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**IN THE UNITED STATES DISTRICT COURT
FOR THE EASTERN DISTRICT OF MICHIGAN**

**GUARDIAN INDUSTRIES CORP. and
CENTRE LUXEMBOURGEOIS DE
RECHERCHES POUR LE VERRE ET LA
CERAMIQUE S.A. (C.R.V.C.)**

Plaintiffs,

vs.

AFG INDUSTRIES, INC.

Defendant.

R. Terrance Rader (P28747)
Lisa R. Mikalonis (P39485)
RADER, FISHMAN & GRAUER, PLLC
39533 Woodward Avenue, Suite 140
Bloomfield Hills, Michigan 48304
Tel: 248-594-0600
Fax: 248-594-0610
Attorneys for Plaintiffs

Case No. 03-73722

Hon. Arthur J. Tarnow

Magistrate Judge R. Steven Whalen

JURY TRIAL DEMANDED

David A. Breuch (P45368)
Brian M. Ziff (P58124)
CLARK HILL PLC
500 Woodward Avenue, Suite 3500
Detroit, Michigan 48226-34354
Tel: 313-965-8300
Fax: 313-965-8252
Attorneys for Defendant

FIRST AMENDED COMPLAINT

Plaintiffs Guardian Industries Corp. ("Guardian") and Centre Luxembourgeois de Recherches pour le Verre et la Ceramique S.A. (C.R.V.C.) (collectively "Plaintiffs"), by their

undersigned attorneys, for their First Amended Complaint against defendant AFG Industries, Inc. ("AFG"), allege as follows:

NATURE OF THE ACTION

1. This is an action for patent infringement arising out of AFG's infringement of U.S. Plaintiffs' Patent No. 6,576,349, Guardian's U.S. Patent No. 6,602,608, and Plaintiff's U.S. Patent No. 6,686,050, in violation of the patent laws of the United States, 35 U.S.C. §§ 271 and 281-285.

THE PARTIES

2. Guardian Industries Corp. is a corporation organized and existing under the laws of the State of Michigan, having a principal place of business in Auburn Hills, Michigan.

3. Centre Luxembourgeois de Recherches pour le Verre et la Ceramique S.A. (C.R.V.C.) is a corporation organized and existing under the laws of the country of Luxembourg, having a principal place of business in Dudelange, Grand Duchy of Luxembourg.

4. On information and belief, AFG Industries, Inc. is a corporation organized and existing under the laws of the State of Tennessee, having a principal place of business in Kingsport, Tennessee.

JURISDICTION AND VENUE

5. This action arises under the patent laws of the United States, Title 35 of the United States Code.

6. This Court has jurisdiction over the subject matter of this action pursuant to 28 U.S.C. § 1338(a).

7. Venue is proper in this judicial district under 28 U.S.C. §§ 1391(b), 1391(c) and 1400(b).

BACKGROUND

8. On June 10, 2003, United States Patent No. 6,576,349 ("the '349 patent"), entitled "Heat Treatable Low-E Coated Articles and Methods of Making Same," was duly and legally issued to Philip J. Lingle et al. The patent is assigned to Guardian Industries Corp. and Centre Luxembourgeois de Recherches pour le Verre et la Ceramique S.A. (C.R.V.C.) A true and correct copy of the '349 patent is attached hereto as **Exhibit A**.

9. On August 5, 2003, United States Patent No. 6,602,608 ("the '608 patent"), entitled "Coated Article with Improved Barrier Layer Structure and Method of Making the Same," was duly and legally issued to Grzegorz Stachowiak. The patent is assigned to Guardian Industries Corp. A true and correct copy of the '608 patent is attached hereto as **Exhibit B**.

10. On February 3, 2004, United States Patent No. 6,686,050 ("the '050 patent"), entitled "Heat Treatable Low-E Coated Articles and Methods of Making Same," was duly and legally issued to Philip J. Lingle et al. The patent is assigned to Guardian Industries Corp. and Centre Luxembourgeois de Recherches pour le Verre et la Ceramique S.A. (C.R.V.C.) A true and correct copy of the '050 patent is attached hereto as **Exhibit C**.

COUNT I

(Patent Infringement)

11. AFG has directly infringed the '349 patent by making, offering to sell, selling, or using within the United States, articles covered by one or more of the claims of Plaintiffs' '349 patent.

12. On information and belief, since at least June 10, 2003, AFG has had notice of Plaintiffs' exclusive rights secured by the '349 patent.

13. On information and belief, AFG has proceeded in a willful and deliberate manner to infringe the '349 patent.

14. On information and belief, AFG's actions constitute willful infringement of the '349 patent, in violation of 35 U.S.C. §§ 271 and 281-284.

15. Plaintiffs have been irreparably harmed by AFG's infringing conduct.

16. AFG's infringing conduct will continue unless enjoined by the Court.

COUNT II

(Patent Infringement)

17. AFG has directly infringed the '608 patent by making, offering to sell, selling, or using within the United States, articles covered by one or more of the claims of Guardian's '608 patent.

18. AFG has directly infringed the '608 patent by making, offering to sell, selling, or using within the United States, articles covered by one or more of the claims of Guardian's '608 patent.

19. On information and belief, since at least August 5, 2003, AFG has had notice of Guardian's exclusive rights secured by the '608 patent.

20. On information and belief, AFG has proceeded in a willful and deliberate manner to infringe the '608 patent.

21. On information and belief, AFG's actions constitute willful infringement of the '608 patent, in violation of 35 U.S.C. §§ 271 and 281-284.

22. Guardian has been irreparably harmed by AFG's infringing conduct.

23. AFG's infringing conduct will continue unless enjoined by the Court.

COUNT III

(Patent Infringement)

24. AFG has directly infringed the '050 patent by making, offering to sell, selling, or using within the United States, articles covered by one or more of the claims of Plaintiffs' '050 patent.

25. On information and belief, since at least February 3, 2004, AFG has had notice of Plaintiffs' exclusive rights secured by the '050 patent.

26. On information and belief, AFG has proceeded in a willful and deliberate manner to infringe the '050 patent.

27. On information and belief, AFG's actions constitute willful infringement of the '050 patent, in violation of 35 U.S.C. §§ 271 and 281-284.

28. Plaintiffs have been irreparably harmed by AFG's infringing conduct.

29. AFG's infringing conduct will continue unless enjoined by the Court.

RELIEF REQUESTED

WHEREFORE, Plaintiffs respectfully request this Court to enter a judgment and order that:

- A. AFG has directly infringed the '349, '608, and '050 patents;
- B. AFG's infringement has been willful and deliberate;
- C. AFG and its officers, agents, representatives, employees and all others in concert or participation with them, directly or indirectly, be preliminarily and permanently enjoined from infringing, inducing others to infringe, or contributing to the infringement of the '349, '608, and '050 patents;
- D. Plaintiffs be awarded damages adequate to compensate for AFG's infringement of the '349, '608, and '050 patents together with pre-judgment interest pursuant to 35 U.S.C. § 284;
- E. Plaintiffs be awarded treble damages and its costs and reasonable attorneys' fees and expenses in this action in accordance with 35 U.S.C. §§ 284 and 285; and


F. Plaintiffs be awarded such other and further relief as this Court may deem just and proper.

JURY DEMAND

Guardian hereby requests a trial by jury of all triable issues.

Respectfully submitted,

RADER, FISHMAN AND GRAUER PLLC

Date: July 19, 2004 By: 

R. Terrance Rader (P28747)

Lisa R. Mikalonis (P39485)

39533 Woodward Avenue, Suite 140

Bloomfield Hills, Michigan 48304

Tel.: (248) 594-0600

Fax: (248) 594-0610

Attorneys for Plaintiff

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CERTIFICATE OF SERVICE

I hereby certify that on July 19, 2004, I served copies of the First Amended Complaint with exhibits via first class mail, on the following persons:

David A. Breuch
Brian M. Ziff
Clark Hill PLC
500 Woodward Avenue, Suite 3500
Detroit, MI 48226-3435

Martin Zoltick
Joseph A. Hynds
Rothwell, Figg, Ernst & Manbeck
1425 K. Street NW, Suite 800
Washington, DC 20005

I also hereby certify that on July 19, 2004, I served copies of the First Amended Complaint without exhibits via facsimile, on the following persons:

David A. Breuch
Brian M. Ziff
Clark Hill PLC
313-965-8252

Martin Zoltick
Joseph A. Hynds
Rothwell, Figg, Ernst & Manbeck
202-783-6031



Raimi Blackerby



(12) **United States Patent**
Lingle et al.

(10) Patent No.: **US 6,576,349 B2**
(45) Date of Patent: **Jun. 10, 2003**

(54) **HEAT TREATABLE LOW-E COATED
ARTICLES AND METHODS OF MAKING
SAME**

(75) Inventors: Philip J. Lingle, Temperance, MI (US);
Anton Dietrich, Azmoos (CH); Ronald
E. Laird, Dexter, MI (US); Jean-Marc
Lemmer, Luxembourg (LU)

(73) Assignees: Guardian Industries Corp., Auburn
Hills, MI (US); Centre
Luxembourgeois de Recherches pour
le Verra et la Ceramique
S.A.(C.R.V.C.), Grand Duchy (LU)

(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 142 days.

(21) Appl. No.: 09/794,224

(22) Filed: Feb. 28, 2001

(65) Prior Publication Data

US 2002/0064662 A1 May 30, 2002

Related U.S. Application Data

(60) Provisional application No. 60/217,101, filed on Jul. 10,
2000.

(51) Int. Cl.⁷ B32B 5/14

(52) U.S. Cl. 428/610; 428/426; 428/428;
428/432; 428/446; 428/448; 428/450; 428/469;
428/472; 428/666; 428/673; 428/680; 428/697;
428/698; 428/699; 428/702; 428/701

(58) Field of Search 428/426, 428,
428/432, 469, 472, 673, 697, 698, 699,
701, 702, 610

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Primary Examiner—Deborah Jones

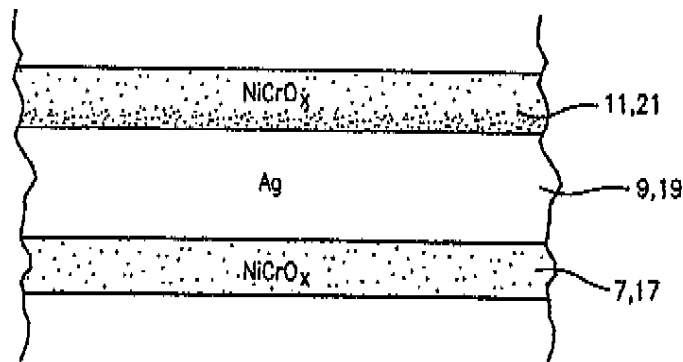
Assistant Examiner—Andrew T Piziali

(74) Attorney, Agent, or Firm—Nixon & Vanderhuy P.C.

(57) **ABSTRACT**

A heat treatable coated article (e.g., vehicle windshield, IG unit, etc.) is provided with a dual-silver low-E coating. Before and/or after heat treatment (HT), the coating and/or coated article has a visible transmittance of at least 70%, more preferably at least 75%. Moreover, the coating and/or coated article is designed so as to have approximately the same color when viewed over a wide range of viewing angles. In certain embodiments, at least one contact layer (e.g., of or including NiCrO_x) that contacts an infrared (IR) reflecting layer (e.g., Ag) is oxidation graded so that it progressively becomes less oxidized through its thickness as it nears the IR reflecting layer. In still other embodiments, a Si-rich silicon nitride layer(s) may be utilized to reduce haze.

52 Claims, 6 Drawing Sheets



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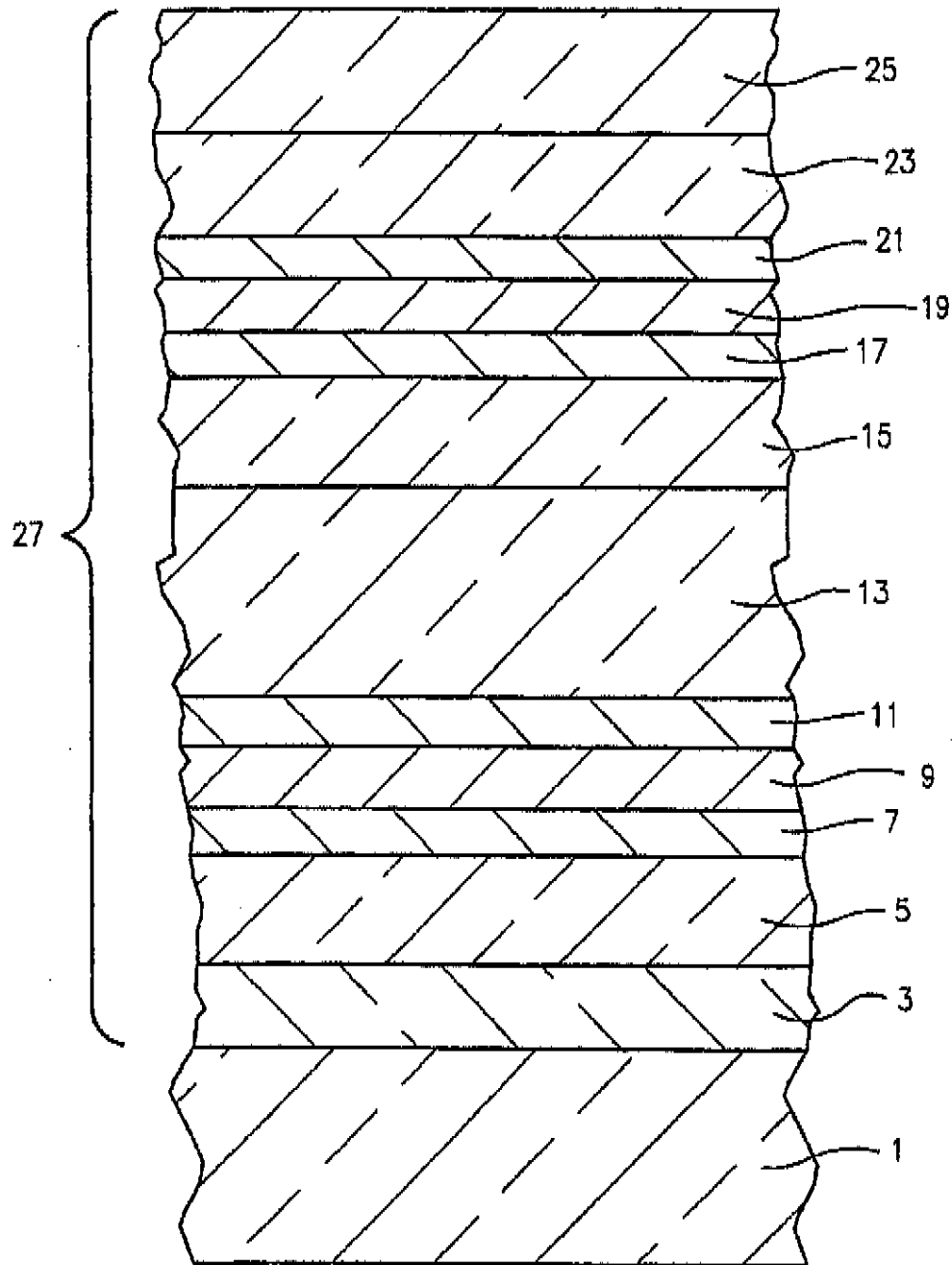


FIG. 1

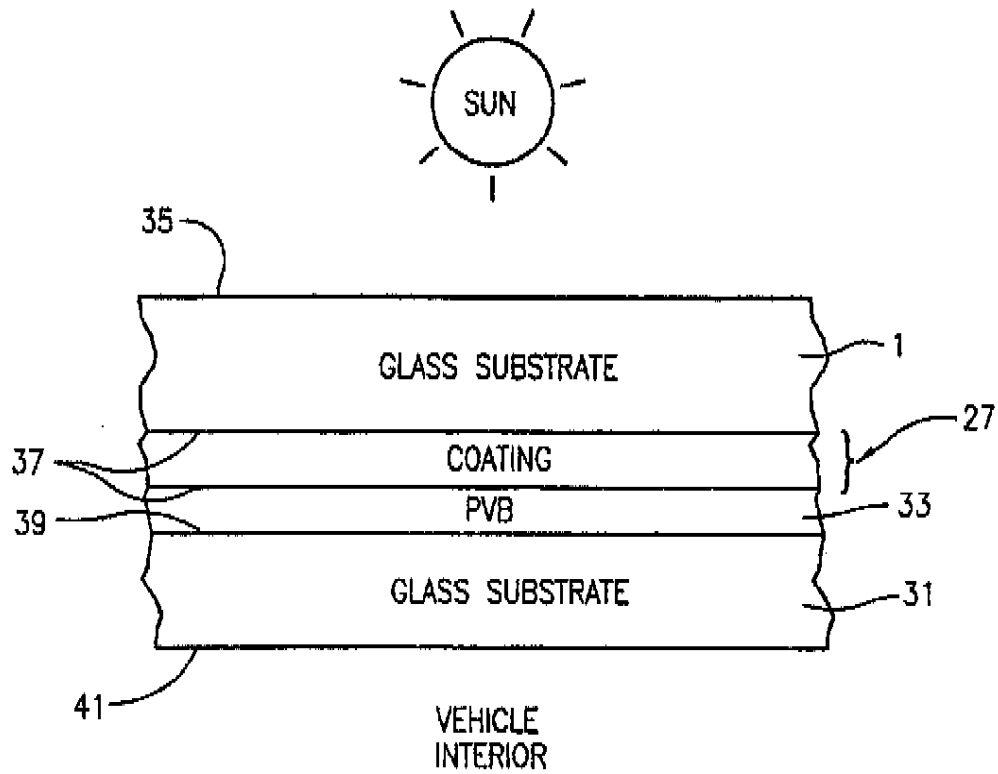


FIG. 2

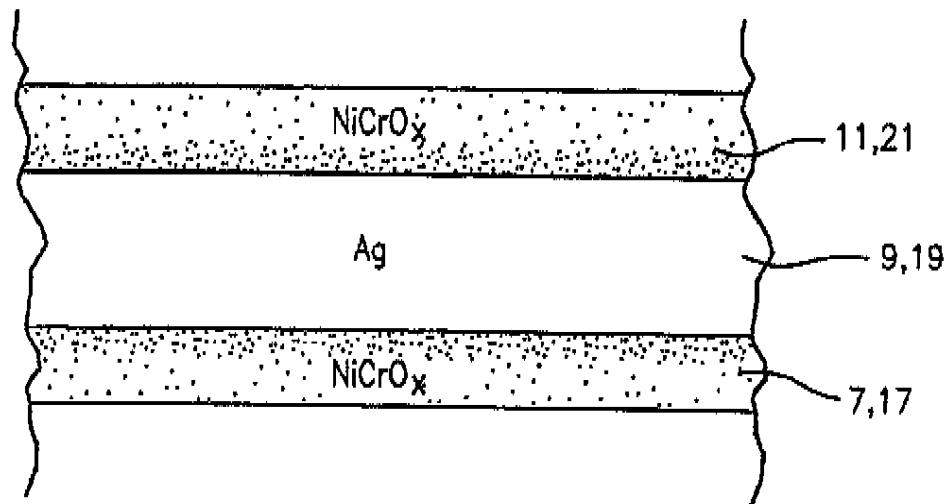


FIG. 3(a)

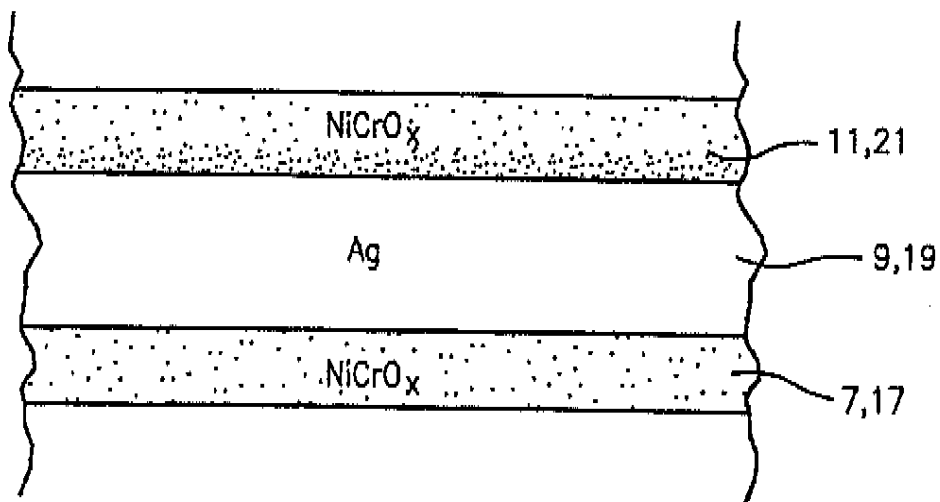


FIG. 3(b)

