37

Receipt Number
552299

IN THE UNITED STATES DISTRICT COURT
FOR THE EASTERN DISTRICT OF MICHIGAN Exhibits A-B

GUARDIAN INDUSTRIES CORP. and CENTRE LUXEMBOURGEOIS DE RECHERCHES POUR LE VERRE ET LA CERAMIQUE S.A. (C.R.V.C.) Plaintiffs, v. AFG INDUSTRIES, INC. Defendant.	Case: 2:06-cv-15728 Assigned To: Roberts, Victoria A Referral Judge: Pepe, Steven D Filed: 12-26-2006 At 01:40 PM CMP GUARDIAN IND CORP V. AFG INDUST RIES (TAM) **JURY TRIAL DEMANDED**

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 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. Patent No. 6,936,347 ("the '347 patent") and U.S. Patent No. 7,067,175 ("the '175 patent"), in violation of the patent laws of the United States, 35 U.S.C. §§ 271 and 281-285.

THE PARTIES

2. Guardian is a corporation organized and existing under the laws of the State of Delaware, 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 is a corporation organized and existing under the laws of the State of Delaware, 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. §§ 1331 and 1338(a).

7. Upon information and belief, this Court has personal jurisdiction over AFG. AFG has conducted and continues to conduct business in this judicial district purposefully, has placed its infringing low-emissivity glass products into the stream of commerce knowing and intending that this judicial district was and is a likely destination of those products, has caused injury to Plaintiffs in this judicial district and has committed acts of infringement in this judicial district.

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

BACKGROUND

9. The U.S. Patent and Trademark Office ("PTO") duly and legally issued the '347 patent, entitled "Coated Article with High Visible Transmission and Low Emissivity," to Ronald E. Laird et al. on August 30, 2005. The '347 patent is assigned to Plaintiffs. A true and correct copy of the '347 patent is attached as Exhibit A.

10. The PTO duly and legally issued the '175 patent, entitled "Method of Making Heat Treatable Coated Article with Diamond-Like Carbon (DLC) Inclusive Layer," to Vijayen S.

Veerasamy on June 27, 2006. The '175 patent is assigned to Guardian. A true and correct copy of the '175 patent is attached hereto as Exhibit B.

COUNT I

(Patent Infringement)

11. AFG has infringed the '347 patent by making, offering to sell, selling or using within the United States low-emissivity glass products covered by one or more claims of the '347 patent, including but not limited to products that, on information and belief, AFG markets as "Ti-AC 36."

12. On information and belief, AFG has had notice of Plaintiffs' exclusive rights secured by the '347 patent since at least August 30, 2005.

13. On information and belief, AFG has proceeded in a willful and deliberate manner to infringe the '347 patent.

14. On information and belief, AFG's actions constitute willful infringement of the '347 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 infringed the '175 patent by making, offering to sell, selling or using within the United States low-emissivity glass products covered by one or more claims of the '175 patent, including but not limited to products that, on information and belief, AFG markets as "Ti-AC 36."

18. On information and belief, AFG has had notice of Guardian's exclusive rights secured by the '175 patent since at least June 27, 2006.

19. On information and belief, AFG has proceeded in a willful and deliberate manner to infringe the '175 patent.

20. On information and belief, AFG's actions constitute willful infringement of the '175 patent, in violation of 35 U.S.C. §§ 271 and 281-284.

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

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

RELIEF REQUESTED

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

A. AFG has infringed the '347 patent;

B. AFG's infringement of the '347 patent 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 enjoined from infringing, inducing others to infringe or contributing to the infringement of the '347 patent;

D. AFG has infringed the '175 patent;

E. AFG's infringement of the '175 patent has been willful and deliberate;

F. AFG and its officers, agents, representatives, employees and all others in concert or participation with them, directly or indirectly, be enjoined from infringing, inducing others to infringe or contributing to the infringement of the '175 patent;

G. Plaintiffs be awarded damages adequate to compensate for AFG's infringement of the '347 and '175 patents together with pre-judgment interest pursuant to 35 U.S.C. § 284;

H. Plaintiffs be awarded treble damages and their costs and reasonable attorneys' fees and expenses in this action in accordance with 35 U.S.C. §§ 284 and 285; and

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

JURY DEMAND

Plaintiffs hereby request a trial by jury of all triable issues.

