 and 6' can also be doped with other materials in certain example embodiments. It is possible for the combination of layers 2 and 3 (or 2' and 3'), for example, to be replaced with a medium index layer (e.g., $NbSiO_x$) having a refractive index (n) of from 1.70 to 2.10, more preferably from 1.75 to 2.0, and even more preferably from 1.75 to 1.95. Medium index layers 7, 7', 9, and 9' each have a refractive index (n) of from 1.70 to 2.10, more preferably from 1.75 to 2.0, and even more preferably from 1.75 to 1.95. In certain example embodiments, medium index layers 7 and 7' can be of a medium index material such as a combination of niobium oxide and silicon oxide (also known as niobium silicon oxide), or another material such as a combination of titanium oxide and silicon oxide (also known as titanium silicon oxide), or any other suitable medium index material. In certain example embodiments, medium index layers 9, and 9' can be of a medium index material such as a combination of zirconium oxide and silicon oxide (also known as zirconium silicon oxide), or any other suitable medium index material. And the zirconium in layers 9, 9' helps improve durability of the respective coatings 10 and 20. It is also noted that stack sequences from either the Fig. 1 or Fig. 2 embodiment can be repeated, so that for example another sequence of layers 2-8 could be provided on top of the layers illustrated in each coating in Figs. 1-2. In certain example embodiments, it is possible for each of the layers to include other materials such as dopants. It will be appreciated of course that other layers can also be provided, or certain layers can be omitted, and different materials can be used, in certain alternative embodiments of this disclosed subject matter.

[0056] Generally, other layer(s) can also be provided in other locations of the coatings. Thus, while the coatings 10 and 20 or layers thereof is/are "on" or "supported by" substrate 1 (directly or indirectly), other layer(s) can be provided therebetween. Thus, for example, a layer or coating is considered "on" the substrate 1 even when other layer(s) can be provided therebetween (i.e., the terms "on" and "supported by" as used herein are not limited to directly contacting). However, there can be the direct contacts shown in Figs. 1 and 2 in example embodiments.

[0057] It has surprisingly and unexpectedly been found that modifying the above-identified coating from Table 11 of U.S. Patent No. U.S. Patent No. 11,112,538, by adding a low index layer (e.g., silicon oxide based, such as SiO_2 based) 5 (and/or 5') and an adjacent high index layer (e.g., niobium oxide based, such as NbO_x based) 6 (and/or 6'), to the middle of the layer stack of, results in one or more of: improved haze values, improved thermal stability upon heat treatment (HT) (i.e., lower reflective ΔE^* value(s)), substantially neutral coloration to a viewer, reduced color variability, low visible reflection, and/or reduced effects of aging (e.g., low reflectance changes upon aging, and/or visible reflectance more stable over time as coated (AC) and/or as heat treated (HT)). The same applies to corresponding layers 5' and 6' of coating 20. Co-sputtered layers 7, 7', 9, 9' can be provided for improved durability. The center low index layer (e.g, SiO_x) 5, 5' has been found with NbO_x 6, 6' to reduce haze, and to reduce color shift upon HT so as to provide improved thermal stability and thus lower reflective ΔE^* value(s). The TiO_x undercoat 2, 2' can be provided for added thermal stability. One or more of SiO_x inclusive layers 3, 5, 8 can be provided for a dense microstructure, leading to lower aging effects.

[0058] In certain example embodiments, the first low index layer 3 can be at least twice as thick as the second low index layer 5 (more preferably at least three times as thick); and/or the third low index layer 8 can be at least twice as thick as the second low index layer 5 (more preferably at least three times as thick, or at least four times as thick). In certain example embodiments, the second and third high index layers 4 and 6 can be substantially the same thickness, namely the same thickness plus/minus about 15%.