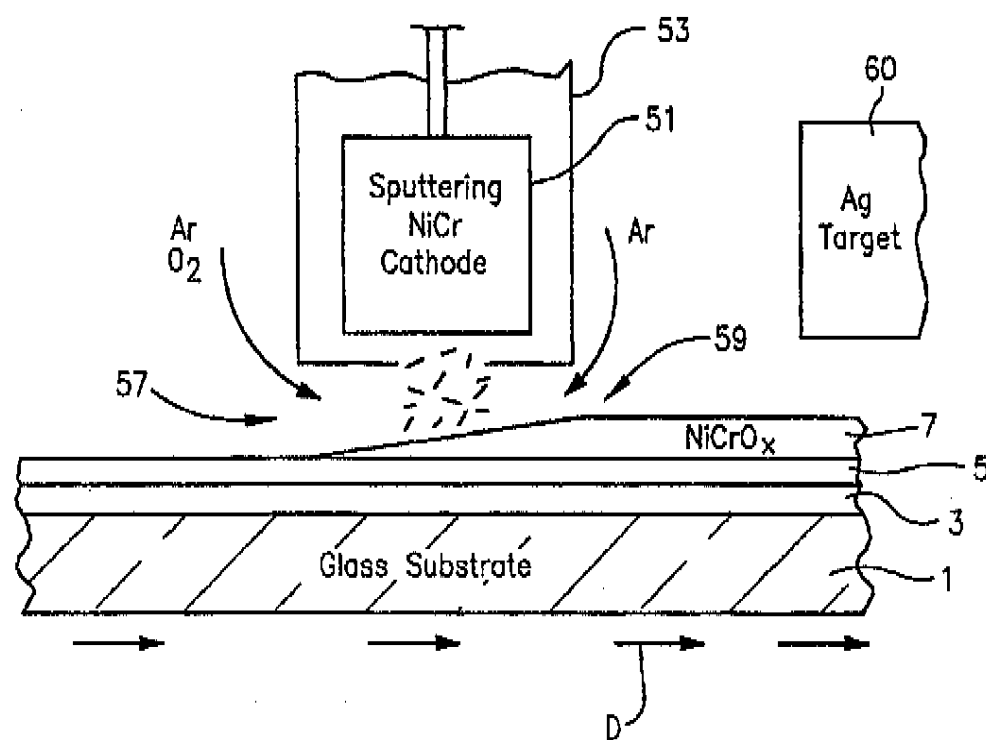


FIG. 4

Examples 1-3

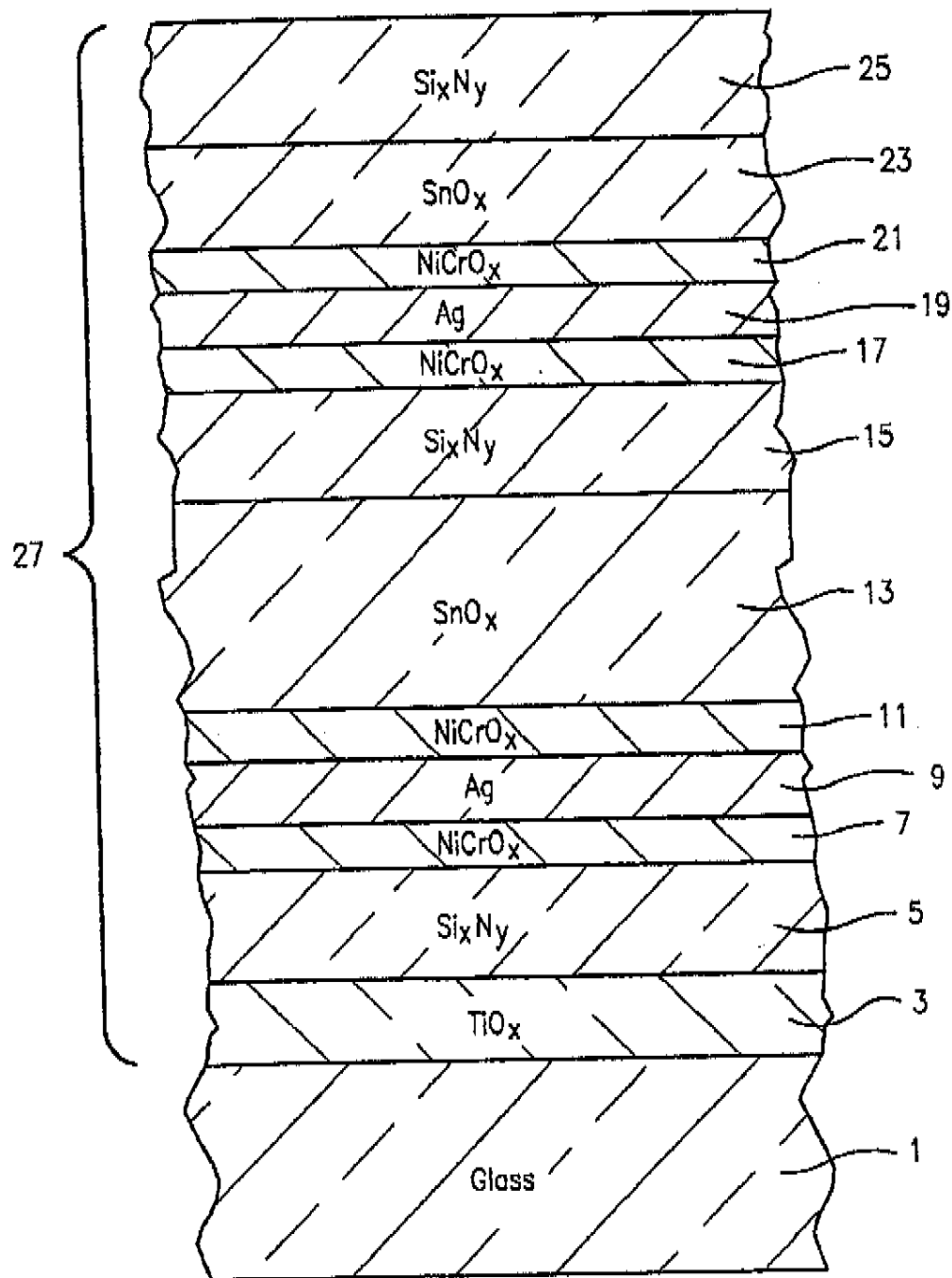


FIG. 5

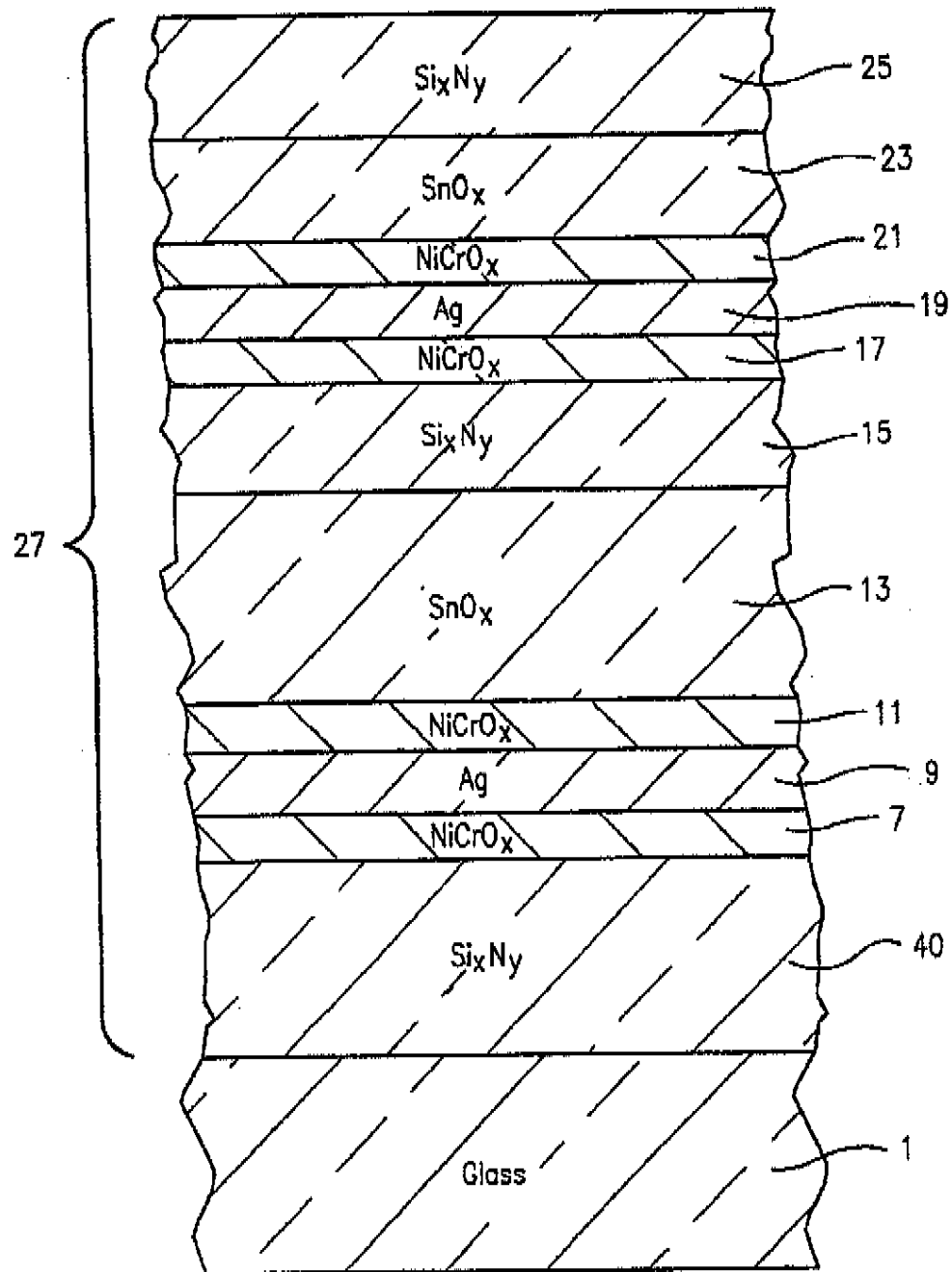


FIG. 6

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HEAT TREATABLE LOW-E COATED ARTICLES AND METHODS OF MAKING SAME

This application claims priority on U.S. Provisional Patent Application Ser. No. 60/217,101, filed Jul. 10, 2000.

This invention relates to heat treatable (low-E) coated articles, and methods of making the same. Such coated articles may be used in the context of vehicle windshields, insulating glass (IG) units, and other suitable applications.

BACKGROUND OF THE INVENTION

Layer coatings provided for solar management purposes are known in the art. Such coatings often seek to reflect infrared (IR) radiation while at the same time enabling a high amount of visible light transmittance. In the automobile industry, for example, vehicle windshields often must have a visible light transmittance of at least 70% in the United States, and at least 75% in Europe, even when laminated with a polyvinyl butyral (PVB) layer provided between opposing glass substrates. This need for high visible transmittance often conflicts with the need for good IR reflection, and it is difficult to obtain both simultaneously. Making low-E coating designs more difficult is the need for a mechanically and/or chemically durable coating, as well as the need for a coating with low visible reflectance (glass side) that does not suffer radical color change when viewed at different viewing angles. It is also desirable for such coatings to be heat treatable, so that they may be used in vehicle windshields where heat bending is required, tempered IG units, and the like.

U.S. Pat. No. 5,584,902 (commonly owned herewith) discloses a low-E coating system including, from the glass substrate outward, a stack of: $\text{Si}_3\text{N}_4/\text{NiCr}/\text{Ag}/\text{NiCr}/\text{Si}_3\text{N}_4$. Unfortunately, while this coating is heat treatable and low-E in nature, it is characterized by rather high emissivity and/or sheet resistance values which lead to rather low R_{total} (total solar energy reflectance) values around 22–24%. For example, one coating reported in the '902 patent had a sheet resistance (R_s) of 14.4 ohms/square and a normal emissivity (E_n) of 0.15 before heat treatment; and a R_s of 10.5 ohms/square and a E_n of 0.11 after heat treatment.

U.S. Pat. No. 5,557,462 (commonly owned herewith) discloses a dual silver low-E coating including from the glass outwardly a stack of: $\text{Si}_3\text{N}_4/\text{NiCr}/\text{Ag}/\text{NiCr}/\text{Si}_3\text{N}_4/\text{NiCr}/\text{Ag}/\text{NiCr}/\text{Si}_3\text{N}_4$. The coating system of the '462 patent is characterized by good emissivity values and good R_{total} values. Unfortunately, the coating systems described in the '462 patent are not heat treatable (e.g., upon heat treatment R_s goes way up, such as from about 3–5 to well over 10, and haze tends to set in). Because the coatings described in the '462 patent are not heat treatable, as a practical matter they cannot be used in applications such as vehicle windshields (where heat bending is required) or other applications requiring heat treatment (HT) such as tempering, heat strengthening, or bending.

Certain other dual-silver coatings are described in the background section of the aforesaid provisional application. See also U.S. Pat. No. 6,060,178. Unfortunately, these coating systems are plagued by poor durability before and/or after heat treatment.

SUMMARY OF THE INVENTION

An object of certain exemplary embodiments of this invention is to provide a heat treatable low-E coating (or layer system) which is mechanically and/or chemically durable before and after heat treatment, the coating system having a visible transmittance of at least about 70%.

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Another object of certain exemplary embodiments of this invention is to provide a dual silver low-E coating which is heat treatable and is mechanically and chemically durable.

Another object of certain exemplary embodiments of this invention is to provide a dual-silver low-E coating including at least one oxidation graded contact layer which contacts an IR reflecting layer, where the degree of oxidation in the contact layer is graded or changes throughout the thickness of the layer. Graded contact layer(s) can help enable the coating to have high visible transmittance coupled with heat treatability.

Another object of certain exemplary embodiments of this invention is to provide a coating including a Ni or NiCr inclusive contact layer(s) (e.g., NiCrO_x layer) which is oxidation graded in thickness so that one portion of the layer is more oxidized than another portion of the layer. Again, it is believed that graded contact layer(s) can help enable the coating to have high visible transmittance coupled with heat treatability.

Another object of certain exemplary embodiments of this invention is to utilize a silicon nitride layer in a layer stack in order to reduce haze experienced upon heat treatment. This silicon nitride layer may be Si-rich in certain embodiments.

Another object of certain exemplary embodiments of this invention is to provide a heat treatable dual-silver coating/layer system designed to: a) be mechanically durable, b) have a visible transmittance of at least about 70%, more preferably of at least about 75%, and c) have a R_{total} value of at least about 26%, more preferably of at least about 28%, and most preferably of at least about 29%.

Another object of certain exemplary embodiments of this invention is to provide a coating according to one or more of the above-listed objects which may be used in the context of an IG window unit and/or a vehicle windshield.

Another object of certain exemplary embodiments of this invention is to provide a heat treatable low-E coating having high visible transmittance combined with a normal emissivity (E_n) of no greater than 0.08 (more preferably no greater than 0.06) before heat treatment, and/or an E_n of no greater than 0.07 (more preferably no greater than 0.05) after heat treatment (HT).

Another object of certain exemplary embodiments of this invention is to provide a heat treatable low-E coating having high visible transmittance combined with a sheet resistance (R_s) of no greater than 10.0 ohms/sq. (more preferably no greater than 8.0 ohms/sq., and most preferably no greater than about 5.0 ohms/sq.) before heat treatment; and/or a R_s of no greater than 8.0 ohms/sq. (more preferably no greater than 6.0 ohms/sq., and most preferably no greater than about 4.0 ohms/sq.) after heat treatment.

Another object of certain exemplary embodiments of this invention is to provide a heat treatable low-E coating which is characterized by substantial reflective color stability with shifts in viewing angle (VA). For example, in certain exemplary embodiments, coated articles of this invention may experience a glass side reflective color coordinate a^* shift (i.e., Δa^*) of no more than 4.0, more preferably no more than 3.0, and most preferably no more than 2.0, given a VA shift of about 60 degrees.

Another object of certain exemplary embodiments of this invention is to provide a heat treatable low-E dual silver coating with a glass side reflective color coordinate a^* value within the range of from -2.0 to 2.0 before and/or after a 60 degree VA shift from normal, so as to minimize or reduce color change detectable by the human naked eye.

Another object of certain exemplary embodiments of this invention is to provide a heat treatable low-E dual silver coating having a haze value after heat treatment of no greater

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than 0.40, more preferably no greater than 0.30 (monolithic and/or in the context of a laminate such as a windshield).

Another object of certain exemplary embodiments of this invention is to provide a heat treated laminated article having a dual silver low-E coating, with a glass side visible reflectance (R_Y) (Ill. C, 2 degree) of no greater than 11%, more preferably no greater than about 9.0%, and most preferably no greater than 8.5%.

Another object of this invention is to fulfill one or more of the above-listed objects.

Generally speaking, certain example embodiments of this invention fulfill one or more of the above-listed objects by providing a coated article including a coating supported by a glass substrate, the coating comprising:

an infrared (IR) reflecting layer contacting and sandwiched between first and second layers, said second layer comprising NiCrO_x ; and

wherein at least said second layer comprising NiCrO_x is oxidation graded so that a first portion of said second layer close to said infrared (IR) reflecting layer is less oxidized than a second portion of said second layer that is further from said infrared (IR) reflecting layer.

Certain other example embodiments of this invention fulfill one or more of the above-listed objects or needs by providing a coated article including a coating supported by a substrate, the coating comprising:

a metallic infrared (IR) reflecting layer contacting and sandwiched between first and second contact layers; and

wherein said second contact layer is oxidation graded and becomes progressively more oxidized through its thickness proceeding further from said infrared (IR) reflecting layer.

Certain other example embodiments of this invention fulfill one or more of the above-listed needs or objects by providing a coated article comprising:

a coating provided on a glass substrate, said coating comprising from the glass substrate outwardly:

- a) at least one dielectric layer;
- b) a first contact layer that is at least partially oxidized;
- c) a first IR reflecting layer comprising Ag;
- d) a second contact layer that is at least partially oxidized, said first IR reflecting layer contacting each of said first and second contact layers;
- e) at least one additional dielectric layer;
- f) a third contact layer that is at least partially oxidized;
- g) a second IR reflecting layer comprising Ag;
- h) a fourth contact layer that is at least partially oxidized, said second IR reflecting layer contacting each of said third and fourth contact layers;
- i) at least one additional dielectric layer;

wherein after being heat treated (HT) and laminated said coated article has a visible transmittance of at least about 70%, a T_{total} no greater than about 50%, an R_{total} of at least 26%, and a sheet resistance (R_s) of no greater than 8.0 ohms/sq; and

wherein at least two of said first, second, third and fourth contact layers comprise at least Ni or a Ni alloy.

Certain other example embodiments of this invention fulfill one or more of the above listed needs or objects by providing a coated article comprising:

a coating provided on a glass substrate, said coating comprising from the glass substrate outwardly:

- a) at least one dielectric layer comprising silicon nitride;
- b) a first contact layer comprising Ni or a Ni alloy at least partially oxidized;

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c) a first IR reflecting layer comprising Ag;

d) a second contact layer comprising Ni or a Ni alloy at least partially oxidized;

e) at least one additional dielectric layer;

f) a third contact layer comprising Ni or a Ni alloy at least partially oxidized;

g) a second IR reflecting layer comprising Ag;

h) a fourth contact layer comprising Ni or a Ni alloy at least partially oxidized;

i) at least one additional dielectric layer;

wherein after being heat treated (HT) said coated article has a visible transmittance of at least 70%, a T_{total} no greater than 50%, an R_{total} of at least 26%, and a sheet resistance (R_s) of no greater than 8.0 ohms/sq.

Certain other example embodiments of this invention fulfill one or more of the above-listed needs or objects by providing a method of sputtering an oxidation graded layer, the method comprising:

providing a substrate;

providing a sputtering apparatus including at least one target;

directing a first gas portion proximate a first side of the target and a second gas portion proximate a second side of the target, the first gas portion including more oxygen than the second gas portion so that as the substrate passes below the target an oxidation graded layer is formed on an IR reflecting layer, the oxidation graded layer being more oxidized at one portion thereof than at another portion thereof.

Certain other embodiments of this invention fulfill one or more of the above listed objects by providing a coated article comprising:

a layer system supported by a glass substrate, the layer system comprising from the substrate outwardly:

a Si-rich silicon nitride Si_xN_y layer where x/y is from 0.76 to 1.5 in at least part of the layer;

a first contact layer; and

an IR reflecting layer.

In different embodiments of this invention, part of all of Si-rich silicon nitride layers may be Si-rich.

This invention will now be described with respect to certain example embodiments thereof as illustrated in the following drawings, wherein:

IN THE DRAWINGS

FIG. 1 is a side cross sectional view of a coated article according to an embodiment of this invention.

FIG. 2 is a schematic partial cross sectional view of a laminated vehicle windshield according to an embodiment of this invention, in which coatings according to any embodiment of this invention may be used.

FIG. 3(a) is cross sectional view of a portion of a coating according to an embodiment of this invention illustrating a pair of oxidation graded contact layers (e.g., NiCrO_x layers) surrounding an IR reflecting layer (e.g., Ag).