Dated: December 26, 2006

Respectfully submitted,

Reising, Ethington, Barnes, Kisselle P.C.

By:

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(248) 689-3500

A

US006936347B2

(12) United States Patent
Laird et al.

(10) **Patent No.: US 6,936,347 B2**
(45) **Date of Patent: Aug. 30, 2005**

(54) **COATED ARTICLE WITH HIGH VISIBLE TRANSMISSION AND LOW EMISSIVITY**

(75) Inventors: **Ronald E. Laird**, deceased, late of Dexter, MI (US); by **Carole Laird**, legal representative, Dexter, MI (US); **Uwe Kriltz**, Jena, MI (US)

(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.), Dudelange (LU)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 251 days.

(21) Appl. No.: **09/978,184**

(22) Filed: **Oct. 17, 2001**

(65) **Prior Publication Data**

US 2003/0150711 A1 Aug. 14, 2003

(51) **Int. Cl.**^{7} **B32B 17/06**
(52) **U.S. Cl.** **428/432**; 428/428; 428/448; 428/472; 428/673; 428/697; 428/698; 428/699; 428/701; 428/702
(58) **Field of Search** 428/428, 432, 428/448, 450, 472, 673, 697, 698, 699, 701, 702

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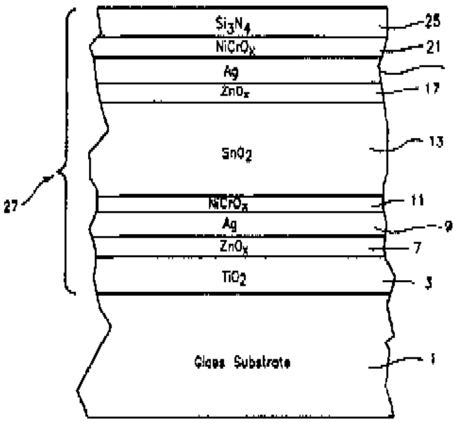
Primary Examiner—Terrel Morris
Assistant Examiner—Andrew T Piziali
(74) *Attorney, Agent, or Firm*—Nixon & Vanderhye P.C.

(57) **ABSTRACT**

A coated article that can be used in applications such as insulating glass (IG) units, so that resulting IG units can achieve high visible transmission of at least 70% (e.g., when using clear glass substrates from 1.0 to 3.5 mm thick), combined with at least one of: (a) SHGC no greater than about 0.45, more preferably no greater than about 0.40; (b) SC no greater than about 0.49, more preferably no greater than about 0.46; (c) chemical and/or mechanical durability; (d) neutral transmissive color such that transmissive a* is from −5.0 to 0 (more preferably from −3.5 to −1.5), and transmissive b* is from −2.0 to 4.0 (more preferably from 1.0 to 3.0); and (e) neutral reflective color from the exterior of the IG unit (i.e., Rg/R_{out}) such that reflective a* is from −3.0 to 2.0 (more preferably from −2.0 to 0.5), and reflective b* is from −5.0 to 1.0 (more preferably from −4.0 to −1.0). In certain example non-limiting embodiments, coated articles herein comprise: substrate/TiO_x/ZnO_x/Ag/$NiCrO_x$/SnO_x/ZnO_x/Ag/$NiCrO_x$/SnO_x/Si_xN_y.