[0059] Turning back to the Fig. 1-2 embodiments, various thicknesses can be used consistent with one or more of the needs discussed herein. According to certain example embodiments of this disclosed subject matter, example thicknesses (in angstroms) and materials for the respective layers 2-9 of the coating 10 on the glass substrate 1 are as follows in certain example embodiments for achieving desired visible transmission, low visible reflection, fairly neutral reflective coloration, low haze, and thermal stability upon optional HT (layers are listed in order moving away from the glass substrate 1). Table 1 below provides example materials and thicknesses for AR coating 10 and/or 20, before and/or after optional HT. Similar materials/ thicknesses can of course be provide for layers 2'-9' of coating 20.

Table 1 (Example Coating Materials/Thicknesses)

Layer	Example (Å)	Preferred (Å)	Most Preferred (Å)
Glass Substrate 1			
titanium oxide (e.g., TiO_2; layer 2):	40-200 Å	60-120 Å	80-105 Å
silicon oxide (e.g., SiO_2; layer 3):	100-800 Å	350-470 Å	400-440 Å
niobium oxide (e.g., Nb_2O_5; layer 4):	150-800 Å	350-480 Å	400-450 Å
silicon oxide (e.g., SiO_2; layer 5):	40-400 Å	60-160 Å	80-120 Å
niobium oxide (e.g., Nb_2O_5; layer 6):	150-800 Å	340-480 Å	380-430 Å
niobium silicon oxide (layer 7):	50-900 Å	100-500 Å	200-300 Å
silicon oxide (e.g., SiO_2; layer 8):	200-1000 Å	560-700 Å	590-650 Å
zirconium silicon oxide (layer 9):	30-400 Å	40-200 Å	50-150 Å

[0060] Before any optional heat treatment (HT) such as thermal tempering, heat bending, and/or heat strengthening, in certain example embodiments of this disclosed subject matter coated articles according to the Fig. 1 and/or Fig. 2 embodiment(s) can have color/optical characteristics as follows in Table 2 according to Illuminant C, 2 degree observer. And Table 3 provides example data after HT. It is noted that TY and T_{vis} stand for visible transmission through the Fig. 1 coated article in Table 2, RY stands for visible reflectance of the coated article from the point of view of the intended viewer, and that the a* and b* values under RY stand for the respective CIE visible reflectance colorations of the overall coated article from the point of view of the intended viewer and indicate neutral reflective coloration of the overall coated article. Subscript “g” indicates from the glass side of the coated article (e.g., Fig. 1 embodiment), and subscript “f” indicates from the film/coating side of the coated article. The a*, b* values under R_fY relate to “film” side reflective coloration values, and the a*, b* values under R_gY relate to glass side reflective coloration values. The ΔE* values in Table 3, indicating thermal stability, are at the normal viewing angle, or at about an 8 degree viewing angle.

Table 2: Optical Characteristics (Fig. 1 and/or 2 coated article; as-coated & pre-HT)

	General	Preferred	Most Preferred
T_{vis} (TY):	≥ 60%	≥ 70%	≥ 80%
Ta*:	-4 to +4	-2 to +2	-1 to +1
Tb*:	-4 to +4	-2 to +2	-1 to +1
R_fY:	≤ 5 or 1%	≤ 0.90%	≤ 0.80%
a*:	-5 to +4	-4 to 0	-3 to -1
b*:	-13 to +3	-10 to -5	-9 to -6
R_gY:	≤ 5 or 1%	≤ 0.90%	≤ 0.80%
a*:	-5 to +4	-4 to 0	-3 to +1
b*:	-13 to +3	-10 to -5	-9 to -6
Haze Value:	≤ 2	≤ 0.50	≤ 0.30

Table 3: Optical Characteristics (Fig. 1 and/or 2 coated article; after optional HT)

	General	Preferred	Most Preferred
T_{vis} (TY):	≥ 60%	≥ 70%	≥ 80%
Ta*:	-4 to +4	-2 to +2	-1 to +1
Tb*:	-4 to +4	-2 to +2	-1 to +1
R_fY:	≤ 5 or 1%	≤ 0.90%	≤ 0.75%

a*:	-5 to +4	-4 to 0	-3 to +1
b*:	-13 to +3	-10 to -5	-9 to -6
R_gY:	≤ 5 or 1%	≤ 0.80%	≤ 0.70%
a*:	-5 to +4	-4 to 0	-3 to +1
b*:	-13 to +3	-10 to -5	-9 to -6
Haze Value:	≤ 1.0	≤ 0.50	≤ 0.45
ΔE*:	≤ 5.0 or 3.0	≤ 2.50	≤ 2.0 or 1.5

[0061] It can be seen from Table 2 (pre-HT) and Table 3 (post-HT) above that the overall coated article has high visible transmission, low visible reflectance due to the AR coating(s) 10 and/or 20, good thermal stability, low haze, and neutral appearance from the point of view of the intended viewer.