FIG. 3(b) is cross sectional view of a portion of a coating according to another embodiment of this invention illustrating an IR reflecting layer (e.g., Ag) surrounded by a pair of contact layers (e.g., NiCrO_x layers), only one of which is oxidation graded.

FIG. 4 is a schematic and partial cross sectional view illustrating how a graded contact layer (e.g., NiCrO_x layer) is deposited via sputtering in accordance with an embodiment of this invention.

FIG. 5 is a cross sectional view of the layer stack of coatings of Examples 1-3.

FIG. 6 is a cross sectional view of a coated article according to another embodiment of this invention.

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DETAILED DESCRIPTION OF CERTAIN EXEMPLARY EMBODIMENTS OF THE INVENTION

Referring now more particularly to the accompanying drawings in which like reference numerals indicate like parts or layers throughout the several views.

Certain embodiments of this invention provide a low-E coating or layer system that may be used in applications such as vehicle windshields, other vehicle windows, skylights, glass doors, IG units, and the like. Coatings according to certain embodiments of this invention preferably have low-E characteristics as well as high visible transmittance, and are heat treatable. Preferably, coatings of certain embodiments herein are mechanically durable before and/or after heat treatment (HT), and HT does not cause a significant jump in sheet resistance (R_s) and/or haze. As is known in the art, such HT often necessitates heating the coated substrate to temperatures of from 1100° F. (593° C.) to 1450° F. (788° C.) for a sufficient period of time to attain the desired result (e.g., tempering, bending, and/or heat strengthening).

FIG. 1 is a side cross sectional view of a coated article according to an embodiment of this invention. The coated article includes substrate 1 (e.g., clear, green, bronze, or blue-green glass substrate from about 1.0 to 10.0 mm thick, more preferably from about 1.8 mm to 4 mm thick), first dielectric anti-reflection layer 3, second dielectric haze-reducing layer 5, first lower contact layer 7 (which contacts layer 9), first conductive metallic infrared (IR) reflecting layer 9, first upper contact layer 11 (which contacts layer 9), third dielectric layer 13 (which may be deposited in one or multiple steps in different embodiments of this invention), fourth dielectric layer 15, second lower contact layer 17 (which contacts layer 19), second conductive metallic IR reflecting layer 19, second upper contact layer 21 (which contacts layer 19), fifth dielectric layer 23, and finally sixth protective dielectric layer 25. The "contact" layers each contact at least one IR reflecting layer. The aforesaid layers 3-25 make up heat treatable low-E (i.e., low emissivity) coating 27 which is provided on glass or plastic substrate 1.

In certain embodiments of this invention, first dielectric layer 3 may be of or include titanium dioxide (TiO_2 , where x is from 1.7 to 2.3, most preferably 2.0), silicon nitride (Si_3N_4 , where x/y may be about 0.75 (i.e., Si_3N_4), or alternatively x/y may be from about 0.76 to 1.5 in Si-rich embodiments), silicon dioxide (SiO_2 , where x is from 1.7 to 2.3, most preferably about 2.0), niobium oxide (e.g., Nb_2O_5), SiZrN , tin oxide, zinc oxide, silicon oxynitride, or any other suitable dielectric material. First dielectric layer 3 functions as an antireflection layer in certain embodiments of this invention.

Second dielectric layer 5 may function to reduce haze in certain embodiments of this invention, and is preferably of or includes silicon nitride (e.g., Si_3N_4 , or alternatively silicon-rich silicon nitride Si_xN_y , where x/y is from 0.76 to 1.5, more preferably from 0.85 to 1.2). When sputtering silicon nitride layer(s) herein, a Si target may be used, or alternatively a target including Si admixed with up to 3-20% by weight aluminum and/or stainless steel (e.g. SS#316) may be used, with about this amount of aluminum and/or steel then appearing in the layer(s) so formed. Other materials may also be used for haze reducing layer 5, including but not limited to SiZrN .

While Si_3N_4 may be used for layer 5 (and/or layer 15) in certain embodiments, it has been found that a silicon rich type of silicon nitride as layer 5 is better at reducing haze and/or improving mechanical durability in certain embodiments of this invention. Absent this layer 5 (and/or 15), haze tends to be at least 0.45; whereas with this layer(s) it is reduced to no greater than 0.4 as discussed herein. In Si-rich

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silicon nitride embodiments, layer 5 (and/or layer 15) is of or includes Si_xN_y , where x/y is from 0.76 to 1.5, more preferably from about 0.85 to 1.2. Si_3N_4 has an index of refraction "n" of about 2.04, and an extinction coefficient "k" of about 0. However, Si-rich silicon nitride according to certain embodiments of this invention may have an index of refraction of at least about 2.05, more preferably of at least about 2.07, and may be 2.08 (at 632 nm) in exemplary embodiments. Also, Si-rich silicon nitride according to certain embodiments of this invention may have an extinction coefficient "k" of at least about 0.001, and more preferably of at least about 0.003. In a first monolithic example after HT of a Si-rich nitride layer 5 (and/or 15), "n" was 2.099 and "k" was 0.0034; while in a second monolithic example after HT "n" was 2.168 and "k" was 0.014. Si-rich silicon nitride, in addition to being better at reducing haze than Si_3N_4 , has also been found to adhere better to the titanium oxide of layer 3 in example embodiments. Surprisingly, it has also been found that Si-rich silicon nitride under the NiCrO_x and Ag layers in FIGS. 1, 5 and 6 provides a lower sheet resistance (R_s).

Infrared (IR) reflecting layers 9 and 19 are preferably metallic and conductive, and may be made of or include silver (Ag), gold, or any other suitable IR reflecting material. However, metallic Ag is the material of choice for the IR reflecting layers 9 and 19 in certain example embodiments of this invention. These IR reflecting layers help enable coating 27 to have low-E characteristics.

Contact layers 7, 11, 17, and 21 are of or include nickel (Ni) oxide, or a nickel alloy oxide such as nickel chrome oxide (NiCrO_x), in preferred embodiments of this invention. NiCrO_x layers 7, 11, 17, and/or 21 may be fully oxidized in certain embodiments of this invention (i.e., fully stoichiometric), or may be at least about 75% oxidized in other embodiments of this invention. While NiCrO_x is a preferred material for layers 7, 11, 17 and/or 21, those skilled in the art will recognize that other materials may instead be used (e.g., oxides of Ni, oxides of Ni alloys, oxides of Cr, oxides of Cr alloys, NiCrO_xN_y , or any other suitable material) for one or more of these layers. It is noted that contact layers 7, 11, 17 and/or 21 may or may not be continuous in different embodiments of this invention.

When layers 7, 11, 17 and/or 21 comprise NiCrO_x in certain embodiments, the Ni and Cr may be provided in different amounts, such as in the form of nichrome by weight about 80-90% Ni and 10-20% Cr. An exemplary sputtering target for depositing these layers includes not only SS-316 which consists essentially of 10% Ni and 90% other ingredients, mainly Fe and Cr, but Haynes 214 alloy as well, which by weight consists essentially of (as a nominal composition) the following materials which may also show up in these layers:

Element	Weight %
Ni	75.45
Fe	4.00
Cr	16.00
C	.04
Al	4.50
Y	.01

One or more of contact layers 7, 11, 17, and/or 21 (e.g., of or including NiCrO_x) is/are preferably oxidation graded in certain embodiments of this invention so that the degree of oxidation in the layer(s) changes throughout the thickness of the layer(s). For example, one or more of contact layers (7, 11, 17 and/or 21) may be graded so as to be less oxidized at the contact interface with the immediately adjacent IR

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reflecting layer (9 or 19) than at a portion of the contact layer(s) further or more/most distant from the immediately adjacent IR reflecting layer. It is believed that oxidation grading of one or more of contact layer(s) 7, 11, 17 and/or 21 enables the low-E coating 27 to achieve the combination of heat treatability and high visible transmission (which was not previously achievable using NiCrO_x contact layers in a dual silver low-E coating system; e.g., see the aforesaid '462 patent). This will be explained in more detail below with reference to FIGS. 3(a) and 3(b).

Turning back to FIG. 1, third dielectric layer 13 acts as a coupling layer between the two halves of the coating 27, and is of or includes tin oxide in certain embodiments of this invention. However, other dielectric materials may instead be used for layer 13, including but not limited to silicon nitride, titanium dioxide, niobium oxide, silicon oxynitride, zinc oxide, or the like. Fourth dielectric layer 15 functions as a haze reducer in certain embodiments of this invention, and is preferably of or includes silicon nitride (e.g., Si_3N_4 , or alternatively silicon-rich silicon nitride discussed above). However, in alternative embodiments of this invention, other materials (e.g., SiZrN) may instead be used for dielectric layer 15.

Fifth dielectric layer 23 may be of or include tin oxide in certain embodiments of this invention. However, other dielectric materials may instead be used for layer 23, including but not limited to silicon nitride, titanium dioxide, niobium oxide, silicon oxynitride, zinc oxide, or the like. Protective overcoat dielectric layer 25 is provided at least for durability purposes, and may be of or include silicon nitride (e.g., Si_3N_4) in certain embodiments of this invention. However, other dielectric materials may instead be used for layer 25, including but not limited to titanium dioxide, silicon oxynitride, tin oxide, zinc oxide, niobium oxide, SiZrN , or the like.

Other layer(s) below or above the illustrated coating 27 may also be provided. Thus, while the layer system or coating 27 is "on" or "supported by" substrate 1 (directly or indirectly), other layer(s) may be provided therebetween. Thus, for example, coating 27 of FIG. 1 may be considered "on" and "supported by" the substrate 1 even if other layer(s) are provided between layer 3 and substrate 1. Moreover, certain layers of coating 27 may be removed in certain embodiments, while others may be added in other embodiments of this invention without departing from the overall spirit of certain embodiments of this invention.

FIG. 2 illustrates a laminate (e.g., vehicle windshield) according to an embodiment of this invention, including coating 27 of FIG. 1. As shown in FIG. 2, the laminate (e.g., windshield) includes first glass substrate 1 on which coating 27 is provided, and second glass substrate 31. PVB layer 33 is provided between the substrates in a known manner, so as to contact coating 27 on one side thereof. In the FIG. 2 embodiment, coating 27 is provided at/on the second (or #2) surface 37 of the laminate. The first surface 35 is at the exterior of the laminate exposed to the outside of the vehicle, second surface 37 is on the interior or inside of outer substrate 1, third surface 39 is on the inside of the interior substrate 31, and fourth surface 41 is at the interior of the vehicle. Coatings 27 herein are preferably provided on either the second 37 or third 39 surface(s) of such laminates (the same is also true with regard to IG units).

Turning back to FIG. 1, while various thicknesses may be used consistent with one or more of the objects discussed herein, exemplary preferred thicknesses and example materials for the respective layers on the glass substrate 1 in the FIG. 1 embodiment are as follows:

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TABLE 1

(Example Materials/Thicknesses; FIG. 1 Embodiment)

Layer	Preferred Range (Å)	More Preferred (Å)	Example (Å)
TiO_2 (layer 3)	0-400 Å	50-250 Å	100 Å
Si_3N_4 (layer 5)	0-400 Å	50-250 Å	170 Å
NiCrO_x (layer 7)	5-100 Å	10-50 Å	18 Å
Ag (layer 9)	50-250 Å	80-120 Å	105 Å
NiCrO_x (layer 11)	5-100 Å	10-50 Å	16 Å
SnO_2 (layer 13)	0-800 Å	500-850 Å	650 Å
Si_3N_4 (layer 15)	0-800 Å	50-250 Å	170 Å
NiCrO_x (layer 17)	5-100 Å	10-50 Å	18 Å
Ag (layer 19)	50-250 Å	80-120 Å	105 Å
NiCrO_x (layer 21)	5-100 Å	10-50 Å	16 Å
SnO_2 (layer 23)	0-800 Å	100-300 Å	150 Å
Si_3N_4 (layer 25)	0-500 Å	100-300 Å	250 Å

FIG. 6 illustrates a low-E heat treatable coating 27 according to another embodiment of this invention. The FIG. 6 coating 27 is the same as the FIG. 1 coating described above, except that either (i) dielectric layer 3 is removed, or (ii) layers 3 and 5 are replaced with a single silicon nitride layer 40. Silicon nitride layer 40 may be of or include Si_3N_4 in certain embodiments of this invention. In other embodiments, silicon nitride layer 40 may be of or include Si_xN_y , where x/y may be from about 0.65 to 0.80, or alternatively from about 0.76 to 1.5 in silicon rich embodiments. In another embodiment of the particular FIG. 6 embodiment, layer 40 may be of or include SiZrN . Nitride layer 40 is advantageous because it functions to reduce haze, and is preferably from about 10 to 500 Å thick, more preferably from about 200-400 Å thick. In this embodiment, upper IR reflecting layer 19 may also be thickened by about 0 to 10 Å, and/or the top dielectric 25 may be thickened by about 0-10%. In another aspect of the FIG. 6 embodiment, silicon nitride may be used for layer 40 but in a manner such that the lower portion of the layer is of or includes Si_3N_4 , while the upper portion is of the silicon rich type silicon nitride discussed above. As with all embodiments herein, Si-rich silicon nitride has improved performance in reducing haze compared to Si_3N_4 . The FIG. 6 embodiment tends to have reduced visible transmission (but still at least 70%) relative to the FIG. 1 embodiment, but may be more durable under certain circumstances, and R_{color} may be higher than in the FIG. 1 embodiment which is of course beneficial.

In certain exemplary embodiments of this invention, coating/layer systems 27 according to all embodiments above have the following low-E characteristics before/after heat treatment (HT) when in monolithic form, as set forth in Table 2:

TABLE 2

Monolithic Before/After Heat Treatment (HT)

Characteristic	General	More Preferred	Most Preferred
R_s (ohms/sq) (before HT):	<= 10.0	<= 8.0	<= 3.0
R_s (ohms/sq) (after HT):	<= 8.0	<= 6.0	<= 4.0
E_n (before HT):	<= 0.08	<= 0.06	n/a
E_n (after HT):	<= 0.07	<= 0.05	n/a
Haze (after HT):	<= 0.40	<= 0.30	<= 0.28

Coatings 27 according to certain exemplary embodiments of this invention (e.g., FIGS. 1-6) have the following color/transmission/reflection/haze characteristics (e.g., preferred greyish color can be seen below) when on a clear soda lime silica glass substrate (e.g., 2.1 mm thick) in laminated

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form with another similar clear soda lime silica glass substrate (e.g., in the form of a vehicle windshield with PVB or index oil between the two substrates) as shown in FIG. 2 (i.e., on the #2 surface of the laminate), as set forth in Table 3. In Table 3 below, R_Y is visible reflection from the exterior of the vehicle as shown in FIG. 2, and R_Y is visible reflection from the other side of the laminate such as from the vehicle interior in FIG. 2, and the a^* , b^* values under these respective reflection parameters also correspond to glass (g) side (e.g., outside vehicle in FIG. 2) and film (f) side (e.g., vehicle interior in FIG. 2), respectively.

TABLE 3

Color/Transmission After HT Laminated Form		
Characteristic	General	More Preferred
T_{vis} (Ill. A, 2 deg.):	$\geq 70\%$	$\geq 75\%$ (FIG. 1 only)
T_{vis} (Ill. C, 2 deg.):	$\geq 70\%$	$\geq 75\%$ (FIG. 1 only)
R_Y (Ill. A, C; 2 deg.):	$\leq 11\%$	$\leq 9\%$
a^* (Ill. A, C; 2°):	-2.0 to +2.0	-1.0 to +1.0
b^* (Ill. A, C; 2°):	-10.0 to +1.0	-8.0 to -2.0
R_Y (Ill. A, C; 2 deg.):	$\leq 11\%$	$\leq 9\%$
a^* (Ill. A, C; 2°):	-3.0 to +1.0	-2.0 to 0.0
b^* (Ill. A, C; 2°):	-5.0 to 0.0	-4.0 to -1.0
R_{total} :	$\geq 26\%$	$\geq 28\%$
Haze:	≤ 0.4	≤ 0.3
T_{total} :	$\leq 50\%$	$\leq 48\%$

Surprisingly, it has been found that layer stacks according to certain embodiments of this invention are characterized by rather low visible color shifts due to viewing angle (VA) change when viewed from the glass side of the article (e.g., from the exterior of the vehicle in FIG. 2). For example, Table 4 below illustrates the low Δa^* values associated with laminated coated articles of certain embodiments of this invention when viewed from a normal viewing angle (i.e., straight on) vs. a 60 degree off axis viewing angle. In other words, Table 4 below illustrates that according to certain embodiments of this invention Δa^* can be kept rather low even given a viewing angle (VA) shift of 60 degrees so that coated articles do not appear to change color to the naked eye when viewed at different angles. It is noted that Δb^* values are not deemed as important as Δa^* values, because a^* changes are typically more noticeable to the naked human eye than are corresponding b^* changes. In certain exemplary embodiments, a^* is within the range of -2.0 to +2.0 both before and after the 60 degree viewing angle (VA) shift, so that a^* remains proximate the b^* axis (i.e., the b^* axis is vertical blue(-)/yellow(+), while the a^* axis is horizontal green(-)/red(+)) even through this radical change in viewing angle thereby minimizing the appearance of color change.

TABLE 4

Color Change with 60° Viewing Angle (VA) Change			
Characteristic	General	More Preferred	Best
R_Y (normal VA):	$\leq 11\%$	$\leq 9\%$	$\leq 8\%$
a^* (normal VA):	-2.0 to +2.0	-1.0 to +1.0	-1.0 to 0.0
R_Y (60° VA):	$\leq 18\%$	$\leq 16\%$	$\leq 15\%$
a^* (60° VA):	-2.0 to +4.0	0.0 to +4.0	0.0 to 2.0
Δa^* (60° VA change):	≤ 3.0	≤ 2.0	n/a

It was mentioned above that the dual silver low-E coating system of U.S. Pat. No. 5,557,462 (i.e., glass/ Si_3N_4 /NiCr/Ag/NiCr/ Si_3N_4 /NiCr/Ag/NiCr/ Si_3N_4) is not heat treatable at least because upon heat treatment R_v goes way up, e.g., from about 3-5 to well over 10, and haze tends to set in. It is currently believed that if one were to significantly increase the thickness of the NiCr layers of the '462 patent in an

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attempt to achieve heat treatability, this would unfortunately result in visible transmittance going down well below 70% which would of course render the coated articles non-useable in vehicle windshield applications.

However, it has surprisingly been found that by oxidation grading one or more of the non-crystalline contact layers 7, 11, 17, and/or 21, the resulting coated article can maintain high visible transmission, low-E characteristics including low R_v , and good durability upon heat treatment (e.g., tempering, heat bonding, etc.). Reference is made to FIGS. 3(a) and 3(b) in this regard.

As shown in FIG. 3(a), both contact layers 7 and 11 (and/or 17 and 21) on either side of the applicable IR reflecting layer 9 (and/or 19) are oxidation graded so that they are less oxidized (including not oxidized at all in some optional embodiments) at the IR reflecting layer (e.g., Ag) interface. In other words, the two contact layers on either side of the Ag layer 9 are progressively less oxidized through their respective thicknesses as they near Ag layer 9. Accordingly, in certain embodiments of this invention, the portions (e.g., 5 Å thick portions) of layers 7 and 11 (or 17 and 21) closest to layer 9 (or 19) are from about 0 to 40% oxidized, more preferably from about 0 to 20% oxidized, and most preferably from about 0 to 10% oxidized. Meanwhile, the portions (e.g., 5 Å thick portions) of layer 7 and 11 (or 17 and 21) furthest from layer 9 (or 19) are at least about 50% oxidized, more preferably at least about 60% oxidized, even more preferably at least about 75% oxidized, and most preferably at least about 85% oxidized.

Thus, the contact layers become progressively less oxidized through their respective thicknesses as they approach the IR reflecting layer 9, 19. In certain embodiments, this causes the contact layers 7 and 11 (or 17 and 21) to be conductive or at least semi-conductive at the interface with the IR reflecting layer 9 (or 19), and substantially non-conductive at other parts of the layers 7 and 11 (or 17 and 21) such as in the 5 Å thick portion furthest from layer 9 (or 19). Thus, when the contact layers are of or include graded $NiCrO_x$, the x value progressively decreases through the thickness of the layer toward the IR reflecting layer 9, 19. This value x may even approach or equal zero near the immediately adjacent IR reflecting layer in certain instances.

It is believed that the less oxidized portions of the contact layers 7 and 11 (and/or 17 and 21) near the IR reflecting layer 9 (or 19) interface enable the coating 27 to withstand heat treatment (HT) and provide good adhesion to layer 9, 19. However, these less (or no) oxidized portions of the contact layers are also less transparent to visible light than are the more oxidized portions of the contact layers. Thus, when oxidation graded: (a) the highly oxidized portions of graded contact layers 7 and 11 (and/or 17 and 21) are more transparent to visible light and enable the coating 27 to maintain its high visible transmission characteristics, while (b) the less oxidized portions of the graded contact layers better support the IR reflecting layer(s) 9, 19 during HT and provide good adhesion thereto, and enable the coating to withstand the same.