46 Claims, 4 Drawing Sheets



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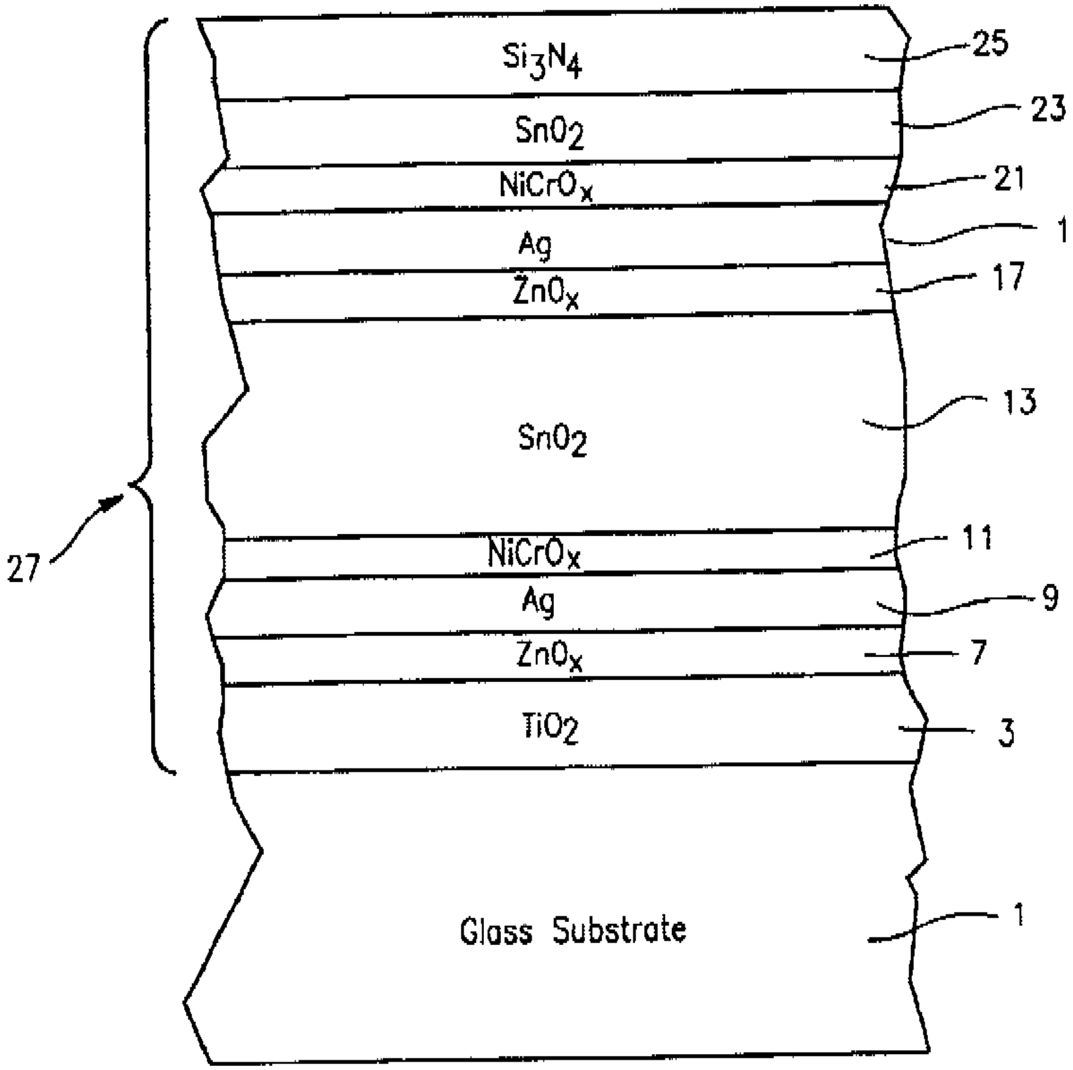
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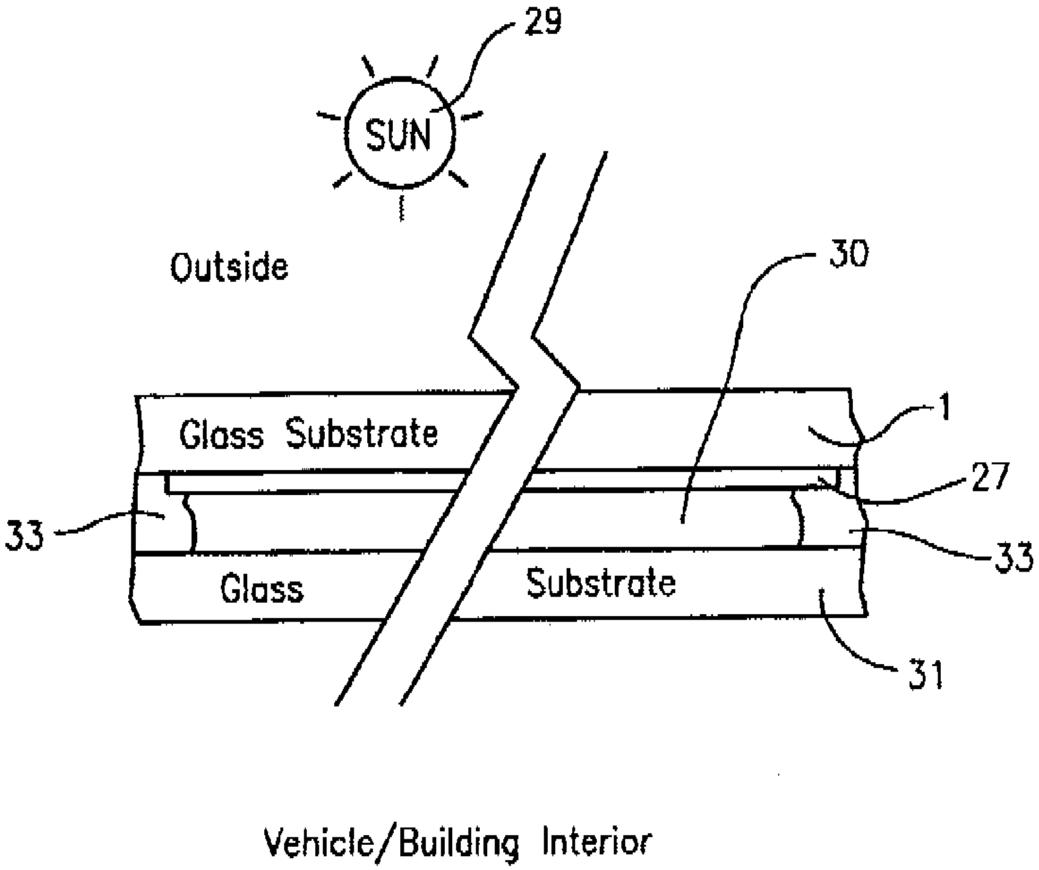
SnO_2
23
$NiCrO_x$
21
Ag
19
ZnO_x
17
SnO_2
13
27
$NiCrO_x$
11
Ag
9
ZnO_x
7
TiO_2
3
Glass Substrate
1