[0062] While embodiments of the present disclosure have been generally discussed, the present disclosure can be further understood by the following, non-limiting examples.

EXAMPLES

[0063] Example 1 according to an example embodiment of this disclosed subject matter is compared below to Comparative Example (CE) 1. Each, as shown in Fig. 2 of the instant application, has the same coating on both sides of the glass substrate 1 so as to represent symmetrical coatings. In particular, each has an AR coating, where the Example 1 coating shown below was provided in a symmetrical manner on both sides of the glass substrate 1 for Example 1 as shown in Fig. 2 of the instant application, and the coating of CE 1 on both sides of the glass substrate is based on the coating from Table 11 of U.S. Patent No. U.S. Patent No. 11,112,538.

Example 1 Coating:

Material	Thickness [nm]
AIR	
SiZrOx	8.5
SiOx	62.8
NbSiOx	25

NbOx	40.4
SiOx	10
NbOx	42.6
SiOx	41.3
TiOx	9.1
GLASS	total 239.6

Comparative Example (CE) 1 Coating:

	Thickness [nm]
Air	
SiZrOx	10
SiOx	56
NbSiOx	25
NbOx	98
SiOx	37
TiOx	10
Glass	total: 236 nm

[0064] Measured monolithically, both before and after thermal tempering (HT), with a Perkin Elmer device, the coatings on the glass substrate of Example 1 and Comparative Example 1 (CE 1) had the following optical characteristics. These measurements were taken with the same coating on both sides of the glass substrate, for example as shown in Fig. 2 for Example 1. Note that all coatings had visible transmission well over 70%, before and after HT at a temperature of at least 580 degrees C (e.g., thermal tempering, heat strengthening, and/or heat bending). The data for Example 1 is in the two right-most columns, whereas data for CE 1 is in the second and third columns from the left edge of the table. "AC" stands for as coated which is before HT such as thermal tempering, whereas "HT" stands for heat treatment/heat treated such as thermal tempering. It is noted that, for example, if coating 20 was removed from Fig. 2/Example 1, then the ΔE* values would be approximately half what they are shown below when both coatings 10 and 20 are present.

Table 4.

	Comparative Example 1 (CE 1)		Example 1	
	AC	HT	AC	HT
TY (UC)	98.3	98.4	97.6	98.2
Ta*	0.44	0.56	0.33	0.33
Tb*	0.63	0.21	0.81	0.3
Rf Y	0.8	0.73	0.77	0.70
Rf L*	7.37	6.84	7.0	6.3
Rf a*	2.98	0.47	-1.9	-0.8
Rf b*	-8.92	-2.5	-8.0	-8.6
Rg Y	0.81	0.72	0.79	0.69
Rg L*	7.46	6.67	7.14	6.2
Rg a*	-2.77	-0.67	-1.99	-0.82
Rg b*	-9.05	-2.39	-8.51	-8.76
ΔE* (film side R)	6.9		1.5	
ΔE* (glass side R)	7.027		1.5	
RfY after aging	>1.0		<1.0	
Haze	0.20	0.9	0.2	0.4

[0065] It can be seen from the above table that Example 1, with the addition of layers 5 and 6 to the coating as shown in Figs. 1-2, had unexpectedly and surprisingly improved values with respect to haze and thermal stability (ΔE*), compared to Comparative Example 1 (CE 1). For example, upon HT, Example 1 had a desirably low ΔE* value of 1.5, whereas Comparative Example 1 had an undesirably high ΔE* value of 6.9. This demonstrates that the addition of layers 5 and 6 to the coating surprising and unexpectedly improved thermal stability of the coated article in a significant manner. Glass side thermal stability was similarly improved. As another example, after HT, Example 1 had a desirably low haze value of 0.4, whereas Comparative Example 1 had an undesirably high haze value of 0.9. This demonstrates that the addition of layers 5 and 6 to the coating surprising and unexpectedly reduced the haze value of the coated article. It can also be seen that Example 1 had slightly better (lower) film side reflection (R_fY) compared to CE 1. The table above also shows that aging did not adversely affect Example 1 as much as CE 1, with respect to film side reflection (R_fY).