The FIG. 3(b) embodiment of this invention is similar to the FIG. 3(a) embodiment, except that only one of the contact layers contacting an IR reflecting layer is graded. In this particular embodiment, the upper contact layer(s) 11, 21 is oxidation graded as discussed above, while the lower one is not and is substantially oxidized, or at least about 50% oxidized. In certain embodiments of this invention, all four non-crystalline contact layers 7, 11, 17 and 21 may be oxidation graded in such a manner, while in other embodiments only the upper contact layers 11 and 21 may be graded. In still further embodiments of this invention, three of the contact layers may be graded, or alternatively only one of the contact layers may be oxidation graded. While $NiCrO_x$ is a preferred material for graded contact layers

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herein, it will be appreciated by those skilled in the art that other materials may instead be used (e.g., including but not limited to NiCrO_xN_x , nickel oxide, chromium oxide, nickel-alloy oxide, etc.), and may be oxidation graded to enable a dual silver coating system to maintain high transmission and good low-E characteristics even in view of HT.

FIG. 4 illustrates how an oxidation graded contact layer 7, 17 may be deposited on a substrate as part of a coating according to an exemplary embodiment of this invention, using an asymmetric introduction of oxygen gas at a target area. Substrate 1 with part of a layer system thereon proceeds in direction D through the sputter coater. Sputtering cathode target 51 within shield 53 may comprise NiCr or any of the Ni inclusive targets discussed above when the contact layer (e.g., layer 7) is to be of or include NiCrO_x . Other metallic or ceramic targets may be used when other materials are to be used as contact layer(s). When the substrate 1 is moving in direction D beneath target 51, gas is introduced around the target on two sides 57 and 59 thereof. On one side 57 of target 51, at least oxygen (e.g., O_2) gas (e.g., oxygen flow of about 30–60 mL/min. at 4.1 kW), and optionally a mixture of oxygen and an inert gas such as argon (Ar), is fed into the coating zone beneath and/or proximate the target. However, on the other side 59 of target 51, less oxygen gas is used and more of another gas such as Ar is introduced into the coating zone beneath and/or proximate the target. For purposes of example, on side 57 of the target the gas flow may comprise any of (a) 100% oxygen, (b) a 70/30 mixture of oxygen/argon, (c) a 50/50 mixture of oxygen/argon, (d) a 30/70 mixture of oxygen/argon, or (e) a 50/25/25 mixture of oxygen/argon/nitrogen; while on the other side 59 of the target the gas flow may comprise any of (a) 100% argon or some other inert gas, (b) a 50/50 mixture of argon/nitrogen, or (c) a 90/10 mixture of argon/oxygen. Thus, there is more oxygen gas flow on side 57 of the target than on the other side 59. Thus, as the substrate 1 passes under the target 51, the first portion of layer 7 to be deposited is highly oxidized because of the presence of the oxygen gas on side 57 of the target, but the latter portion of layer 7 to be deposited is much less oxidized because of the lack of oxygen gas at the exit side 59 of the target. Thus, proximate target 51, the substrate first passes through an oxygen gas enriched sputter coating area and thereafter passes through an oxygen gas depleted sputter coating area having less oxygen gas. After layer 7 has been deposited in FIG. 4, the substrate moves on so that target 60 can be used to sputter coat layer 9 onto the substrate over the already deposited layers.

The amounts of oxygen and/or other gas(es) can of course be adjusted to oxidation grade contact layers in any desired manner. When it is desired to grade the contact layer(s) 11, 21 on the upper side of the IR reflecting layer 9, 19, the gas flow shown in FIG. 4 and described above is inverted so that the higher oxygen inclusive flow is at the exit side 59 of the target and the lower/no oxygen gas flow is at the entry side 57 of the target.

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EXAMPLES 1–3

The following three Example coated articles were made in accordance with certain embodiments of this invention. For each of the three Examples, the coating/layer system 27 shown in FIG. 5 was sputtered onto a clear 2.1 mm thick large soda lime silica float glass substrate 1, and then cut into at least a 3"x3" sample. A Leybold Terra-G six-chamber sputter coating apparatus was used to sputter the coatings 27 onto the substrates 1. Five cathodes were in each chamber, so there were a total of 30 cathode targets in the sputter coater. Cathode numbering utilizes the first digit to refer to the coater chamber, and the second digit to refer to the cathode position in that chamber. For example, cathode #32 was the second cathode (second digit) in the third (first digit) sputter chamber. Cathode #s C13, C14, C23, C62, C31, C32, C62, C64 and C65 were Twin Mag II type cathodes; cathode #C42 was a dual C-Mag type cathode; and cathode #s C44, C51, and C53 were planar cathodes. As will be appreciated by those skilled in the art, the first half of a coating 27 may be deposited in a sputter coater, and then the article may be again run through the coater to sputter the second half of the coating onto the substrate. In the sputter coater, layers 7–11 and 17–21 were sputtered onto the substrate using DC power sputtering, while the other layers were sputtered onto the substrate using a mid-frequency AC type system. Below, "Al" means Al content of approximately 10%. The line speed for each Example was 2.6 meters per minute (m/min.). The coater/process setups for the three Examples are in Table 5. All gas flows (e.g., oxygen, argon, nitrogen) are presented in units of mL/minute. In the below examples, though not shown in the charts, the oxygen flow was turned off at the sides of the NiCr targets discussed above in order to oxidation grade the contact layers 11 and 21 as shown in FIG. 3(b) (i.e., only the two contact layers 11 and 21 above the respective silver layers were oxidation graded in these Examples). Volts refers to cathode volts, and amps (A) refers to cathode amps. "Tr" stands for trim; and trim (Tr) console, trim (Tr) Mid, and trim (Tr) pump are all measured in mL/minute. Pressure is measured in mbar $\times 10^{-3}$. Trim gas refers to individually adjusted gas flows along the cathode length to make corrections regarding layer thickness uniformity. The NiCr targets were approximately 80/20 NiCr. The process for each Example is broken into three separate charts (i.e., Part #s 1–3) because so much information is presented; only the cathode and target data is provided for all three charts in each example for ease of reference. Both silicon nitride layers 5 and 15 were Si-rich through their entire thickness(es); as can be seen by the fact that much more inert argon (Ar) gas than nitrogen gas was used in sputtering these silicon nitride layers.

Example 1

Example #1

Part #1

TABLE 5

Coater Setup/Processes for Examples 1–3

Cathode	Target	Volts (V)	Power (kW)	Ar Flow (mL/min)	O ₂ Flow (mL/min)	N ₂ Flow
#13	Ti	743	73	200	25	80
#14	Ti	703	64	200	35	50
#23	Ti	738	83.5	200	35	50
#42	Si*	456	29.7	225	0	165
#44	NiCr	370	4.3	150	38	0
#51	Ag	432	3.2	100	0	0
#53	NiCr	386	4.1	150	48	0
#62	Sn	431	18.3	200	240	100
#31	Sn	477	24.2	200	290	100

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TABLE 5-continued

Coster Setup/Processes for Examples 1-3						
Cathode	Target	Volt (V)	Power (kW)	Ar Flow (mL/min)	O ₂ Flow (mL/min)	N ₂ Flow
#32	Sn	428	24.5	200	300	100
#42	Si*	453	30.2	225	0	165
#44	NiCr	360	4.2	150	38	0
#51	Ag	430	3.2	100	0	0
#53	NiCr	380	4.1	130	48	0
#62	Sn	442	18.4	200	240	100
#64	Si*	554	40.6	200	0	200
#65	Si*	545	40.3	250	0	200

Example #1

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Part #2 Continued from Part #1 Above[Cathode/
Target in Common]

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Cathode	Target	Thick			Trim Gas	
		Amps (A)	Voltage (V)	Freq. (kHz)		
#13	Ti	128	364	26.7	O ₂	25
#14	Ti	125	346	26.7	O ₂	
#23	Ti	110	344	26.5	O ₂	
#42	Si*	n/a	230	26.18	N ₂	30
#44	NiCr	11.4	0	0	Ar	
#51	Ag	7.4	0	0	Ar	
#53	NiCr	10.7	0	0	Ar	35
#62	Sn	45	203	25.03	O ₂	
#31	Sn	61	224	25.6	O ₂	
#32	Sn	60	225	25.64	O ₂	40
#42	Si*	n/a	230	26.18	N ₂	
#44	NiCr	11.6	0	0	Ar	
#51	Ag	7.4	0	0	Ar	45
#53	NiCr	10.5	0	0	Ar	
#62	Sn	42	208	25.1	O ₂	
#64	Si*	93.5	264	26.4	N ₂	50
#65	Si*	93.5	273	26.2	N ₂	

Example #1

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Part #3 Continued from Parts #1-2 Above[Cathode/
Target in Common]

Cathode	Target	Tr Console	Tr Mid	Tr Pump	Pressure	Lambda	Lambda active
#13	Ti	7.5	15	7.5	2.79E ⁻⁰³	252	True
#14	Ti	12.5	25	12.5	3.03E ⁻⁰³	252	True
#23	Ti	7.5	35	7.5	4.83E ⁻⁰³	252	True
#42	Si*	50	5	45	2.18E ⁻⁰³	0	False
#44	NiCr	15	70	15	2.26E ⁻⁰³	0	False
#51	Ag	15	70	15	1.37E ⁻⁰³	0	False
#53	NiCr	15	70	15	2.16E ⁻⁰³	0	False
#62	Sn	15	70	15	2.12E ⁻⁰³	220	True
#31	Sn	15	70	15	2.97E ⁻⁰³	220	True
#32	Sn	15	70	15	3.19E ⁻⁰³	220	True
#42	Si*	50	5	45	2.52E ⁻⁰³	0	False
#44	NiCr	15	70	15	2.30E ⁻⁰³	0	False
#51	Ag	15	70	15	1.44E ⁻⁰³	0	False
#53	NiCr	15	70	15	2.38E ⁻⁰³	0	False
#62	Sn	15	70	15	2.24E ⁻⁰³	220	True

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-continued

Cathode	Target	Ty Console	Ty Mid	Ty Pump	Pressure	Lambda	Lambda active
#64	Si*	20	60	20	2.88E ⁻⁰³	0	False
#65	Si*	20	60	20	3.61E ⁻⁰³	0	False

Example 2

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Example #2

Part #1

Cathode	Target	Voltage (V)	Power (kW)	Ar Flow (mL/min)	O ₂ Flow (mL/min)	N ₂ Flow
#13	Ti	729	74.6	200	25	80
#14	Ti	703	68	200	35	50
#23	Ti	738	63.5	200	35	50
#42	Si*	451	29.7	225	0	165
#44	NiCr	371.5	4.3	150	38	0
#51	Ag	434	3.2	100	0	0
#53	NiCr	390	4.1	150	48	0
#62	Sn	427	18.4	200	240	100
#31	Sn	476	24.6	200	290	100
#32	Sn	427	25.3	200	300	100
#42	Si*	458	29.3	225	0	165
#44	NiCr	368	4.3	150	38	0
#51	Ag	431	3.2	100	0	0
#53	NiCr	386	4.1	150	48	0
#62	Sn	435	18.4	200	240	100
#64	Si*	552	40.6	200	0	200
#65	Si*	548	40.6	250	0	200

Example #2

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Part #2 Continued from Part #1 Above[Cathode/
Target in Common]

Cathode	Target	Amps (A)	Tank Voltage (V)	Freq. (kHz)	Trim Gas
#13	Ti	346	364	26.7	O ₂
#14	Ti	325	346	26.7	O ₂
#23	Ti	310	344	26.5	O ₂
#42	Si*	n/a	230	26.18	N ₂
#44	NiCr	11.4	0	0	Ar
#51	Ag	7.3	0	0	Ar
#53	NiCr	10.3	0	0	Ar
#62	Sn	45.5	203	25.03	O ₂
#31	Sn	62	225	25.6	O ₂

-continued

			Tank			
	Cathode	Target	Amps (A)	Voltage (V)	Freq. (kHz)	Trim Gas
40	#32	Sn	61	226	25.64	O ₂
	#42	Si*	n/a	230	26.18	N ₂
	#44	NiCr	11.6	0	0	Ar
	#51	Ag	7.4	0	0	Ar
	#53	NiCr	10.5	0	0	Ar
	#62	Sn	44	206	25.1	O ₂
	#64	Si*	93.5	264	26.4	N ₂
45	#65	Si*	93.5	273	26.2	N ₂

Example #2

Part #3 Continued from Parts #1-2 Above[Cathode/
Target in Common]

Cathode	Target	Ty Console	Ty Mid	Ty Pump	Pressure	Lambda	Lambda active
#13	Ti	7.5	15	7.5	2.79E ⁻⁰³	252	True
#14	Ti	12.5	25	12.5	3.03E ⁻⁰³	252	True
#23	Ti	7.5	35	7.5	4.83E ⁻⁰³	252	True
#42	Si*	50	5	45	2.13E ⁻⁰³	0	False
#44	NiCr	15	70	15	2.26E ⁻⁰³	0	False
#51	Ag	15	70	15	1.35E ⁻⁰³	0	False
#53	NiCr	15	70	15	2.34E ⁻⁰³	0	False
#62	Sn	15	70	15	2.13E ⁻⁰³	220	True
#31	Sn	15	70	15	3.22E ⁻⁰³	220	True
#32	Sn	15	70	15	3.25E ⁻⁰³	220	True
#42	Si*	50	5	45	2.21E ⁻⁰³	0	False
#44	NiCr	15	70	15	2.26E ⁻⁰³	0	False

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-continued

Cathode	Target	Ti Console	Ti Mid	Ti Pump	Pressure	Lambda	Lambda active
#51	Ag	15	70	15	1.39E ⁻⁰³	0	False
#53	NiCr	15	70	15	2.18E ⁻⁰³	0	False
#62	Sn	15	70	15	2.15E ⁻⁰³	220	True
#64	Si*	20	60	20	2.75E ⁻⁰³	0	False
#65	Si*	20	60	20	3.35E ⁻⁰³	0	False

Example 3

Example #3

Part #1

Cathode	Target	Voltage (V)	Power (kW)	Ar Flow (ml/min)	O ₂ Flow (ml/min)	N ₂ Flow
#13	Ti	743	73	200	25	60
#14	Ti	703	64	200	35	50
#23	Ti	738	63.5	200	35	50
#42	Si*	456	29.7	225	0	165
#44	NiCr	370	4.3	150	38	0
#51	Ag	432	3.2	100	0	0
#53	NiCr	386	4.1	150	48	0
#62	Sn	431	18.3	200	240	100
#31	Sn	481	25.2	200	290	100
#32	Sn	439	25.9	200	300	100
#42	Si*	449	30.4	225	0	165
#44	NiCr	364	4.2	150	38	0
#51	Ag	427	3.2	100	0	0
#53	NiCr	383	4.0	150	48	0
#62	Sn	452	19.5	200	240	100
#64	Si*	553	40.6	200	0	200
#65	Si*	545	40.3	250	0	200

Example #3

Part #2 Continued from Part #1 Above[Cathode/
Target in Common]

Cathode	Target	Amps (A)	Tank Voltage (V)	Freq. (kHz)	Trim Gas
#13	Ti	128	364	26.7	O ₂
#14	Ti	125	346	26.7	O ₂
#23	Ti	110	344	26.5	O ₂
#42	Si*	n/a	230	26.18	N ₂
#44	NiCr	11.4	0	0	Ar
#51	Ag	7.4	0	0	Ar
#53	NiCr	10.7	0	0	Ar
#62	Sn	45	203	25.03	O ₂
#31	Sn	62	226	25.6	O ₂

-continued

Cathode	Target	Amps (A)	Tank Voltage (V)	Freq. (kHz)	Trim Gas
#32	Sn	62	229	25.64	O ₂
#42	Si*	n/a	230	26.18	N ₂
#44	NiCr	11.4	0	0	Ar
#51	Ag	7.5	0	0	Ar
#53	NiCr	10.5	0	0	Ar
#62	Sn	45.4	212	25.1	O ₂
#64	Si*	94	264	26.4	N ₂
#65	Si*	93.5	273	26.2	N ₂

Example #3

Part #3 Continued from Parts #1-2 Above[Cathode/
Target in Common]

Cathode	Target	Ti Console	Ti Mid	Ti Pump	Pressure	Lambda	Lambda active
#13	Ti	7.5	15	7.5	2.79E ⁻⁰³	252	True
#14	Ti	12.5	25	12.5	3.03E ⁻⁰³	252	True
#23	Ti	7.5	35	7.5	4.83E ⁻⁰³	252	True
#42	Si*	50	5	45	2.18E ⁻⁰³	0	False
#44	NiCr	15	70	15	2.26E ⁻⁰³	0	False
#51	Ag	15	70	15	1.37E ⁻⁰³	0	False
#53	NiCr	15	70	15	2.16E ⁻⁰³	0	False
#62	Sn	15	70	15	2.12E ⁻⁰³	220	True
#31	Sn	15	70	15	3.01E ⁻⁰³	220	True

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-continued

Cathode	Target	Tr Console	Tr Mid	Tr Pump	Pressure	Lambda	Lambda active
#32	Sa	15	70	15	3.24E ⁻⁰³	220	True
#42	Si*	50	5	45	2.58E ⁻⁰³	0	False
#44	NiCr	15	70	15	2.27E ⁻⁰³	0	False
#51	Ag	15	70	15	1.41E ⁻⁰³	0	False
#53	NiCr	15	70	15	2.37E ⁻⁰³	0	False
#62	Sa	15	70	15	2.26E ⁻⁰³	220	True
#64	Si*	20	60	20	2.90E ⁻⁰³	0	False
#65	Si*	20	60	20	3.69E ⁻⁰³	0	False

After coatings 27 of Examples 1-3 were sputtered onto respective substrates 1 in accordance with the above, they 15 were tested/measured as follows in Table 6 (i.e., in a monolithic state). Heat treatment was performed by placing the coated articles into a furnace heated to about 625 degrees C. for about five (5) minutes.

TABLE 6

Exs. 1-3, Monolithic Before/After Heat Treatment (HT)			
Characteristic	Example 1	Example 2	Example 3
T _{vis} Ill. A, 2° (before HT):	>=70%	>=70%	>=70%
T _{vis} Ill. A, 2° (after HT):	>=78%	>=78%	>=78%
R _g (ohms/sq.) (before HT):	4.43	4.37	4.27
R _g (ohms/sq.) (after HT):	3.46	3.33	3.44
E _g (before HT):	<=0.06	<=0.06	<=0.06
E _g (after HT):	<=0.05	<=0.05	<=0.05
Haze (after HT):	0.15	0.28	0.22

Thereafter, the monolithic heat treated coated articles of Examples 1-3 were each laminated to another corresponding clear 2.1 mm thick 3 inch by 3 inch soda lime silica float glass substrate 1, with a layer of PVB (about 0.8 mm thick) being located between the substrates in a known manner, and coating 27 provided on the #2 surface as shown in FIG. 2. The resulting laminated coated articles (see FIG. 2) were then tested/measured and were found to exhibit the following characteristics set forth in Table 7. In Table 7, the glass (G) side is the same as outside the vehicle in FIG. 2, while the film (F) side is the same as the vehicle interior in FIG. 2.

TABLE 7

Color of Exs. 1-3 in Laminated Form Post-HT (i.e., as in FIG. 2)			
Value/M Measurement	Example 1	Example 2	Example 3
Ill. C, 2°			
Transmission (TY or T _{vis}) %:	75.37	75.32	74.68
a* _T :	-2.92	-3.17	-2.25
b* _T :	3.87	4.39	4.07
Reflectance as viewed from glass (G) side: R _G Y (%)	7.93	8.02	8.22
a* _G :	0.59	0.93	0.29
b* _G :	-5.23	-7.10	-5.64
Reflectance as viewed from film/coating (F) side: R _F Y (%)	7.83	7.85	8.11
a* _F :	-1.59	-1.23	-1.68
b* _F :	-2.75	-3.74	-2.73
Ill. D65, 2°			
Transmission (TY or T _{vis}) %:	75.69	75.34	74.71
a* _T :	-2.81	-3.05	-2.16
b* _T :	3.85	4.35	4.07
Reflectance as viewed from glass (G) side: R _G Y (%)	7.93	8.03	8.22

TABLE 7-continued

Color of Exs. 1-3 in Laminated Form Post-HT (i.e., as in FIG. 2)			
Value/M Measurement	Example 1	Example 2	Example 3
20			
a* _G :	0.26	0.57	-0.01
b* _G :	-5.17	-7.03	-5.58
Reflectance as viewed from film/coating (F) side: R _F Y (%)	7.84	7.85	8.12
a* _F :	-1.79	-1.48	-1.88
b* _F :	-2.71	-3.69	-2.69
25			
Ill. A, 2°			
Transmission (TY or T _{vis}) %:	75.27	75.23	74.78
a* _T :	-1.95	-2.05	-1.37
b* _T :	3.28	3.74	3.68
30			
Ill. C, 10°			
Transmission (TY or T _{vis}) %:	75.16	75.08	74.91
a* _T :	-2.39	-2.59	-2.78
b* _T :	3.93	4.45	4.02
Reflectance as viewed from glass (G) side: R _G Y (%)	8.01	8.14	8.31
a* _G :	0.11	0.28	-0.15
b* _G :	-5.21	-7.03	-5.60
Reflectance as viewed from film/coating (F) side: R _F Y (%)	7.87	7.90	8.16
a* _F :	-1.54	-1.30	-1.62
b* _F :	-2.79	-3.78	-2.77
35			
Ill. D65, 10°			
Transmission (TY or T _{vis}) %:	75.19	75.12	74.92
a* _T :	-2.29	-2.49	-2.66
b* _T :	3.92	4.45	3.99
Reflectance as viewed from glass (G) side: R _G Y (%)	8.01	8.14	8.31
a* _G :	-0.09	0.01	-0.37
b* _G :	-5.20	-7.02	-5.58
Reflectance as viewed from film/coating (F) side: R _F Y (%)	7.88	7.91	8.16
a* _F :	-1.69	-1.49	-1.78
b* _F :	-2.77	-3.76	-2.75
40			
Ill. A, 10°			
Transmission (TY or T _{vis}) %:	75.20	75.15	74.85
a* _T :	-1.41	-1.63	-1.75
b* _T :	3.34	3.98	4.02

Moreover, each of Examples 1-3 was found to be chemically and mechanically durable as these terms are defined below, both before and after HT.