FIG. 1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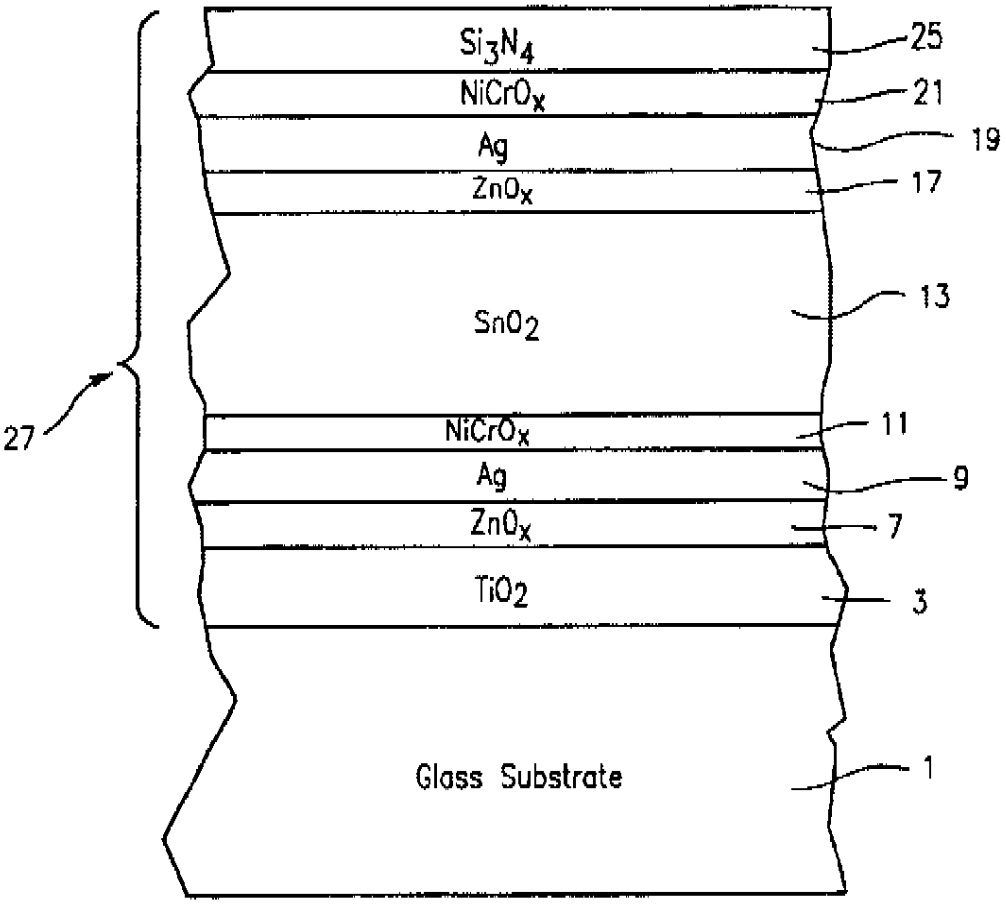
SUN
Outside
30
Glass Substrate
1
27
33
33
Glass
Substrate
31
Vehicle/Building Interior