[0066] These and other modifications and variations to the presently disclosed subject matter can be practiced by those of ordinary skill in the art, without departing from the spirit and scope of the presently disclosed subject matter, which is more particularly set forth in the appended claims. In addition, it should be understood that aspects of the various embodiments can be interchanged both in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the presently disclosed subject matter so further described in such appended claims. :

WHAT IS CLAIMED IS:

1. A coated article including a first antireflective (AR) coating supported by a glass substrate, wherein the first coating comprises, moving away from the glass substrate:
a dielectric first high index layer;
a dielectric first low index layer;
a dielectric second high index layer;
a dielectric second low index layer;
a dielectric third high index layer;
a dielectric first medium index layer;
a dielectric third low index layer; and
an overcoat layer;
wherein the first coating contains no IR reflecting layer based on silver and/or gold;
wherein, from the perspective of a viewer of the coated article, the first coating is configured so that the coated article has a film side reflective ΔE* value of no greater than 3.0 upon heat treatment of at least about 580 degrees C.

2. The coated article of claim 1, wherein the third high index layer is located between and directly contacting the second low index layer and the first medium index layer.

3. The coated article of any one of the proceeding claims, wherein the first coating is configured so that the coated article has a film side reflective ΔE* value of no greater than 2.5.

4. The coated article of any one of the proceeding claims, wherein the first coating is configured so that the coated article has a film side reflective ΔE* value of no greater than 2.0.

5. The coated article of any one of the proceeding claims, wherein the first coating is configured so that the coated article has a glass side reflective ΔE* value of no greater than 2.5.

6. The coated article of any one of the proceeding claims, wherein the first coating is configured so that the coated article has a glass side reflective ΔE* value of no greater than 2.0.

7. The coated article of any one of the proceeding claims, wherein the first coating on the glass substrate has a visible reflectance of no greater than 5%.

8. The coated article of any one of the proceeding claims, wherein the first coating on the glass substrate has a visible reflectance of no greater than 1%.

9. The coated article of any one of the proceeding claims, wherein the coated article has a visible transmission of at least 70%.

10. The coated article of any one of the proceeding claims, wherein the coated article has a visible transmission of at least 90%.

11. The coated article of any one of the proceeding claims, wherein said AR coating is provided on only one side of the glass substrate, so that no AR coating is provided on the side of the glass substrate opposite said AR coating.

12. The coated article of any one of the proceeding claims, wherein all layers of the first coating are transparent dielectric layers.

13. The coated article of any one of the proceeding claims, wherein the coated article is heat treated, and has a haze value no greater than 0.50.

14. The coated article of any one of the proceeding claims, wherein the coated article is thermally tempered.

15. The coated article of any one of the proceeding claims, wherein the first coating is configured so that the coated article has film side reflective a* value of from -4 to 0, and a film side reflective b* value of from -10 to -5, before and/or after any optional heat treatment.

16. The coated article of any one of the proceeding claims, wherein the first coating is configured so that the coated article has film side reflective a* value of from -3 to -1, and a film side reflective b* value of from -9 to -6, before and/or after any optional heat treatment.

17. The coated article of any one of the proceeding claims, wherein the first, second, and third high index layers each have a refractive index (n) of at least 2.15, and the first, second, and third low index layers each have a refractive index (n) of no greater than 1.7.

18. The coated article of any one of the proceeding claims, wherein the dielectric second low index layer comprises an oxide of silicon.

19. The coated article of any one of the proceeding claims, wherein the dielectric third high index layer comprises an oxide of niobium.