As can be seen above, in depositing each of the silicon nitride layers, more Ar gas than N gas was used in the sputtering process. In the Examples the ratio Ar/N is about 225/165 (or 1.36) as can be seen above. In preferred embodiments of this invention the ratio Ar/N is from about 1.15 to 3.0, more preferably from about 1.20 to 2.0, and most preferably from about 1.2 to 1.5. This ratio which uses more of an inert gas (e.g., Ar) than nitrogen in sputtering the silicon nitride layers enables the resulting silicon nitride layers to be Si-rich as discussed above.

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Table 8 below compares, for the HT laminate of Example 1, viewing characteristics at a normal viewing angle (VA) versus at a 60° off axis VA (i.e., the 60° VA is 60 degrees from the normal VA). As can be seen, Example 1 is characterized by substantial color stability over this wide range of viewing angles, so that a viewer looking at the laminate of Example 1 at both a normal VA (i.e., straight on so that the line or site is perpendicular to the plane of the article) and a 60° VA would not notice much if any color change. This is due to the low reflective Δa^* value from the glass (G) side (i.e., Δa^* means the difference between a^* at the normal VA and the 60° off-axis VA). Note: the sixty degree color is Ill. D65, 10 degree standard observer.

TABLE 8

Color Change with 60° Viewing Angle (VA) Change (Ex. 1)		
Characteristic	Ex. 1 (Normal VA)	Ex. 1 (60° off-axis VA)
T_{vis}	75.27%	n/a
a^*_{vis}	-2.2	n/a
b^*_{vis}	4.2	n/a
T_{total}	46.75%	
R_{total}	30.15	36.11
$R_g Y$	7.8%	14.56%
$a^*_{g^*}$	-0.23	1.6
$b^*_{g^*}$	-5.59	-1.33
$\Delta a^*_{g^*}$ (60° VA change)	1.83	same
$\Delta L^*_{g^*}$ (60° VA change)	11.4	same

As can be seen above in Table 8, $\Delta a^*_{g^*}$ (60° VA change) reflective in accordance with certain embodiments of this invention is preferably no greater than 3.0, and more preferably no greater than 2.0. In Table 8, it was 1.83. Moreover, T_{total} is preferably no greater than 50% in certain embodiments of this invention, even more preferably no greater than 48%, and most preferably no greater than about 47%.

Certain embodiments of this invention after heat treatment and lamination are characterized as follows regarding glass (G) side reflective color:

TABLE 9

Parameter	Normal VA	60° off-axis VA
a^*	-2.0 to +2.0	-2.0 to +3.0
b^*	-1.0 to +1.0	0 to +9.0

Certain terms are prevalently used in the glass coating art, particularly when defining the properties and solar management characteristics of coated glass. Such terms are used herein in accordance with their well known meaning. For example, as used herein:

Intensity of reflected visible wavelength light, i.e., "reflectance" is defined by its percentage and is reported as $R_g Y$ or $R_f Y$ (i.e. the Y value cited below in ASTM E-308-85), wherein "X" is either "G" for glass side or "F" for film side. "Glass side" (e.g. "G") means, as viewed from the side of the glass substrate opposite that on which the coating resides, while "film side" (i.e. "F") means, as viewed from the side of the glass substrate on which the coating resides.

Color characteristics are measured and reported herein using the CIE LAB 1976 a^* , b^* coordinates and scale (i.e. the CIE 1976 a^*b^* diagram, Ill. CIE-C 2 degree observer), wherein:

L^* is (CIE 1976) lightness units

a^* is (CIE 1976) red-green units

b^* is (CIE 1976) yellow-blue units

Other similar coordinates may be equivalently used such as by the subscript "h" to signify the conventional use of the Hunter method (or units) Ill. C, 10° observer, or the CIE

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LUV u^*v^* coordinates. These scales are defined herein according to ASTM D-2244-93 "Standard Test Method for Calculation of Color Differences From Instrumentally Measured Color Coordinates" Sep. 15, 1993 as augmented by ASTM E-308-95, Annual Book of ASTM Standards, Vol. 06.01 "Standard Method for Computing the Colors of Objects by 10 Using the CIE System" and/or as reported in IES LIGHTING HANDBOOK 1981 Reference Volume.

The terms "emissivity" (or emittance) and "transmittance" are well understood in the art and are used herein according to their well known meaning. Thus, for example, the term "transmittance" herein means solar transmittance, which is made up of visible light transmittance (TY of T_{vis}), infrared energy transmittance (T_{IR}), and ultraviolet light transmittance (T_{uv}). Total solar energy transmittance (TS or T_{total}) can be characterized as a weighted average of these other values. With respect to these transmittances, visible transmittance may be characterized for architectural purposes by the standard Illuminant C, 2 degree technique; while visible transmittance may be characterized for automotive purposes by the standard Ill. A 2 degree technique (for these techniques, see for example ASTM E-308-95, incorporated herein by reference). For purposes of emissivity a particular infrared range (i.e. 2,500-40,000 nm) is employed. Various standards for calculating/measuring any and/or all of the above parameters may be found in the aforesaid provisional application upon which priority is claimed herein.

The term R_{total} refers to total solar energy reflectance (glass side herein), and is a weighted average of IR reflectance, visible reflectance, and UV reflectance. This term may be calculated in accordance with the known DIN 410 and ISO 13837 (December 1998) Table 1, p. 22 for automotive applications, and the known ASHRAE 142 standard for architectural applications, both of which are incorporated herein by reference.

"Haze" is defined as follows. Light diffused in many directions causes a loss in contrast. The term "haze" is defined herein in accordance with ASTM D 1003 which defines haze as that percentage of light which in passing through deviates from the incident beam greater than 2.5 degrees on the average. "Haze" may be measured herein by a Byk Gardner haze meter (all haze values herein are measured by such a haze meter and are unitless).

"Emissivity" (or emittance) (E) is a measure, or characteristic of both absorption and reflectance of light at given wavelengths. It is usually represented by the formula:

$$E = 1 - \text{Reflectance}_{\mu m}$$

For architectural purposes, emissivity values become quite important in the so-called "mid-range", sometimes also called the "far range" of the infrared spectrum, i.e. about 2,500-40,000 nm., for example, as specified by the WINDOW 4.1 program, LBL-35298 (1994) by Lawrence Berkeley Laboratories, as referenced below. The term "emissivity" as used herein, is thus used to refer to emissivity values measured in this infrared range as specified by ASTM Standard E 1585-93 entitled "Standard Test Method for Measuring and Calculating Emittance of Architectural Flat Glass Products Using Radiometric Measurements". This Standard, and its provisions, are incorporated herein by reference. In this Standard, emissivity is reported as hemispherical emissivity (E_h) and normal emissivity (E_n).

The actual accumulation of data for measurement of such emissivity values is conventional and may be done by using, for example, a Beckman Model 4260 spectrophotometer with "VW" attachment (Beckman Scientific Inst. Corp.). This spectrophotometer measures reflectance versus wavelength, and from this, emissivity is calculated using the aforesaid ASTM Standard 1585-93.

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Another term employed herein is "sheet resistance". Sheet resistance (R_s) is a well known term in the art and is used herein in accordance with its well known meaning. It is here reported in ohms per square units. Generally speaking, this term refers to the resistance in ohms for any square of a layer system on a glass substrate to an electric current passed through the layer system. Sheet resistance is an indication of how well the layer or layer system is reflecting infrared energy, and is thus often used along with emissivity as a measure of this characteristic. "Sheet resistance" may for example be conveniently measured by using a 4-point probe ohmmeter, such as a dispensable 4-point resistivity probe with a Magnetron Instruments Corp. head, Model M-800 produced by Signatone Corp. of Santa Clara, Calif.

"Chemical durability" or "chemically durable" is used herein synonymously with the term of art "chemically resistant" or "chemical stability". Chemical durability is determined by boiling a 2"x5" sample of a coated glass substrate in about 500 cc of 5% HCl for 5 minutes (i.e. at about 220° F.). The sample is deemed to pass this test (and thus the layer system is "chemically resistant" or is deemed to be "chemically durable" or to have "chemical durability") herein if at least half of the sample's layer system remains after the 5 minutes.

"Mechanical durability" as used herein is defined by the following tests. The test uses a Pacific Scientific Abrasion Tester (or equivalent) wherein a 2"x4"x1" nylon brush (e.g., as made by Wright Bernet of Franklin Park, Ill., Model 1280 Hand & Nail Brush) is cyclically passed over the layer system in 500 cycles employing 150 gm of weight, applied to a 6"x17" sample. In this test, if no substantial, noticeable scratches appear when viewed with the naked eye under visible light, the test is deemed passed, and the article is said to be "mechanically durable" or to have "mechanical durability".

The terms "heat treatment" and "heat treating" as used herein mean heating the article to a temperature sufficient to enabling thermal tempering, bending, or heat strengthening of the glass inclusive article. This definition includes, for example, heating a coated article to a temperature of at least about 1100 degrees F. (e.g., to a temperature of from about 550 degrees C. to 900 degrees C.) for a sufficient period to enable tempering.

Once given the above disclosure many other features, modifications and improvements will become apparent to the skilled artisan. For example, and without limitation, the aforesaid oxidation graded contact layer(s) and Si-rich silicon nitride layer(s) can be used with single silver layer stacks, as well as the illustrated dual silver layer stacks. Such other features, modifications and improvements are therefore considered to be a part of this invention, the scope of which is to be determined by the following claims:

What is claimed is:

1. A heat treated coated article including a coating supported by a glass substrate, the coating comprising:
an infrared reflecting layer contacting and sandwiched between first and second layers, said second layer comprising an oxide of NiCr; and

wherein at least said second layer comprising the oxide of NiCr is oxidation graded so that a first portion of said second layer closer to said infrared reflecting layer is less oxidized than a second portion of said second layer that is further from said infrared reflecting layer;

wherein the second layer comprising the oxide of NiCr that is oxidation graded is sandwiched between and contacts each of the infrared reflecting layer and a nitride layer.

2. The coated article of claim 1, wherein said infrared reflecting layer comprises silver.

3. The coated article of claim 1, wherein said first portion of said second layer comprising the oxide of NiCr is from 0

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to 40% oxidized, and said second portion of said second layer comprising the oxide of NiCr is at least about 50% oxidized.

4. The coated article of claim 3, wherein said first portion of said second layer comprising the oxide of NiCr is from 0 to 20% oxidized.

5. The coated article of claim 3, wherein said first portion of said second layer comprising the oxide of NiCr is from 0 to 20% oxidized, and said second portion of said second layer comprising the oxide of NiCr is at least about 60% oxidized.

6. The coated article of claim 1, wherein said second layer comprising the oxide of NiCr becomes progressively less oxidized through its thickness as it nears said IR reflecting layer.

7. The coated article of claim 1, wherein said first portion of said second layer comprising the oxide of NiCr is conductive or semi-conductive, and said second portion of said second layer comprising the oxide of NiCr is dielectric.

8. The coated article of claim 1, wherein both of said first and second layers comprise an oxide of NiCr and are oxidation graded so that each of said first and second layers comprises a first portion close to said infrared reflecting layer being less oxidized than a second portion further from said infrared reflecting layer than said first portion.

9. The coated article of claim 1, wherein said coating comprises, from the glass substrate outwardly, the following layers:

at least one dielectric layer;

said first layer comprising an oxide of NiCr;

said infrared reflecting layer;

said second layer comprising the oxide of NiCr;

at least one additional dielectric layer;

a third layer comprising an oxide of NiCr;

a second infrared reflecting layer;

a fourth layer comprising an oxide of NiCr; and

at least one additional dielectric layer.

10. The coated article of claim 9, wherein said infrared reflecting layers comprise silver, and wherein said at least one dielectric layer between said substrate and said first layer comprising the oxide of NiCr comprises silicon nitride.

11. The coated article of claim 9, wherein said coated article has a visible transmittance of at least about 70%, an R_{total} of at least 26%, and a sheet resistance after heat treatment of no greater than 8.0 ohms/sq.

12. The coated article of claim 11, wherein said coated article has a visible transmittance of at least about 75%, an R_{total} of at least 28%, and a sheet resistance after heat treatment of no greater than 6.0 ohms/sq.

13. The coated article of claim 1, wherein said second layer is provided between said infrared reflecting layer and said substrate.

14. The coated article of claim 1, wherein said infrared reflecting layer is provided between said second layer and said substrate.

15. A heat treated coated article including a coating supported by a substrate, the coating comprising:

an infrared reflecting layer sandwiched between first and second layers, said second layer comprising an oxide of Ni;

wherein at least said second layer comprising an oxide of Ni is oxidation graded and becomes progressively more oxidized through its thickness proceeding further from said infrared reflecting layer; and

- wherein the second layer comprising an oxide of Ni, that is oxidation graded, is sandwiched between and contacting the infrared reflecting layer and a nitride layer.

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16. The coated article of claim 15, wherein said second layer comprises an oxide of NiCr.

17. The coated article of claim 15, wherein said infrared reflecting layer comprises metallic silver.

18. The coated article of claim 15, wherein a first portion of said second layer closer to said infrared reflecting layer is from 0 to 40% oxidized, and a second portion of said second layer further from said infrared reflecting layer is at least about 50% oxidized.

19. The coated article of claim 18, wherein said first portion is from 0 to 20% oxidized, and said second portion is at least about 60% oxidized.

20. The coated article of claim 15, wherein both of said first and second layers comprise an oxide of NiCr and are oxidation graded so that each of said first and second layers comprises a first portion close to said infrared reflecting layer being less oxidized than a second portion further from said infrared reflecting layer than said first portion.

21. The coated article of claim 15, wherein said coating comprises the following layers:

- at least one dielectric layer;
- said first layer;
- said infrared reflecting layer;
- said second layer comprising an oxide of Ni;
- at least one additional dielectric layer;
- a third layer comprising an oxide of Ni;
- a second infrared reflecting layer;
- a fourth layer comprising an oxide of Ni; and
- at least one additional dielectric layer.

22. A heat treated coated article including a coating supported by a substrate, the coating comprising:

- a metallic infrared reflecting layer contacting and sandwiched between first and second contact layers;
- wherein at least said second contact layer is oxidation graded and becomes progressively more oxidized through its thickness proceeding further from said infrared reflecting layer; and

wherein said second contact layer, that is oxidation graded, is sandwiched between and contacting the metallic infrared reflecting layer and a nitride layer.

23. The coated article of claim 22, wherein said coated article has a visible transmittance of at least about 70%, an R_{sheet} of at least 26%, and a sheet resistance after heat treatment of no greater than 8.0 ohms/sq.

24. The coated article of claim 23, wherein said coated article further comprises a second metallic infrared reflecting layer contacting and sandwiched between third and fourth contact layers, at least one of said third and fourth contact layers being oxidation graded so as to become progressively more oxidized through its thickness proceeding further from said second metallic infrared reflecting layer.

25. The coated article of claim 24, wherein said first and second infrared reflecting layers each comprise silver.

26. The coated article of claim 22, wherein said second contact layer comprises an oxide of NiCr, wherein a first portion of said second contact layer is closer to said infrared reflecting layer than a second portion of said second contact layer, and wherein said first portion is from 0 to 40% oxidized, and said second portion is at least about 50% oxidized so as to be more transmissive to visible light than said first portion.

27. The coated article of claim 25, wherein said coating comprises, from the substrate outwardly, the following layers:

- at least one dielectric layer;
- said first contact layer;

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said infrared reflecting layer comprising Ag;

said second contact layer;

at least one additional dielectric layer;

said third contact layer;

said second infrared reflecting layer comprising Ag;

said fourth layer contact layer, this layer being oxidation graded; and

at least one additional dielectric layer.

28. The coated article of claim 27, wherein said at least one dielectric layer between said substrate and said first contact layer comprises at least a silicon nitride layer.

29. The coated article of claim 27 wherein said coated article has a visible transmittance of at least about 75%, an R_{sheet} of at least 28%, and a sheet resistance after heat treatment of no greater than 6.0 ohms/sq.

30. A heat treated coated article comprising a glass substrate supporting a coating, the coating comprising:

at least first and second dielectric layers;

a layer comprising Ag;

a layer comprising NiCr, wherein the layer comprising NiCr and the layer comprising Ag are provided between at least the first and second dielectric layers; wherein the layer comprising NiCr is more oxidized at a location further from the layer comprising Ag than at a location closer to the layer comprising Ag; and

wherein the layer comprising NiCr, that is more oxidized at a location further from the layer comprising Ag than at a location closer to the layer comprising Ag, is sandwiched between and contacting said layer comprising Ag and one of said dielectric layers which comprises a nitride.

31. The coated article of claim 30, wherein the first and second dielectric layers comprise silicon nitride.

32. The coated article of claim 30, wherein the layer comprising Ag is provided at a location between the glass substrate and the layer comprising NiCr.

33. The coated article of claim 30, wherein the layer comprising NiCr is at least about 50% oxidized at the location further from the layer comprising Ag and from 0-40% oxidized at the location closer to the layer comprising Ag.

34. The coated article of claims 30, wherein the coating has a sheet resistance of no greater than 8.0 ohms/square.

35. The coated article of claim 30, wherein the coated article further comprises another layer comprising Ag, and has a visible transmittance of at least 70%.

36. A heat treated coated article comprising a glass substrate supporting a coating, the coating comprising:

first and second layers comprising Ag;

a layer comprising NiCr located between the first and second layers comprising Ag, the layer comprising NiCr being closer to the first layer comprising Ag than to the second layer comprising Ag;

wherein the layer comprising NiCr is more oxidized at a location further from the first layer comprising Ag than at a location closer to the first layer comprising Ag; and

wherein the layer comprising NiCr, that is more oxidized at a location further from the first layer comprising Ag than at a location closer to the first layer comprising Ag, is sandwiched between and contacting each of the first layer comprising Ag and a layer comprising silicon nitride.

37. The coated article of claim 36, wherein the coating has a sheet resistance of no greater than 8.0 ohms/square.

38. The coated article of claim 36, wherein the coated article has a visible transmittance of at least 70%.

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39. The coated article of claim 36, further comprising a layer comprising silicon nitride located between the substrate and the layers comprising Ag.

40. The coated article of claim 36, wherein the coating further comprises a layer comprising titanium oxide that contacts a layer comprising silicon nitride.

41. A heat treated coated article comprising a glass substrate supporting a coating, the coating comprising:

first and second layers comprising Ag;

a layer comprising NiCr that is closer to the first layer comprising Ag than to the second layer comprising Ag;

wherein the layer comprising NiCr is more oxidized at a location further from the first layer comprising Ag than at a location closer to the first layer comprising Ag; and

wherein the layer comprising NiCr, that is more oxidized at a location further from the first layer comprising Ag than at a location closer to the first layer comprising Ag, is sandwiched between and contacting the first layer comprising Ag and a layer comprising a nitride.

42. The coated article of claim 41, wherein the coating has a sheet resistance of no greater than 8.0 ohms/square.

43. The coated article of claim 41, wherein the coated article has a visible transmittance of at least 70%.

44. The coated article of claim 41, further comprising a layer comprising silicon nitride located between the substrate and the layers comprising Ag.

45. The coated article of claim 41, wherein the coating further comprises a layer comprising titanium oxide that contacts a layer comprising silicon nitride.