FIG. 2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Ag
ZnOx
SnO2
NiCrOx
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ZnOx
TiO2
Glass Substrate
25
21
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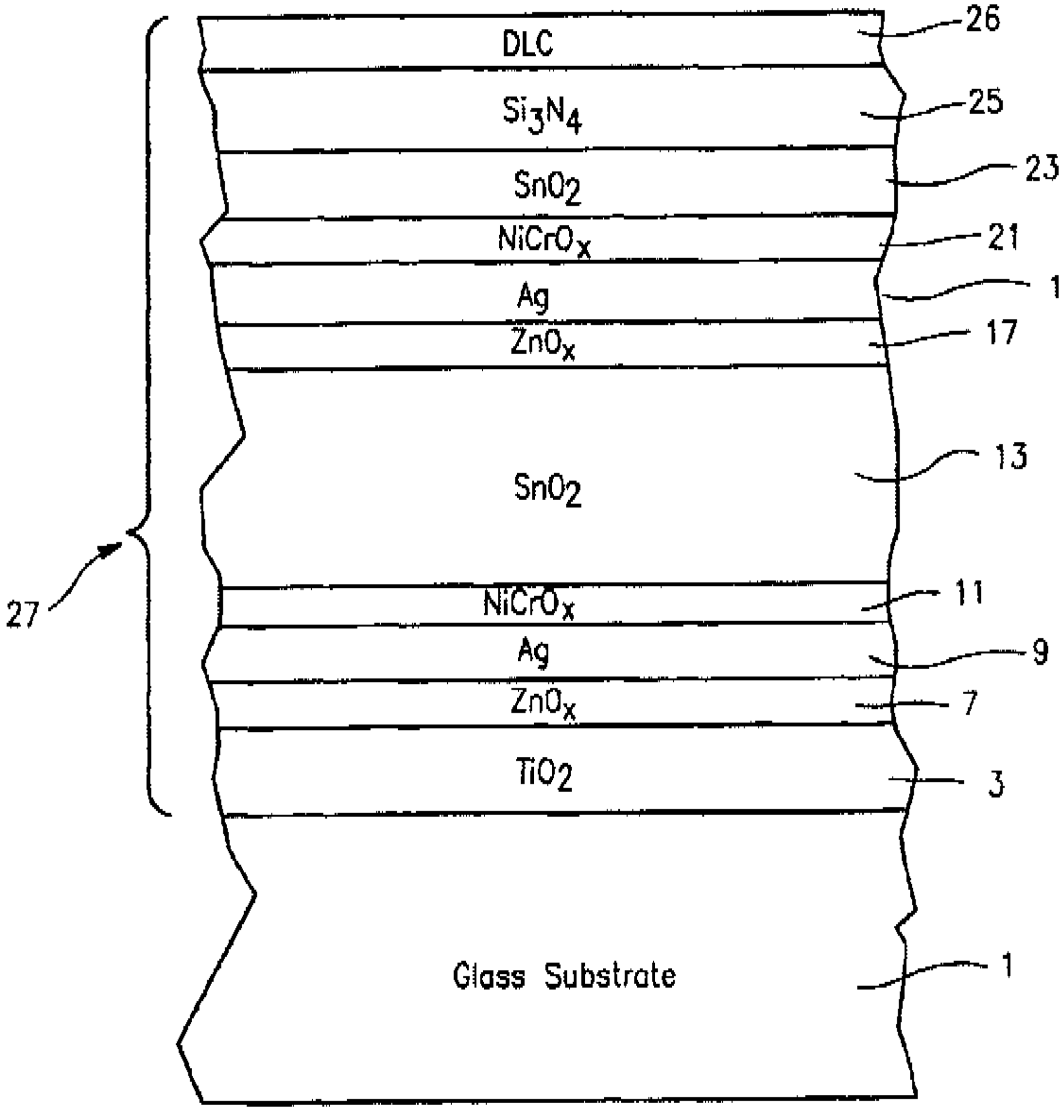
9
7
3
1
27