20. The coated article of any one of the proceeding claims, wherein the first, second, and third low index layers each comprise an oxide of silicon.

21. The coated article of any one of the proceeding claims, wherein the first high index layer comprises an oxide of titanium.

22. The coated article of any one of the proceeding claims, wherein the second and third high index layers each comprise an oxide of niobium.

23. The coated article of any one of the proceeding claims, wherein the medium index layer comprises an oxide of silicon and an oxide of niobium.

24. The coated article of any one of the proceeding claims, wherein the overcoat layer comprises oxide of Zr and Si.

25. The coated article of any one of the proceeding claims, wherein the first low index layer of the first coating is at least twice as thick as the second low index layer of the first coating.

26. The coated article of any one of the proceeding claims, wherein the third low index layer of the first coating is at least twice as thick as the second low index layer of the first coating.

27. The coated article of any one of the proceeding claims, wherein the second and third high index layers are substantially the same thickness, plus/minus 15%.

28. The coated article of any one of the proceeding claims, further comprising a second coating on a side of the glass substrate opposite the first coating, wherein the second coating comprises, moving away from the glass substrate:
a dielectric first high index layer;
a dielectric first low index layer;
a dielectric second high index layer;
a dielectric second low index layer comprising an oxide of silicon;
a dielectric third high index layer comprising an oxide of niobium;
a dielectric first medium index layer, wherein the third high index layer comprising the oxide of niobium is located between and directly contacting the second low index layer comprising the oxide of silicon and the first medium index layer;
a dielectric third low index layer; and
an overcoat layer.

29. A coated article including a first antireflective (AR) coating supported by a glass substrate, wherein the first coating comprises, moving away from the glass substrate:
a dielectric first high index layer;
a dielectric first low index layer;
a dielectric second high index layer;
a dielectric second low index layer comprising an oxide of silicon;
a dielectric third high index layer an oxide of niobium;
a dielectric first medium index layer, wherein the third high index layer is located between and directly contacting the second low index layer and the first medium index layer;
a dielectric third low index layer; and
an overcoat layer;
wherein the first coating contains no IR reflecting layer based on silver and/or gold;
wherein, from the perspective of a viewer of the coated article, the first coating is configured so that the coated article has a film side reflective ΔE* value of no greater than 3.0 upon heat treatment of at least about 580 degrees C.

30. A coated article including first and second antireflective (AR) coatings supported by a glass substrate, wherein the first and second AR coatings are provided on opposite sides of the glass substrate and each comprises, moving away from the glass substrate:
a dielectric first high index layer;
a dielectric first low index layer;
a dielectric second high index layer;
a dielectric second low index layer comprising an oxide of silicon;
a dielectric third high index layer comprising an oxide of niobium;
a dielectric first medium index layer, wherein the third high index layer comprising the oxide of niobium is located between and directly contacting the second low index layer comprising the oxide of silicon and the first medium index layer;
a dielectric third low index layer; and
an overcoat layer;
wherein the first and second coatings ~~contains~~ no IR reflecting layer based on silver and/or gold;
wherein, from the perspective of a viewer of the coated article, the first and second AR coatings are configured so that the coated article has a film side reflective ΔE* value of no greater than 3.0 upon heat treatment of at least about 580 degrees C.

31. A method of making a transparent coated glass product, the method comprising:
having a coated article comprising a first coating on a glass substrate wherein the first coating comprises from the glass substrate moving outwardly: a dielectric first high index layer; a dielectric first low index layer; a dielectric second high index layer; a dielectric second low index layer comprising an oxide of silicon; a dielectric third high index layer comprising an oxide of niobium; a dielectric first medium index layer, wherein the third high index layer comprising the oxide of niobium is located between and directly contacting the second low index layer comprising the oxide of silicon and the first medium index layer; a dielectric third low index layer; and an overcoat layer; wherein the first coating contains no IR reflecting layer based on silver and/or gold; and
heat treating the coated article at a temperature of at least 580 degrees C so that the heat treating causes, from the perspective of a viewer of the coated article, the coated article to realize a film side reflective ΔE* value of no greater than 3.0 due to the heat treating.