46. A heat treated coated article including a coating supported by a glass substrate, the coating comprising:

first and second layers comprising Ag, the first layer comprising Ag being located closer to the glass substrate than the second layer comprising Ag;

first, second and third layers comprising silicon nitride, wherein the first layer comprising silicon nitride is located between the glass substrate and the first layer comprising Ag, wherein the second layer comprising silicon nitride is located between the first and second layers comprising Ag, and wherein the third layer

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comprising silicon nitride is located over both of the first and second layers comprising Ag;

a contact layer that is in direct contact with one of the layers comprising Ag, wherein the contact layer comprises at least one metal and is more oxidized at a location further from the layer comprising Ag that it contacts than at a location closer to the layer comprising Ag that it contacts; and

wherein the contact layer, in addition to contacting one of the layers comprising Ag, also contacts one of the layers comprising silicon nitride on an opposite side thereof.

47. The coated article of claim 46, wherein the contact layer comprises an oxide of Ni and/or Cr.

48. A heat treated coated article including a coating supported by a substrate, the coating comprising:

a layer comprising Ag contacting and sandwiched between first and second contact layers; and

wherein at least said second contact layer comprises a metal and is more oxidized at a location further from said layer comprising Ag than at a location closer to said layer comprising Ag, and wherein said second contact layer is sandwiched between and contacting the layer comprising Ag and a nitride layer.

49. The coated article of claim 48, wherein the coated article is thermally tempered.

50. The coated article of claim 48, wherein the second contact layer, that comprises a metal and is more oxidized at a location further from said layer comprising Ag than at a location closer to said layer comprising Ag, comprises an oxide of Ni.

51. The coated article of claim 48, wherein the second contact layer, that comprises a metal and is more oxidized at a location further from said layer comprising Ag than at a location closer to said layer comprising Ag, comprises an oxide of Cr.

52. The coated article of claim 48, wherein the nitride layer comprises silicon nitride.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 6,576,349 B2
DATED : June 10, 2003
INVENTOR(S) : Lingle et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 27.

Line 25, change "nitrate" to -- nitride --.

Line 29, change "nitrate" to -- nitride --.

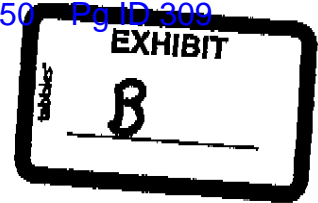
Signed and Sealed this

Twenty-eighth Day of October, 2003

A handwritten signature in black ink, appearing to read "James E. Rogan", written over a horizontal line.

JAMES E. ROGAN

Director of the United States Patent and Trademark Office



(12) **United States Patent**
Stachowiak

(10) Patent No.: **US 6,602,608 B2**
(45) Date of Patent: **Aug. 5, 2003**

(54) **COATED ARTICLE WITH IMPROVED
BARRIER LAYER STRUCTURE AND
METHOD OF MAKING THE SAME**

(75) Inventor: **Grzegorz Stachowiak, Ann Arbor, MI
(US)**

(73) Assignee: **Guardian Industries, Corp., Auburn
Hills, MI (US)**

(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/986,985**

(22) Filed: **Nov. 13, 2001**

(65) **Prior Publication Data**

US 2003/0104221 A1 Jun. 5, 2003

Related U.S. Application Data

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2001.

(51) Int. Cl.⁷ **B32B 17/06**

(52) U.S. Cl. **428/432; 428/428; 428/448;
428/469; 428/472; 428/666; 428/667; 428/673;
428/680; 428/697; 428/698; 428/699; 428/701;
428/702; 428/704**

(58) Field of Search **428/428, 432,
428/448, 469, 472, 693, 697, 698, 699,
701, 702, 666, 667, 680**

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Primary Examiner—Deborah Jones

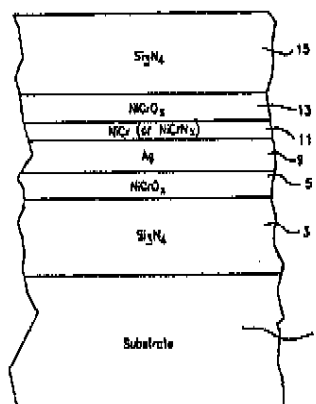
Assistant Examiner—A T Piziali

(74) *Attorney, Agent, or Firm*—Nixon & Vanderhye P.C.

(57) **ABSTRACT**

A coated article, and a corresponding method of making the
same are provided. The coated article includes a coating
supported by a substrate, the coating including a thin metal
or metal nitride contact layer (e.g., NiCr, Ni, Cr, CrN₂, or
NiCrN₂) located directly between and contacting an infrared
(IR) reflecting layer (e.g., Ag) and an oxide barrier layer
(e.g., NiCrO₂).

33 Claims, 3 Drawing Sheets



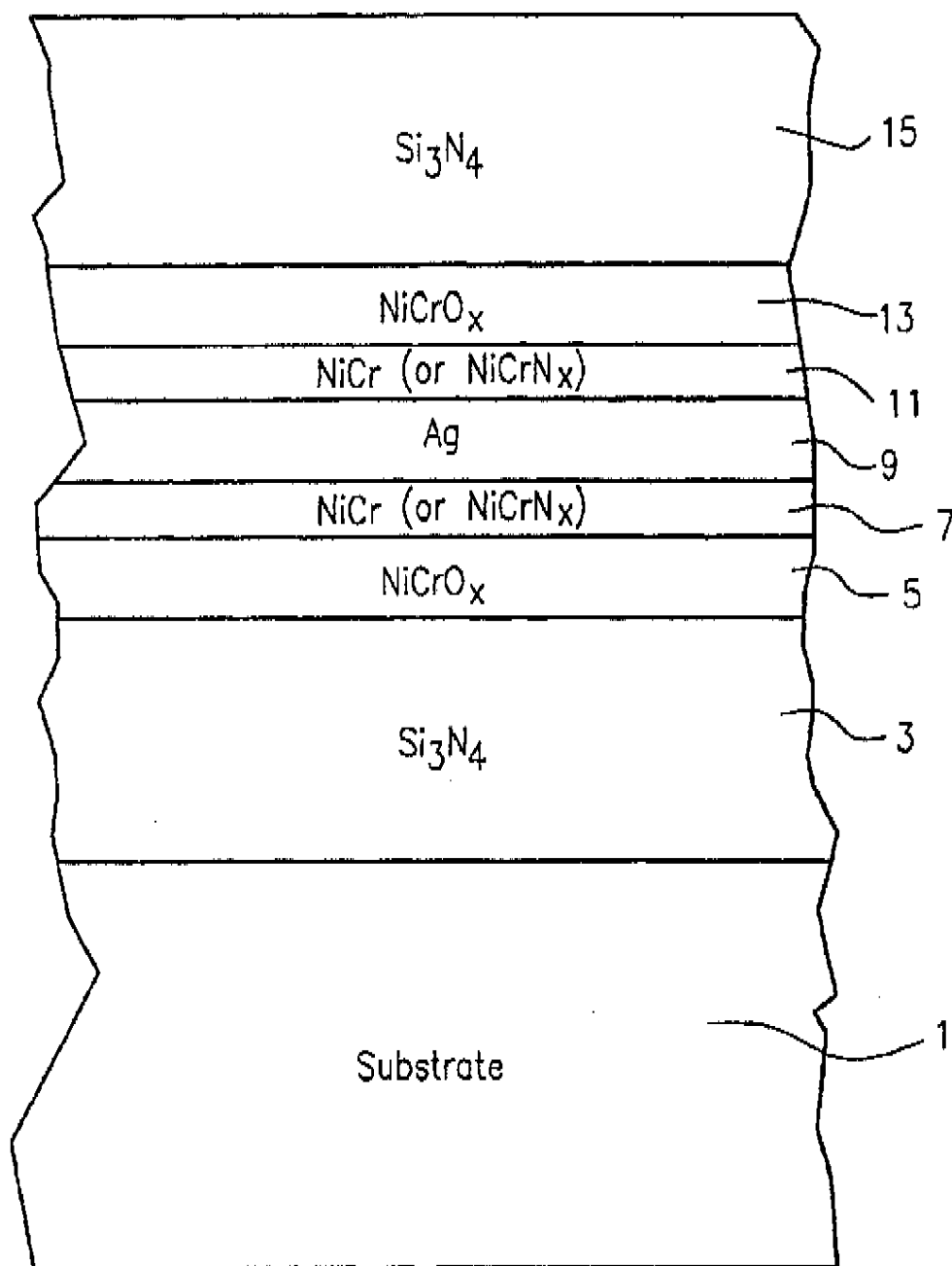


FIG. 1

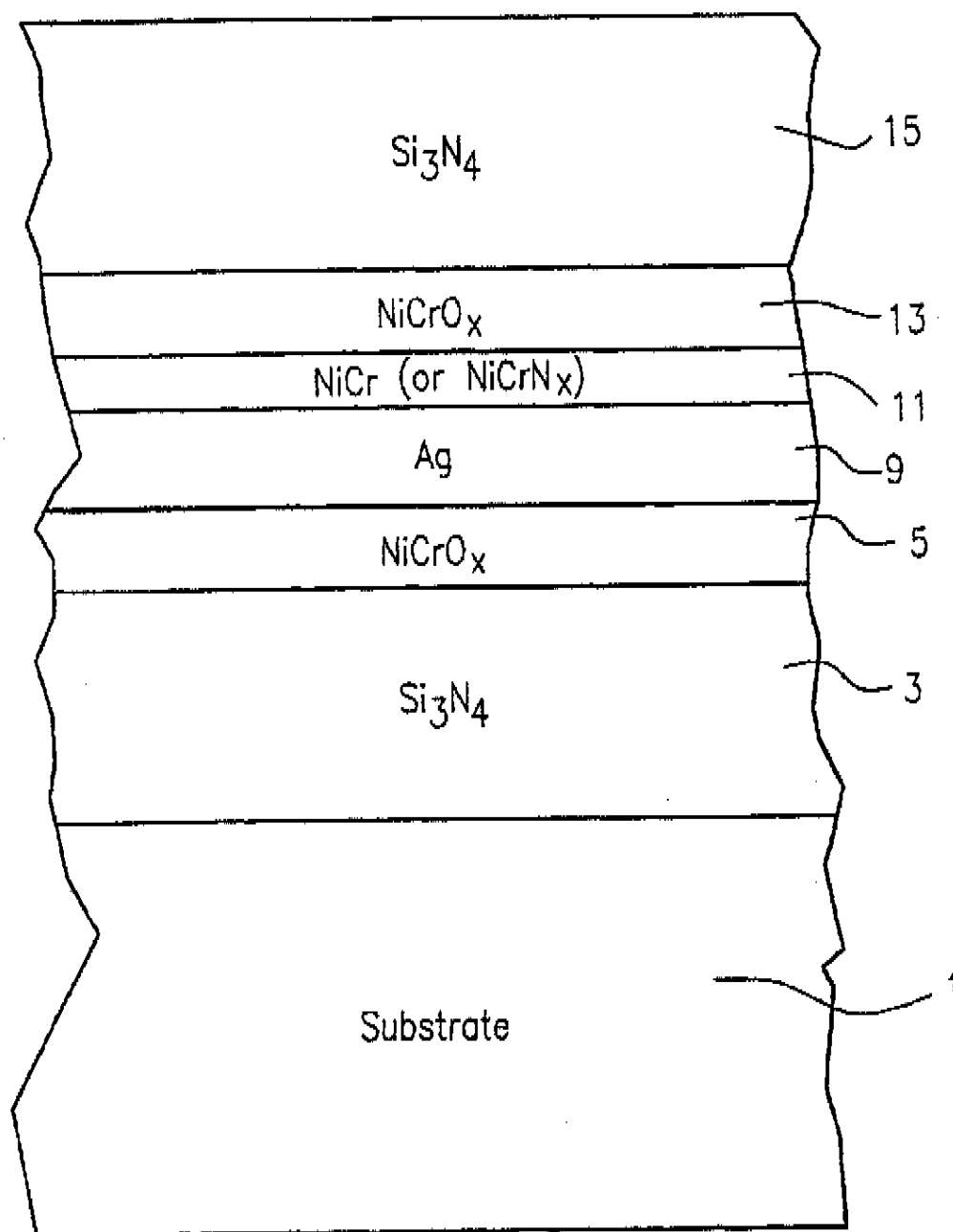


FIG. 2

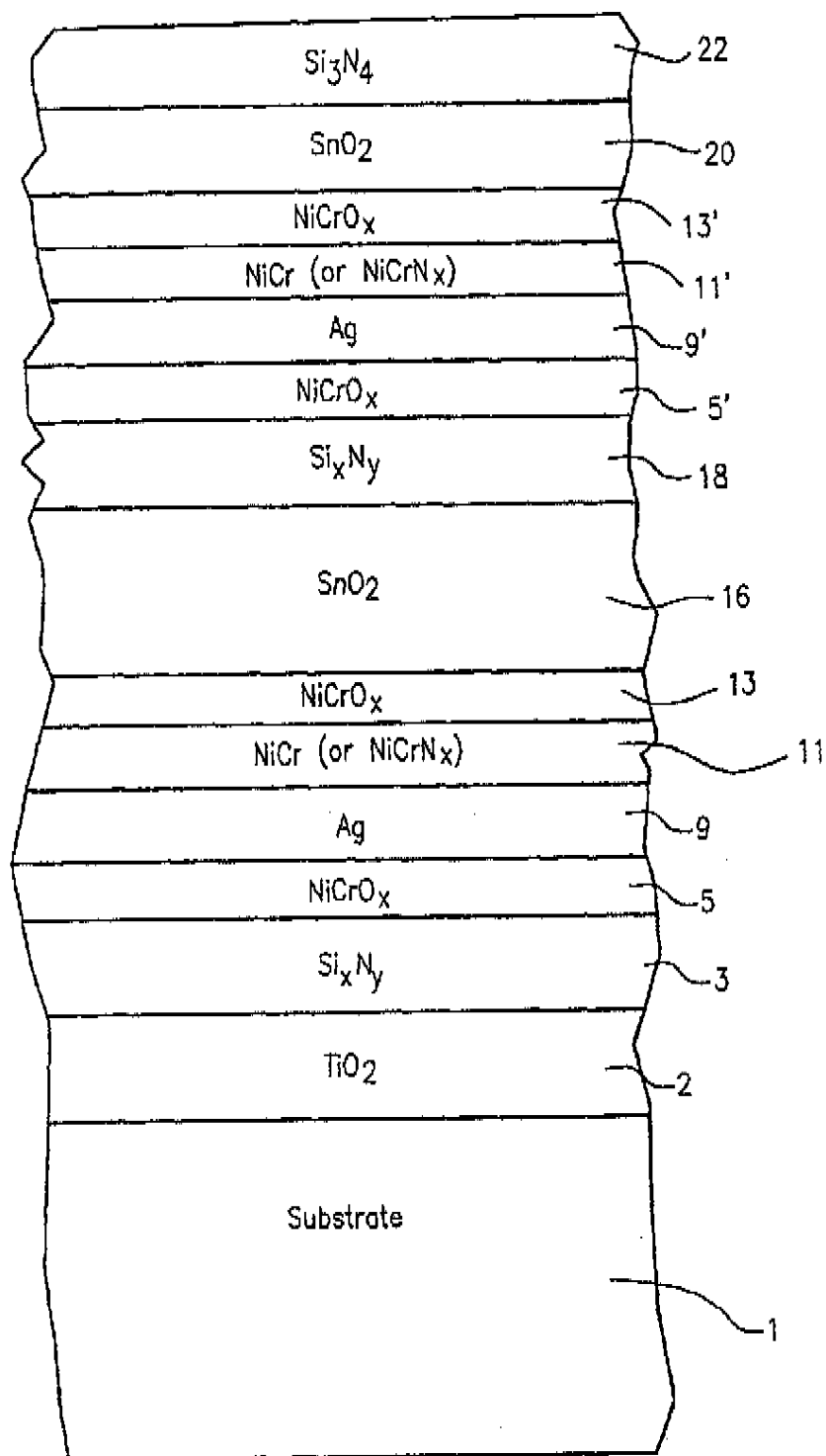


FIG. 3

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COATED ARTICLE WITH IMPROVED BARRIER LAYER STRUCTURE AND METHOD OF MAKING THE SAME

This application claims priority on Provisional U.S. patent application Ser. No. 60/331,160, filed Nov. 9, 2001, the disclosure of which is hereby incorporated herein by reference.

TITLE OF THE INVENTION

This invention relates to a coated article including a metal or metal nitride layer provided between an IR reflecting layer (e.g., Ag layer) and an oxide barrier layer (e.g., NiCrO_x), and a method of making the same.

BACKGROUND OF THE INVENTION

Coated articles provided for solar control purposes are known in the art. For example, see U.S. Pat. No. 5,344,718, which discloses a layer stack of: glass/ Si_3N_4 / NiCr / Ag / NiCr / Si_3N_4 . In coatings such as this, NiCr barrier layers are commonly used to protect the Ag (silver) in low-E type coatings.

Unfortunately, metallic NiCr is characterized by high absorption which reduces transmittance of the final coated article. Due to this high absorption problem, those in the art desiring products with high visible transmission have been forced to use very thin NiCr barrier layers. For example, the NiCr layers in the aforesaid '718 patent are "less than about 7 Å" thick, in order to obtain the desired visible transmission. The thinner such layers are, the less barrier functionality and protection they provide. Consequently, those skilled in the art have been seeking to increase barrier layer transmission by introducing oxygen and/or nitrogen to NiCr barrier layers (e.g., see U.S. Pat. No. 6,014,872 at col. 4, lines 40-50).

Consider a layer stack of glass/ Si_3N_4 / NiCrO_x / Ag / NiCrO_x / Si_3N_4 . While the NiCrO_x protective barrier layers are more transparent than NiCr protective barrier layers, they have their problems. For instance, the use of NiCrO_x protective barrier layers contacting the Ag layer on respective sides thereof can sometimes lead to problems with respect to durability and/or heat treatability. It is believed that during deposition (e.g., via sputtering) of a coating including NiCrO_x protective barrier layers, the Ag layer is exposed to the oxygen plasma (and thus chemically active atomic oxygen in that plasma) used in depositing the NiCrO_x ; this is especially true with respect to the top surface of the Ag layer when an upper NiCrO_x protective barrier is applied directly thereto. The exposure of the Ag to this oxygen inclusive plasma is believed to sometimes lead to Ag adhesion problems.

In view of the above, it will be apparent to those skilled in the art that there exists a need for an improved barrier layer(s) structure for protecting an IR reflecting layer (e.g., Ag).

BRIEF SUMMARY OF THE INVENTION

An object of this invention is to provide an improved barrier layer(s) structure for protecting an IR reflecting layer such as Ag in a coated article, and a corresponding method of making the same.

Another object of this invention is to provide a barrier layer(s) structure which is capable of protecting an IR reflecting layer, and which is both fairly transmissive to visible light and enables a durable final coated article.

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Another object of this invention is to fulfill one or more of the above listed objects and/or needs.

In certain example embodiments of this invention, one or more of the above-listed objects and/or needs is/are fulfilled by providing a coated article comprising: a glass substrate; a coating supported by the glass substrate, wherein the coating comprises a first dielectric layer, a first NiCrO_x inclusive layer, an Ag inclusive layer, a second NiCrO_x inclusive layer, and a second dielectric layer, wherein the Ag inclusive layer is located between the first and second NiCrO_x inclusive layers; and wherein the coating further includes a metal or metal nitride protective contact layer located between and contacting the Ag layer and one of the NiCrO_x inclusive layers.

In other example embodiments of this invention, one or more of the above-listed objects and/or needs is/are fulfilled by providing a coated article including a coating supported by a substrate, the coating comprising: a NiCrO_x inclusive layer; an Ag inclusive layer; and a metal or metal nitride layer located between and contacting each of the NiCrO_x inclusive layer and the Ag inclusive layer.

In other example embodiments of this invention, one or more of the above-listed objects and/or needs is/are fulfilled by providing a coated article including a coating supported by a substrate, the coating comprising: an oxide layer including an oxide of a metal or metal alloy; a metallic infrared (IR) reflecting layer; a metal or metal nitride protective contact layer located between and contacting each of the metallic IR reflecting layer and the oxide layer; and wherein the metal or metal nitride contact layer comprises the same metal or metal alloy as is in the oxide layer.

In still further embodiments of this invention, one or more of the above-listed objects and/or needs is/are fulfilled by providing a method of making a coated article, the method comprising: providing a glass substrate; depositing a first dielectric layer so as to be supported by the substrate; depositing an Ag layer on the substrate over the first dielectric layer; depositing a metal or metal nitride contact layer on the substrate directly over and in contact with the Ag layer; depositing a layer comprising NiCrO_x on the substrate directly over and in contact with the metal or metal nitride contact layer; and

depositing another dielectric layer on the substrate over the layer comprising NiCrO_x .

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross sectional view of a coated article according to an embodiment of this invention.

FIG. 2 is a cross sectional view of a coated article according to another embodiment of this invention.

FIG. 3 is a cross sectional view of a coated article according to yet another embodiment of this invention.

DETAILED DESCRIPTION OF EXAMPLE EMBODIMENTS OF THE INVENTION

Referring now more particularly to the accompanying drawings in which like reference numerals indicate like parts throughout the several views.