FIG. 3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25
SnO_2
23
$NiCrO_x$
21
Ag
19
ZnO_x
17
SnO_2
13
27
$NiCrO_x$
11
Ag
9
ZnO_x
7
TiO_2
3
Glass Substrate
1

FIG. 4

COATED ARTICLE WITH HIGH VISIBLE TRANSMISSION AND LOW EMISSIVITY

This invention relates to a coated article, and a method of making the same. In particular, this invention relates to a coated article having high visible transmission (e.g., absent tempering, heat bending, or other significant heat treatment), neutral color (transmissive and/or reflective), durability (mechanical and/or chemical), and/or low emissivity (low-E) characteristics, and a method of making the same.

BACKGROUND OF THE INVENTION

Coated articles are known in the art. For example, see U.S. Pat. No. 5,800,933 to Hartig (the '933 patent). The '933 patent discloses, inter alia, a layer stack of: glass substate/$TiO_2/Si_3N_4/NiCr/Ag/NiCr/Si_3N_4$. In columns 22–25 of the '933 patent, it can be seen from non-heat-treatable Example A that the resulting insulating glass (IG) unit used 2.3 mm glass sheets and had a visible transmission of 69.5%, a shading coefficient (SC) of 0.48, and thus a solar heat gain coefficient (SHGC) of about 0.418 (i.e., SC=SHGC/0.87). Even using these thin clear glass sheets (2.3 mm thick), the IG unit was still not able to achieve a visible transmission of at least 70%; this is unfortunate in certain non-limiting situations. Moreover, it would sometimes be desirable to have a SC and/or SHGC that was lower than those listed above, for solar management reasons that will be appreciated by those skilled in the art.