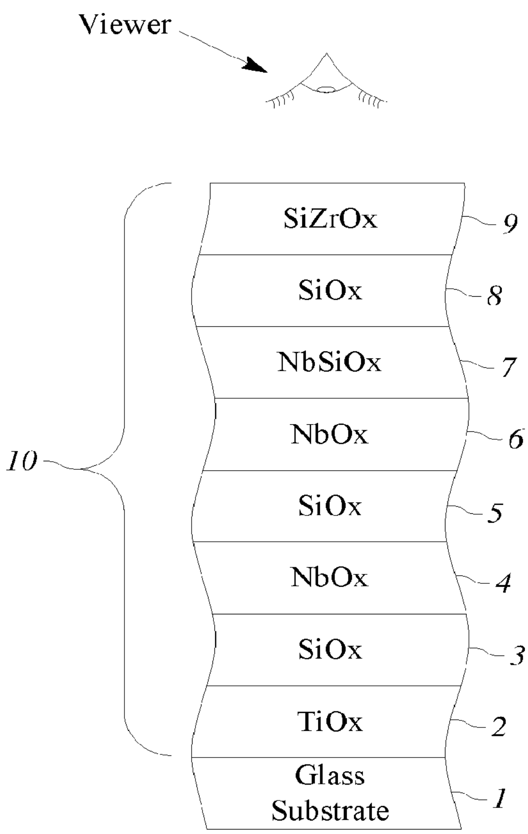
Viewer
SiZrOx
9
SiOx
8
NbSiOx
7
NbOx
6
10
SiOx
5
NbOx
4
SiOx
3
TiOx
2
Glass
Substrate
1

FIG. 1

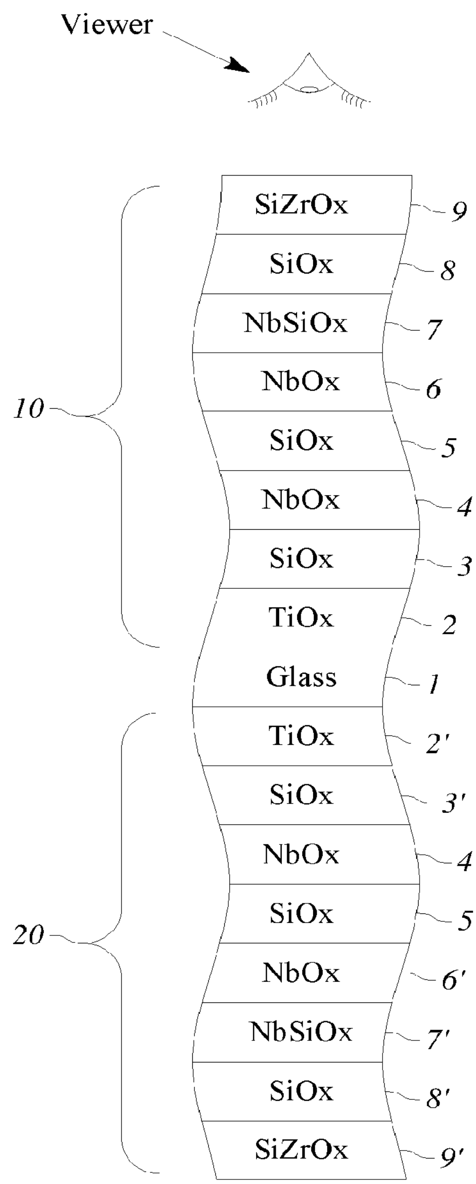
Viewer
SiZrOx
9
SiOx
8
NbSiOx
7
NbOx
6
10
SiOx
5
NbOx
4
SiOx
3
TiOx
2
Glass
1
TiOx
2'
SiOx
3'
NbOx
4'
SiOx
5'
20
NbOx
6'
NbSiOx
7'
SiOx
8'
SiZrOx
9'