Coated articles according to different embodiments of this invention may be used in the context of architectural windows (e.g., IG units), automotive windows, or any other suitable application. Coated articles herein may or may not be heat treated (e.g., thermally tempered, heat bent, or the like) in different embodiments of this invention.

FIG. 1 is a side cross sectional view of a coated article according to an embodiment of this invention. The coated article includes substrate 1 (e.g., clear, green, bronze, or blue-green glass substrate from about 1.0 to 10.0 mm thick,

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more preferably from about 1.8 mm to 4 mm thick), first dielectric layer 3, lower barrier layer 5, lower barrier contact layer 7 (which contacts IR reflecting layer 9), first conductive metallic infrared (IR) reflecting layer 9, upper barrier contact layer 11 (which contacts IR reflecting layer 9), upper barrier layer 13, and upper dielectric layer 15. The "contact" layers 7 and 11 each contact IR reflecting layer 9. Example non-limiting materials for layers 3-15 are illustrated in FIG. 1. The aforesaid layers 3-15 make up a solar control coating (e.g., a low-E or low emissivity type coating) which may be provided on glass or plastic substrates 1. The layer stack 3-15 illustrated in FIG. 1 may, in certain alternative embodiments of this invention, be repeated on substrate 1 one or more times (e.g., another layer stack 3-15 may be provided on top of the stack shown in FIG. 1 on the same substrate—this applies to any and all embodiments herein).

In certain embodiments of this invention, first dielectric layer 3 may be of or include titanium dioxide (TiO_2 , where x is from 1.7 to 2.7, most preferably 2.0 to 2.6), silicon nitride (Si_3N_4 , where x/y may be about 0.75 (i.e., Si_3N_4), or alternatively x/y may be from about 0.76 to 1.5 in Si-rich embodiments), silicon dioxide (SiO_2 , where x is from 1.7 to 2.3, most preferably about 2.0), niobium oxide (e.g., Nb_2O_5), Si_3ZrN , tin oxide, zinc oxide, silicon oxynitride, or any other suitable dielectric material. First dielectric layer 3 may function as an antireflection and/or color modifying layer in certain embodiments of this invention.

Infrared (IR) reflecting layer 9 is preferably metallic and conductive, and may be made of or include silver (Ag), gold (Au), or any other suitable IR reflecting material. However, metallic Ag is the material of choice for IR reflecting layer 9 in certain example embodiments of this invention. The IR reflecting layer(s) helps enable the coating to have low-E characteristics.

Barrier layers 5 and 13 are preferably at least partially oxidized, and in certain embodiments of this invention are of or include nickel (Ni) oxide, or a nickel alloy oxide such as nickel chrome oxide (NiCrO_x), or any other suitable material (s). In the FIG. 1 embodiment, layers 5 and 13 comprise NiCrO_x which may be either fully oxidized/oxidized or only partially oxidized. In particular, NiCrO_x layers 5 and 13 may be fully oxidized in certain embodiments of this invention (i.e., fully stoichiometric), or may be at least about 75% oxidized in other embodiments of this invention. While NiCrO_x is a preferred material for barrier layers 5 and 13, those skilled in the art will recognized that other materials may instead be used (e.g., oxides of Ni, oxides of Ni alloys, oxides of Cr, oxides of Cr alloys, NiCrO_xN_y , NiCrN_x , NbO_x , or any other suitable material) for one or more of these layers. It is noted that barrier layers 5 and 13 may or may not be continuous in different embodiments of this invention.

Still referring to barrier layers 5 and 13, these layers may or may not be oxidation graded in different embodiments of this invention. In some embodiments, barrier layers 5 and 13 are approximately uniformly oxidized throughout their respective thicknesses (i.e., no grading). However, in other embodiments, barrier layers 5 and 13 may be oxidation graded so as to be less oxidized at the contact interface with the immediately adjacent contact layer(s) 7, 11 than at a portion of the barrier layer(s) further or more/most distant from the immediately adjacent contact layer. This may improve adhesion of the metal or metal nitride contact layers 7, 11 to the barrier layers 5, 13, respectively. Such grading may also enable the coating, in certain example non-limiting embodiments, to achieve the combination of heat treatability and high visible transmission. For a more detailed discussion of how layers 5 and/or 13 may be oxidation graded, see pending U.S. Ser. No. 09/794,224, the disclosure of which is hereby incorporated herein by reference.

Contact layers 7 and 11 (which contact IR reflecting layer 9) are preferably more metallic and/or less oxidized than

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their respective adjacent barrier layers 5 and 13. For example, in certain embodiments of this invention, contact layers 7 and 11 may be of or include Ni, Cr, NiCr , CrN_x , or NiCrN_x (it is noted that the term NiCrN_x as used herein includes situations where the Ni in the layer is metallic and the nitriding is mostly with respect to the Cr). In such embodiments, layers 7 and 11 are either not oxidized, or only slightly oxidized to an extent significantly less than barrier layers 5 and 13. Thus, in certain preferred example embodiments of this invention, contact layers 7 and/or 11 are substantially free of oxygen (i.e., less than about 10% oxidized), or are even oxidized from only 0-5% in certain embodiments.

Surprisingly, it has been found that by providing thin metal or metal-nitride protective contact layers 7 and 11 (e.g., NiCr , Ni, Cr, CrN_x , Nb, or NiCrN_x) on the substrate between the IR reflecting layer 9 (e.g., Ag) and the respective barrier layers 5 and 13 (e.g., NiCrO_x), durability can be improved compared to a situation where NiCrO_x barrier layers 5 and 13 where entirely in direct contact with Ag layer 9. The use of thin metal or metal nitride contact layers 7 and/or 11 in contact with barrier layers 5 and/or 13 enables the resulting coated article to have both a high visible transmission (e.g., at least 70% in certain example embodiments), and be durable both before and/or after heat treatment. It is noted that metal or metal nitride contact layers 7 and 11 are provided to be rather thin (to reduce adverse affects of visible light absorption) in certain embodiments, so that the contact layers 7 and 11 may or may not be continuous in different embodiments of this invention.

When NiCr is used in layers 5, 7, 11 and/or 13 in certain embodiments of this invention (i.e., when a NiCr target is used in sputtering any of these layers regardless of whether they are oxidized, nitrided, or neither), the Ni and Cr may be provided in different amounts, such as in the form of nichrome by weight about 80-90% Ni and 10-20% Cr. An exemplary sputtering target for depositing these layers includes not only SS-316 which consists essentially of 10% Ni and 90% other ingredients, mainly Fe and Cr, but Inconel and Haynes 214 alloy as well, which by weight consists essentially of (as a nominal composition) the following materials which may also show up in these layers: Ni: 75.45%; Fe: 4%; Cr: 16%; C: 0.04%; Al: 4.5%; and Y:0.01%. In other embodiments, the NiCr target may be 50/50 Ni/Cr, or any other suitable ratio.

Still referring to FIG. 1, while various materials and/or thicknesses may be used consistent with one or more of the objects discussed herein, exemplary preferred thicknesses and materials for the respective layers on the glass substrate 1 in the FIG. 1 embodiment are as follows:

TABLE 1

(Example Materials/Thicknesses; FIG. 1 Embodiment)

Layer	Preferred Range (Å)	More	
		Preferred (Å)	Example (Å)
Si_3N_4 (layer 3)	0-600 Å	300-600 Å	410-520 Å
NiCrO_x (layer 5)	5-100 Å	10-50 Å	15-30 Å
NiCr (layer 7)	1-25 Å	1-10 Å	3-4 Å
Ag (layer 9)	50-250 Å	80-160 Å	100-140 Å
NiCr (layer 11)	1-25 Å	1-10 Å	3-4 Å
NiCrO_x (layer 13)	5-100 Å	10-50 Å	15-25 Å
Si_3N_4 (layer 15)	0-800 Å	300-600 Å	410-540 Å

Other layer(s) below or above the illustrated coating may also be provided. Thus, while the FIG. 1 layer system or coating is "on" or "supported by" substrate 1 (directly or indirectly), other layer(s) may be provided therebetween.

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Thus, for example, the coating of FIG. 1 may be considered "on" and "supported by" the substrate 1 even if other layer(s) are provided between layer 3 and substrate 1. Moreover, certain layers of the coating may be removed in certain embodiments, while others may be added in other embodiments of this invention without departing from the overall spirit of certain embodiments of this invention.

FIG. 2 is a cross sectional view of a coated article according to another embodiment of this invention. The FIG. 2 embodiment is the same as the FIG. 1 embodiment, except that lower contact layer 7 from the FIG. 1 embodiment is not present in the FIG. 2 embodiment. In particular, a metal or metal nitride contact layer 11 is provided only on the upper side of Ag layer 9 because this is where the Ag layer is most susceptible to problems arising from exposure to oxygen plasma as discussed above. In still further, but less preferred, embodiments of this invention, a metal or metal nitride contact layer may be provided on the bottom of Ag layer 9 but not on top of layer 9 (i.e., the inverse of FIG. 2). In the FIG. 2 embodiment, those skilled in the art will recognize that layer 5 need not be NiCrO_x , but instead may be any other suitable material including but not limited to an oxide of titanium (e.g., TiO_2), ZnAlO_x , or the like.

FIG. 3 is a cross sectional view of yet another embodiment of this invention where metal or metal nitride contact layer(s) 7 and/or 11 can be used. It will be appreciated by those skilled in the art that these layers may be used in a variety of different coating stacks, and dielectric materials of the coating(s) and the number of IR reflecting layer(s) of the coating, are not always of particular relevance with respect to the contact layers described herein. While a metal or metal nitride contact layer (contact layer 11 over the bottom Ag layer 9, and contact layer 11' over the top Ag layer 9'), in other embodiments of this invention metal or metal nitride contact layer(s) may be provided below one or both of these Ag layer(s) as well (e.g., see contact layer 7 in FIG. 1). In the FIG. 3 embodiment, example materials and thicknesses (which are of course non-limiting) are provided below in Table 2.

TABLE 2

(Example Materials/Thicknesses: FIG. 3 Embodiment)

Layer	Preferred Range (Å)	Mon Preferred (Å)	Example (Å)
TiO_2 (layer 2)	0-400 Å	50-250 Å	100-180 Å
Si_3N_4 (layer 3)	0-500 Å	50-400 Å	170-360 Å
NiCrO_x (layer 5)	5-100 Å	10-50 Å	15-30 Å
Ag (layer 9)	50-250 Å	80-120 Å	105 Å
NiCr (layer 11)	1-25 Å	1-10 Å	3-4 Å
NiCrO_x (layer 13)	5-100 Å	10-50 Å	15-30 Å
SnO_2 (layer 16)	0-800 Å	500-850 Å	650 Å
Si_3N_4 (layer 18)	0-800 Å	50-250 Å	170 Å
NiCrO_x (layer 5')	5-100 Å	10-50 Å	15-30 Å
Ag (layer 9')	50-250 Å	80-120 Å	105 Å
NiCr (layer 11')	1-25 Å	1-10 Å	3-4 Å
NiCrO_x (layer 13')	5-100 Å	10-50 Å	15-30 Å
SnO_2 (layer 20)	0-800 Å	100-300 Å	150 Å
Si_3N_4 (layer 22)	0-800 Å	100-300 Å	250 Å

An example of the FIG. 1 embodiment of the instant invention was made and tested, as set forth below. During the sputter coating process in which layers 3-15 were deposited: the line speed for lower silicon nitride layer 3 (using a Si sputtering target) was 55 inches/minute using 8 passes; the line speed for upper silicon nitride layer 15 (using a Si sputtering target) was 50 inches/minute using 8 passes; the line speed for the NiCr contact layers 7 and 11 was 100 inches/minute using 1 pass; and the line speed for the NiCrO_x barrier layers 5 and 13 was 37.5 inches/minute using 2 passes.

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COATER SET-UP FOR EXAMPLE OF FIG. 1 EMBODIMENT

Target Mat'l	Power (kW)	Volts (V)	Ar (sccm)	O ₂ (sccm)	N ₂ (sccm)	Thickness (Å)
Si (layer 3)	1 kW	485 V	40	0	40	470 Å
NiCr (layer 5)	1 kW	415 V	40	10	0	22 Å
NiCr (layer 7)	0.38 kW	370 V	30	0	0	3 Å
Ag (layer 9)	2.95 kW	465 V	30	0	0	$R_s = 16$ ohm/sq.
NiCr (layer 11)	0.38 kW	370 V	30	0	0	3 Å
NiCr (layer 13)	1 kW	415 V	40	10	0	22 Å
Si (layer 15)	1 kW	485 V	40	0	40	510 Å

As will be appreciated by those skilled in the art, the aforesaid coater set-up resulted in a layer stack on glass substrate 1 of (from the substrate outwardly): $\text{Si}_3\text{N}_4/\text{NiCrO}_x/\text{NiCr}/\text{Ag}/\text{NiCr}/\text{NiCrO}_x/\text{Si}_3\text{N}_4$. Of course, in alternative embodiments of this invention contact layer(s) 7 and/or 11 could be nitrided (fully or only partially) by adding nitrogen gas to the sputter coating process of those layers 7 and/or 11. Optical characteristics of this particular example were measure as follows (Ill. C, 2 degree observer technique was used for transmission characteristics):

OPTICAL CHARACTERISTICS OF EXAMPLE

Transmission (T _v) %:	81.25%
a* _v :	-2.24
b* _v :	0.81
Reflectance as viewed from glass (G) side: R _G Y (%)	7.54
L* _G :	33.01
a* _G :	0.54
b* _G :	-7.13
Reflectance as viewed from film/coating (F) side: R _F Y (%)	5.07
a* _F :	3.21
b* _F :	-5.30
R _s (sheet resistance in ohms/sq.):	16.0

This example was characterized by better durability than a comparative example where the metal contact layers were omitted.

Coated articles according to certain embodiments of this invention have a visible transmission of at least 65%, more preferably of at least 70%, and most preferably of at least 75%, and even sometimes at least 80%. Moreover, coated articles according to certain example embodiments of this invention have a sheet resistance (R_s) of no greater than 20 ohms/sq., more preferably no greater than 16 ohms/sq., and sometimes no greater than 12 ohms/sq.

While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not to be limited to the disclosed embodiment, but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

What is claimed is:

1. A heat treated coated article comprising:
a glass substrate;

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a coating supported by the glass substrate, wherein the coating comprises a first dielectric layer, an Ag inclusive layer, a layer comprising an oxide of NiCr, and a second dielectric layer, wherein the Ag inclusive layer is located between the first dielectric layer and the layer which comprise an oxide of NiCr; and

wherein the coating further includes a metal or metal nitride contact layer located directly between and contacting each of the Ag inclusive layer and the layer comprising an oxide of NiCr, wherein said metal or metal nitride contact layer is more metallic than said adjacent layer comprising an oxide of NiCr.

2. The coated article of claim 1, wherein the contact layer is on an upper side of the Ag inclusive layer, and is metallic and consists essentially of nickel.

3. The coated article of claim 1, wherein the layer comprising an oxide of NiCr is located directly between and contacting each of a layer comprising silicon nitride and said contact layer.

4. The coated article of claim 1, wherein the contact layer comprises a nitride of NiCr and is less oxidized than said layer comprising an oxide or NiCr that the contact layer is in contact with.

5. The coated article of claim 1, wherein the layer comprising an oxide of NiCr is more metallic at a location closer to the silver inclusive layer than at another location further from the silver inclusive layer.

6. The coated article of claim 1, wherein the metal or metal nitride contact layer comprises at least one of Ni and a nitride of NiCr.

7. The coated article of claim 1, wherein the coated article has a visible transmission of at least 70%.

8. The coated article of claim 7, wherein the coated article has a visible transmission of at least 75%.

9. The coated article of claim 1, where the coating has a sheet resistance (R_s) of no greater than 20 ohms/sq.

10. The coated article of claim 1, wherein the first dielectric layer comprises silicon nitride.

11. The coated article of claim 10, wherein the second dielectric layer comprises silicon nitride.

12. The coated article of claim 1, wherein the first dielectric layer comprises an oxide of titanium.

13. The coated article of claim 1, wherein the contact layer is provided on the upper surface of the Ag inclusive layer.

14. A heat treated coated article including a coating supported by a substrate, the coating comprising:

a layer comprising an oxide of NiCr;

an Ag inclusive layer; and

a metal or metal nitride layer located between and contacting each of the layer comprising an oxide of NiCr and the Ag inclusive layer, wherein the metal or metal nitride layer is more metallic than is the layer comprising an oxide of NiCr.

15. The coated article of claim 14, wherein the layer comprising an oxide of NiCr is oxidation graded so as to be more metallic at a location closer to the metal or metal nitride layer than at a location further from the metal or metal nitride layer.

16. The coated article of claim 14, wherein the metal or metal nitride layer is of at least one of Ni, a nitride of Cr, and a nitride of NiCr.

17. The coated article of claim 14, wherein the coating has a sheet resistance (R_s) of no greater than 20 ohms/sq.

18. A heat treated coated article including a coating supported by a substrate, the coating comprising:

an oxide layer including an oxide of a metal or metal alloy;

an infrared (IR) reflecting layer;

a metal or metal nitride contact layer located between and contacting each of the IR reflecting layer and the oxide layer;

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wherein the oxide layer is more metallic at a location closer to the metal or metal nitride contact layer than at another location further from the metal or metal nitride contact layer; and

wherein the metal or metal nitride contact layer comprises at least one metal which is also in the oxide layer.

19. The coated article of claim 18, wherein the oxide layer comprises an oxide of NiCr, and wherein the metal or metal nitride contact layer comprises Ni so that said at least one metal that the contact layer and the oxide layer have in common comprises Ni.

20. The coated article of claim 19, wherein the IR reflecting layer comprises Ag.

21. The coated article of claim 18, wherein the metal or metal nitride contact layer is metallic and is of Ni, and is located on an upper side of the IR reflecting layer, and wherein the IR reflecting layer comprises Ag.

22. The coated article of claim 18, wherein the coated article is characterized by a sheet resistance (R_s) of no greater than 20 ohms/sq., and a visible transmission of at least 70%.

23. The coated article of claim 1, wherein the metal or metal nitride contact layer is of a lesser thickness than the layer comprising an oxide of NiCr.

24. The coated article of claim 1, wherein the metal or metal nitride contact layer is from about 1-10 Å thick, and the layer comprising an oxide of NiCr is from about 10-50 Å thick.

25. The coated article of claim 14, wherein the metal or metal nitride layer is from about 1-10 Å thick, and the layer comprising an oxide of NiCr is from about 10-50 Å thick.

26. The coated article of claim 18, wherein the metal or metal nitride contact layer is from about 1-10 Å thick, and the oxide layer which contacts the metal or metal nitride contact layer is from about 10-50 Å thick.

27. The coated article of claim 1, wherein the contact layer is substantially free of oxygen.

28. The coated article of claim 14, wherein the metal or metal nitride layer is oxidized from 0-5%.

29. The coated article of claim 14, wherein the contact layer has at least one metal in common with the layer comprising an oxide of NiCr which is in a contact with the contact layer.

30. The coated article of claim 14, wherein the metal or metal nitride layer has at least one metal in common with the layer comprising an oxide of NiCr which is in contact with the metal or metal nitride layer.

31. A heat treated coated article comprising:

a glass substrate;

a coating supported by the glass substrate, wherein the coating comprises a first dielectric layer, an Ag inclusive layer, a layer comprising an oxide of NiCr, and a second dielectric layer, wherein the Ag inclusive layer is located between the first dielectric layer and the layer comprising an oxide of NiCr;

wherein the coating further includes a contact layer comprising a metal located between and contacting the Ag inclusive layer and the layer comprising an oxide of NiCr; and

wherein the layer comprising an oxide of NiCr is oxidation graded so as to be more metallic at a location closer to the contact layer than at another location further from the contact layer.

32. The coated article of claim 31, wherein the contact layer is metallic and is of Ni.

33. The coated article of claim 31, wherein the contact layer is more metallic and less oxidized than is the layer comprising an oxide of NiCr.

* * * * *



(12) **United States Patent**
Lingle et al.

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(45) Date of Patent: **Feb. 3, 2004**

(54) **HEAT TREATABLE LOW-E COATED
ARTICLES AND METHODS OF MAKING
SAME**

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(75) Inventors: Philip J. Lingle, Temperance, MI (US);
Anton Dietrich, Azmoos (CH); Ronald
E. Laird, Dexter, MI (US); Jean-Marc
Lemmer, Luxembourg (LU)

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(73) Assignees: Guardian Industries Corp., Auburn
Hills, MI (US); Centre
Luxembourgeois de Recherches pour
le Verre et la Ceramique S.A.
(C.R.V.C.), Grand Duché de (LU)

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2000.

(51) Int. Cl.⁷ B32B 17/06

(52) U.S. Cl. 428/432; 428/428; 428/448;
428/469; 428/472; 428/689; 428/697; 428/699;
428/701; 428/702

(58) Field of Search 428/428, 432,
428/448, 469, 472, 689, 697, 699, 701,
702

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Primary Examiner—Deborah Jones

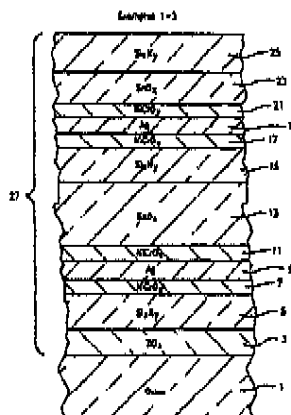
Assistant Examiner—A. Piziali

(74) Attorney, Agent, or Firm—Nixon & Vanderhyc P.C.

(57) **ABSTRACT**

A heat treatable coated article (e.g., vehicle windshield, IG
unit, etc.) is provided with a dual-silver low-E coating.
Before and/or after heat treatment (HT), the coating and/or
coated article has a visible transmittance of at least 70%,
more preferably at least 75%. Moreover, the coating and/or
coated article is designed so as to have approximately the
same color when viewed over a wide range of viewing
angles. In certain embodiments, at least one contact layer
(e.g., of or including NiCrO₂) that contacts an infrared (IR)
reflecting layer (e.g., Ag) is oxidation graded so that it
progressively becomes less oxidized through its thickness as
it nears the IR reflecting layer. In still other embodiments, a
Si-rich silicon nitride layer(s) may be utilized to reduce
haze.

24 Claims, 6 Drawing Sheets



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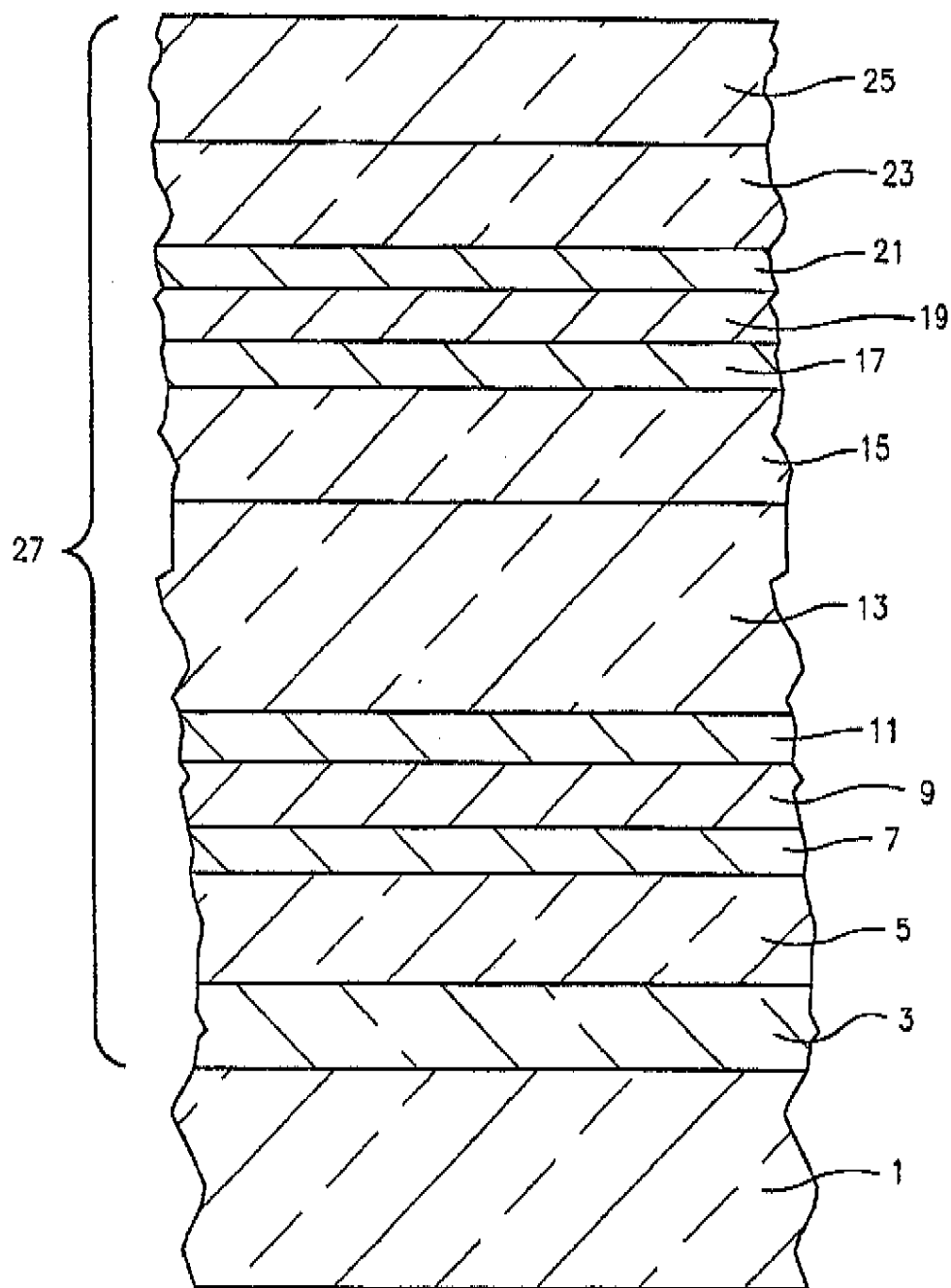


FIG. 1

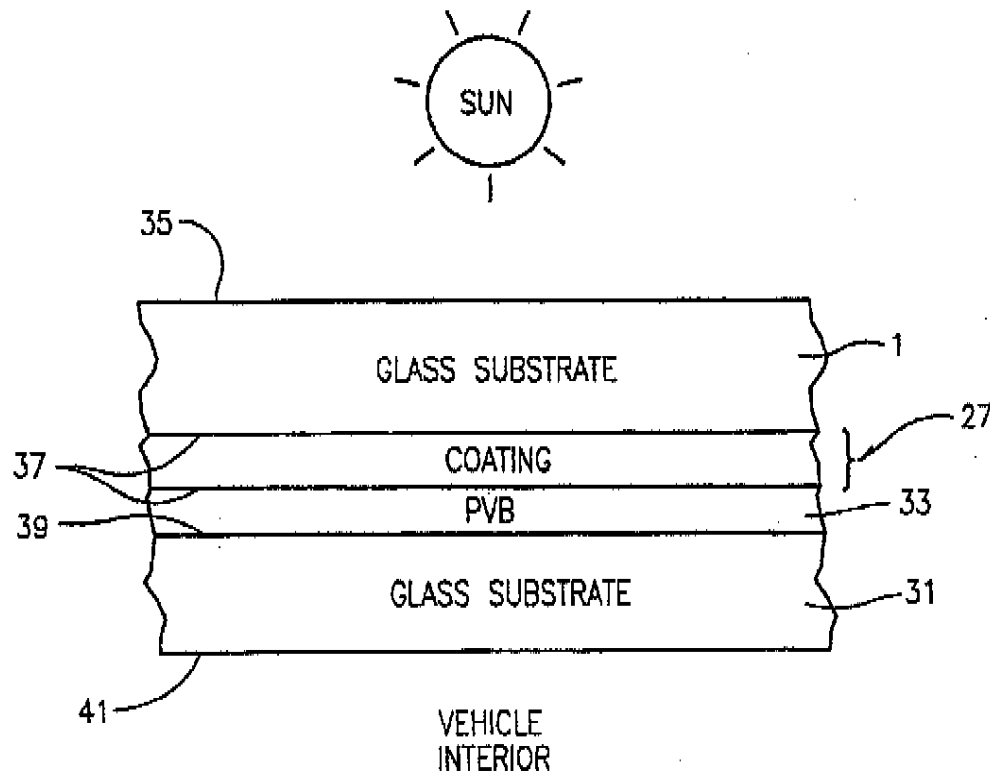


FIG. 2

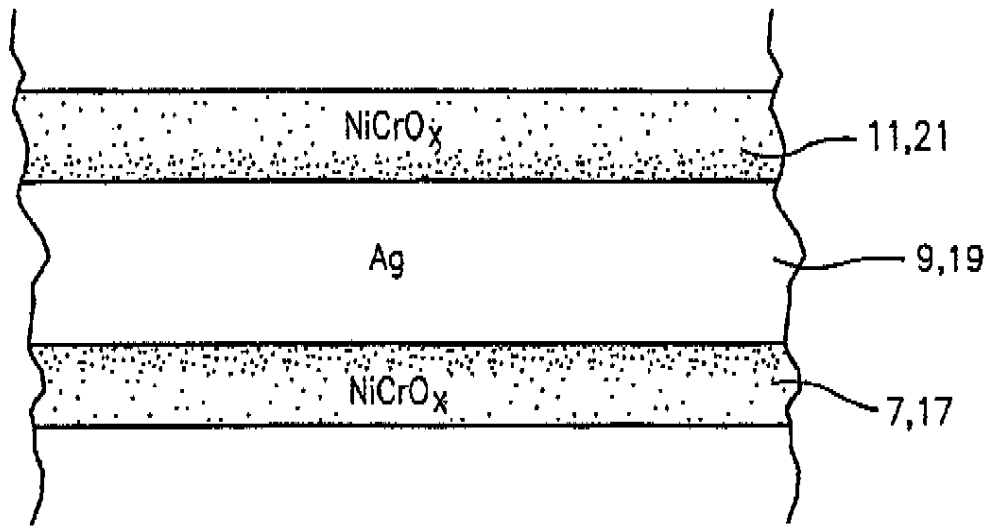


FIG. 3(a)

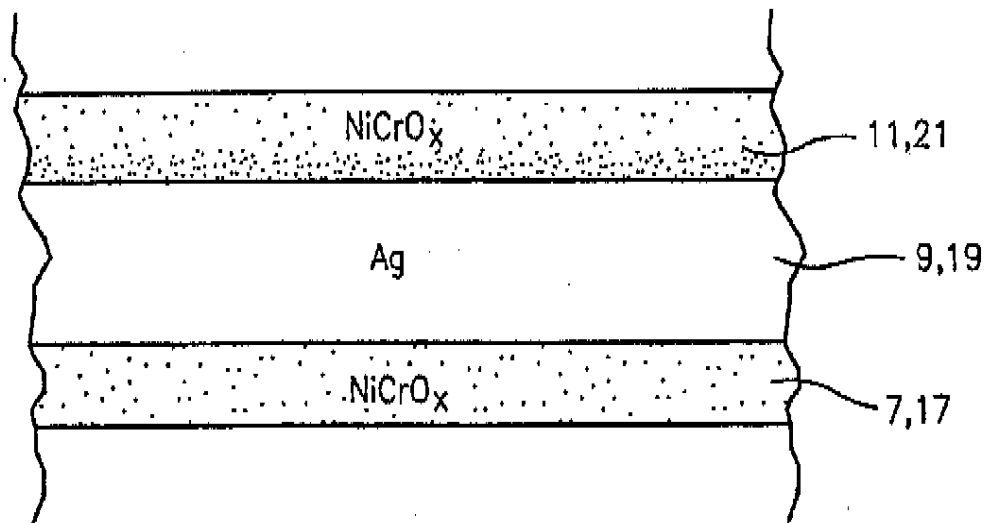


FIG. 3(b)

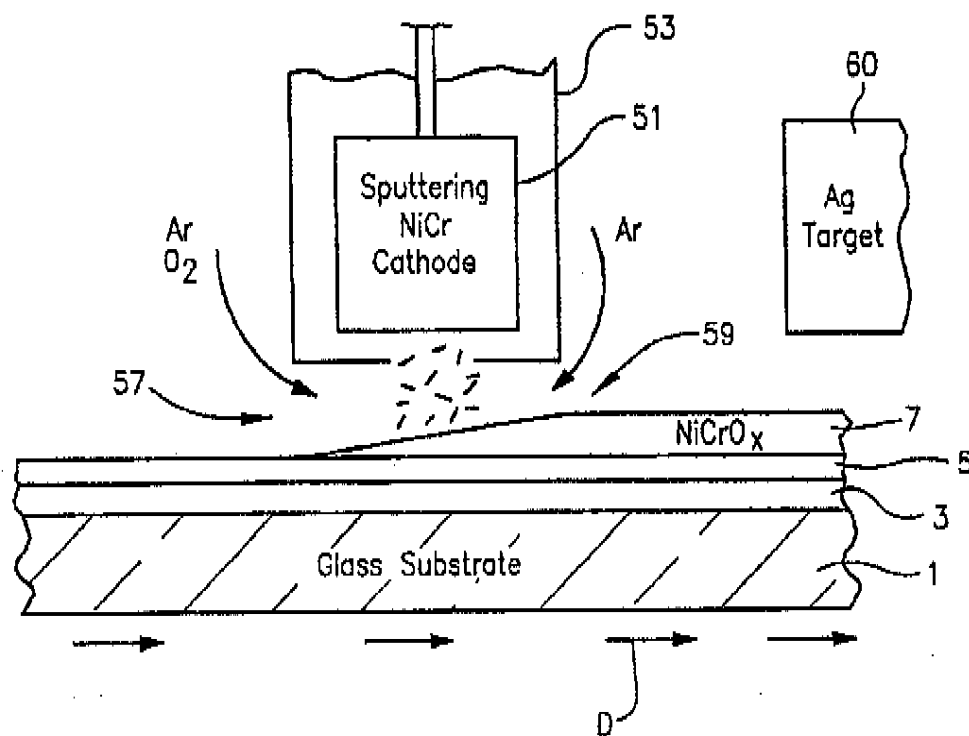


FIG. 4

Examples 1-3

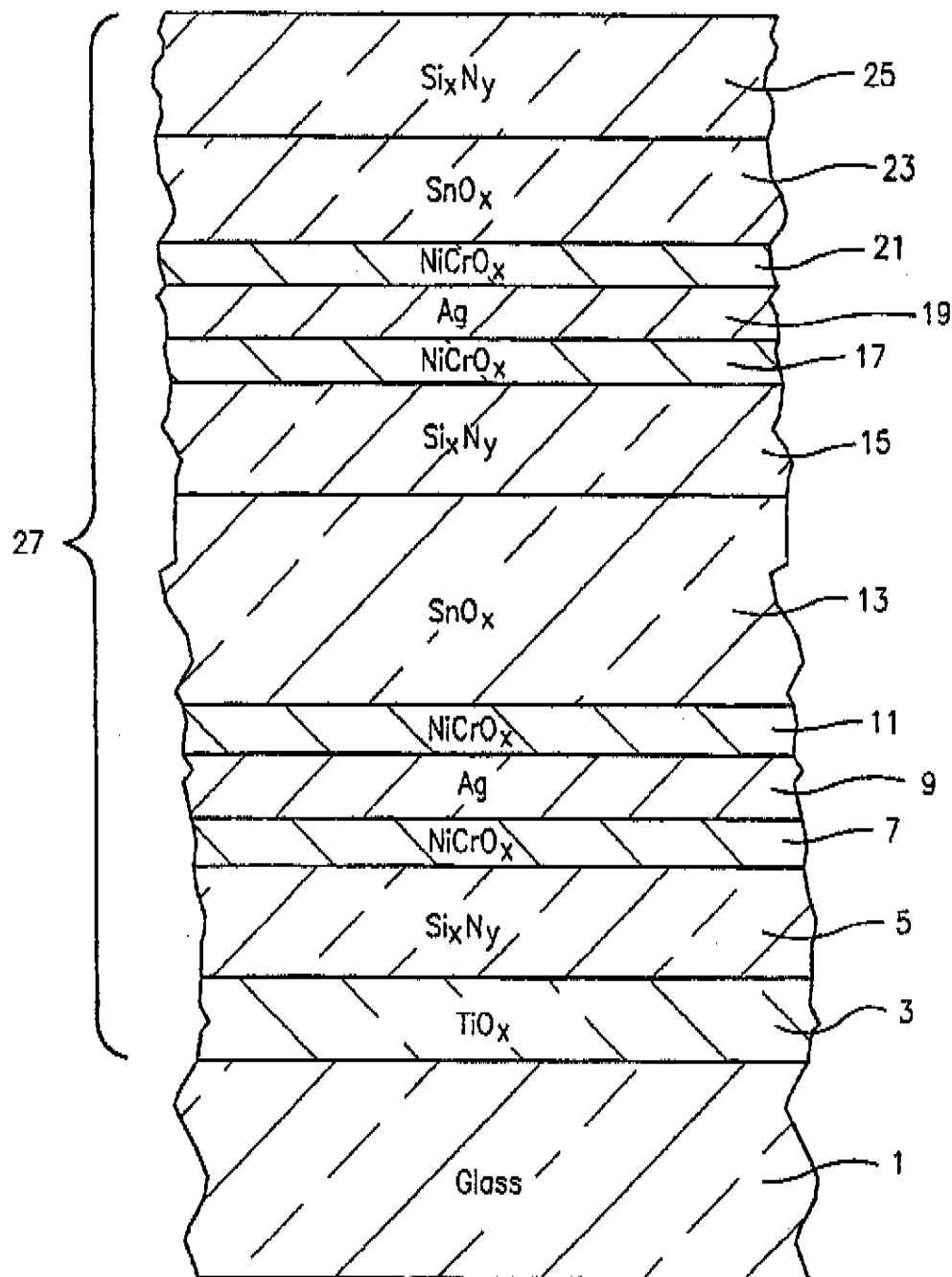


FIG. 5

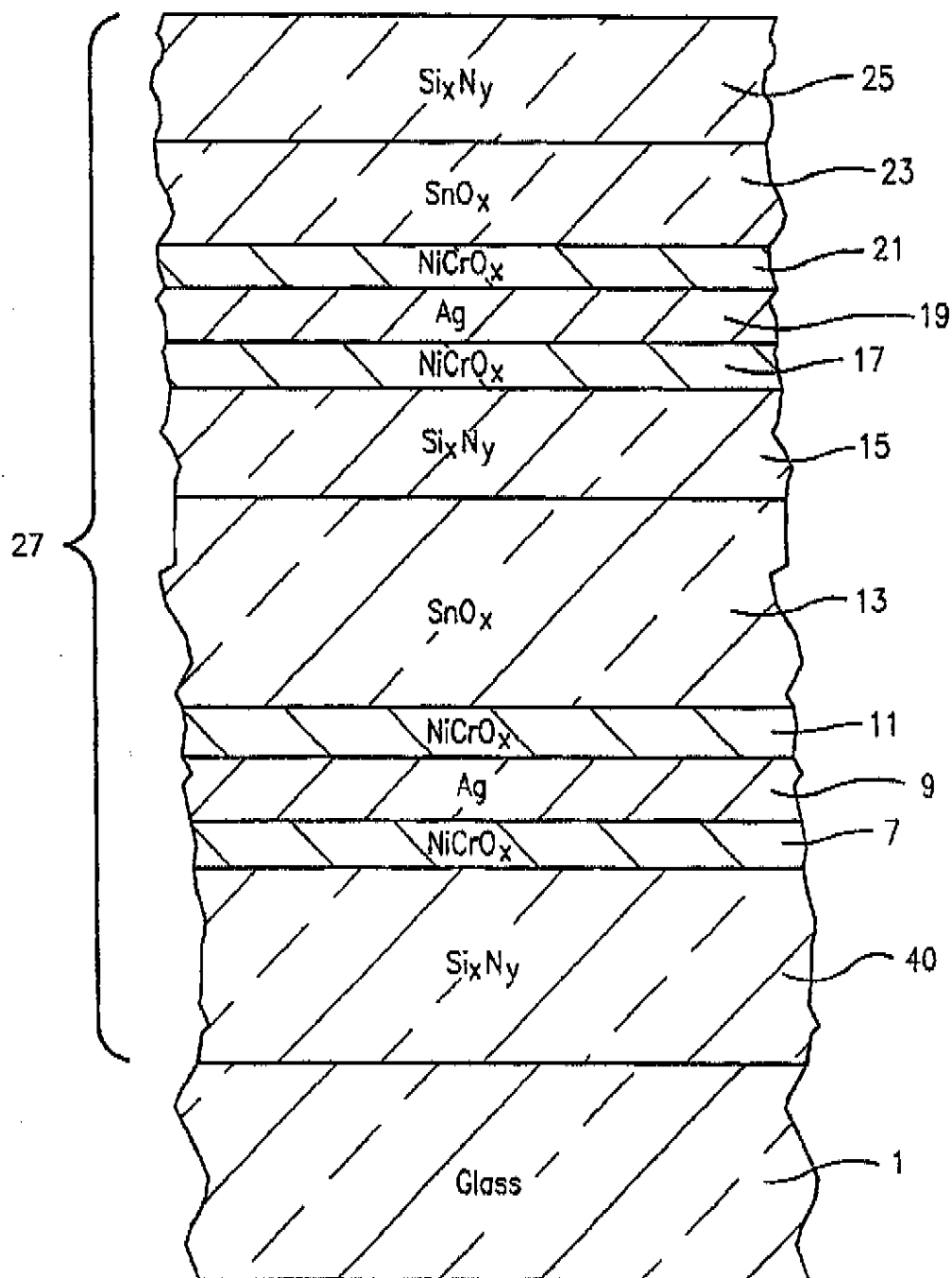


FIG. 6