FIG. 2

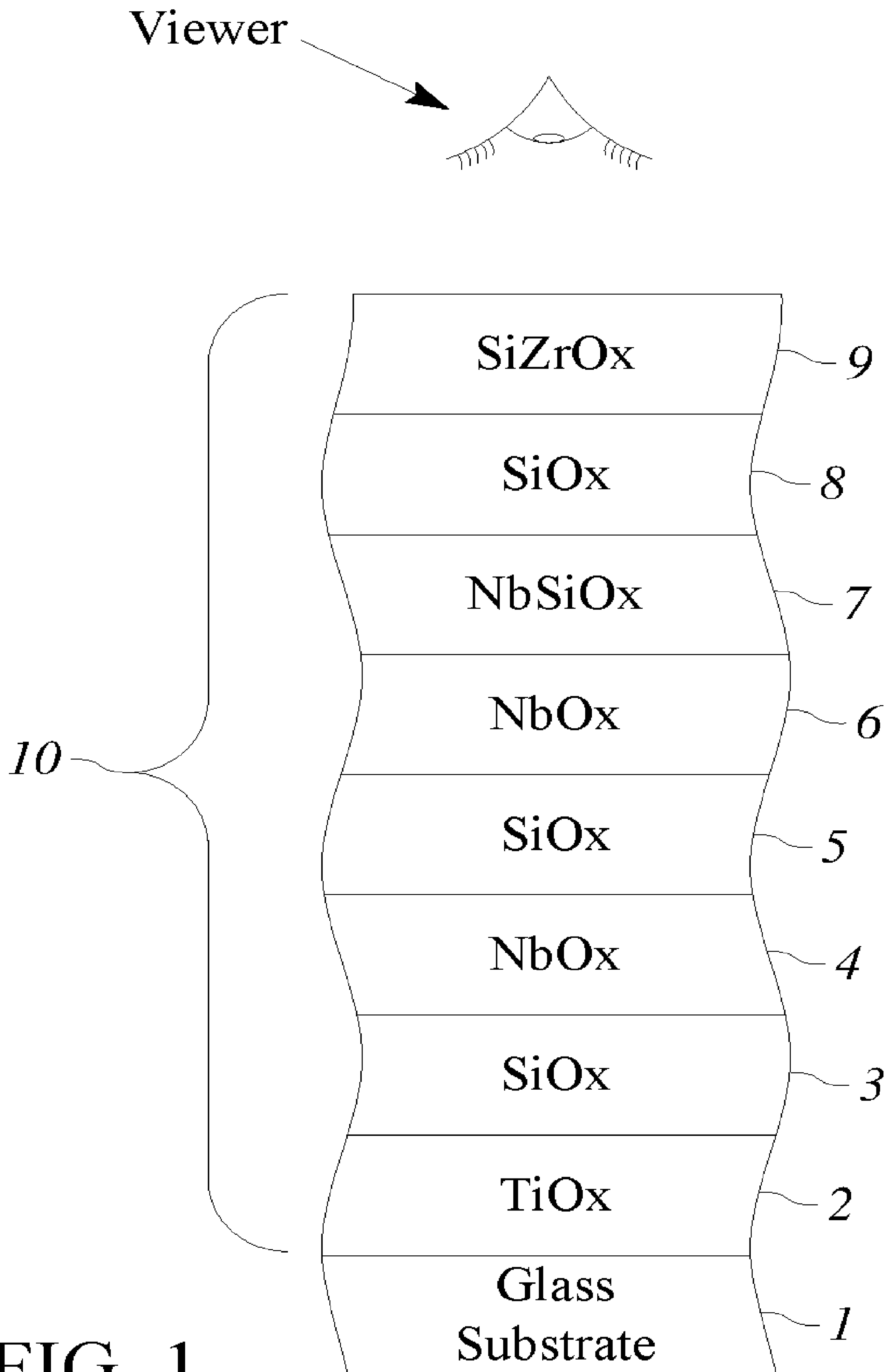
Viewer
SiZrOx
9
SiOx
8
NbSiOx
7
NbOx
6
10
SiOx
5
NbOx
4
SiOx
3
TiOx
2
Glass Substrate
1

FIG. 1