It will be appreciated by those skilled in the art that there exists a need in the art for a coated article that can be used in monolithic applications and/or applications such as IG units, so that resulting IG units can achieve high visible transmission (e.g., visible transmission of at least 70%) combined with one or more of (a) SHGC no greater than about 0.45, more preferably no greater than about 0.40; (b) SC no greater than about 0.49, more preferably no greater than about 0.46; (c) chemical and/or mechanical durability; (d) neutral transmissive color such that transmissive a* is from −5.0 to 0 (more preferably from −3.5 to −1.5), and transmissive b* is from −2.0 to 4.0 (more preferably from 1.0 to 3.0); and (e) neutral reflective color from the exterior of the IG unit (i.e., Rg/R_{out}) such that reflective a* is from −3.0 to 2.0 (more preferably from −2.0 to 0.5), and reflective b* is from −5.0 to 1.0 (more preferably from −4.0 to −1.0).

BRIEF SUMMARY OF THE INVENTION

An object of this invention is to provide a coated article that can be used in applications such as insulating glass (IG) units, so that resulting IG units can achieve high visible transmission of at least 70% (e.g., when using clear glass substrates from 1.0 to 3.5 mm thick), combined with at least one of: (a) SHGC no greater than about 0.45, more preferably no greater than about 0.40; (b) SC no greater than about 0.49, more preferably no greater than about 0.46; (c) chemical and/or mechanical durability; (d) neutral transmissive color such that transmissive a* is from −5.0 to 0 (more preferably from −3.5 to −1.5), and transmissive b* is from −2.0 to 4.0 (more preferably from 1 to 3.0); and (e) neutral reflective color from the exterior of the IG unit (i.e., Rg/R_{out}) such that reflective a* is from −3.0 to 2.0 (more preferably from −2.0 to 0.5), and reflective b* is from −5.0 to 1.0 (more preferably from −4.0 to −1.0).

Another object of this invention is to provide an article having a layer stack comprising:

substrate/$TiO_x/ZnO_x/Ag/NiCrO_x/SnO_x/ZnO_x/Ag/NiCrO_x/SnO_x/Si_xN_y$. In certain example non-limiting embodiments of this invention, such a layer stack may enable one or more of the above-listed objects and/or needs to be met.

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

In certain example non-limiting embodiments of this invention, one or more of the above-listed objects and/or needs is/are satisfied by providing a coated article comprising:

a substrate;

a first dielectric layer supported by the substrate;

a lower contact layer comprising zinc oxide;

an infrared (IR) reflecting layer comprising silver;

an upper contact layer comprising at least one of an oxide of nickel, an oxide of chromium, and nickel chrome oxide; and

wherein the IR reflecting layer comprising silver is located between and in contact with the lower and upper contact layers.

In other example embodiments of this invention, one or more of the above-listed needs and/or objects is/are satisfied by providing an insulating glass (IG) window unit comprising:

first and second substrates spaced from one another,

a coating supported by the first substrate, the coating including first and second IR reflecting layers, each of the IR reflecting layers being sandwiched between and contacting a respective pair of contact layers;

wherein the coating has a sheet resistance (R_s) no greater than 3.5 ohms/square; and

wherein the IG window unit has a visible transmission of at least 70%, a solar heat gain coefficient (SHGC) no greater than 0.45, and outside reflective color characterized by $a^*_{outside\ reflective}$ from −3.0 to 2.0 and $b^*_{outside\ reflective}$ from −5.0 to 1.0.

In other example embodiments of this invention, one or more of the above-listed objects and/or needs is/are satisfied by providing a coated article comprising:

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

a) a titanium oxide inclusive layer;

b) a zinc oxide inclusive contact layer;

c) a silver inclusive layer;

d) a nickel chrome oxide inclusive layer;

e) a tin oxide inclusive layer;

f) a zinc oxide inclusive layer;

g) a silver inclusive layer;

h) a nickel chrome oxide inclusive layer; and

i) a silicon nitride inclusive layer;

wherein the coated article has a visible transmission of at least about 70% and the coating or layer system has a sheet resistance (R_s) of no greater than 5.0 ohms/square.

BRIEF DESCRIPTION OF THE DRAWINGS

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

FIG. 2 is a cross sectional view of an insulating glass (IG) unit utilizing the coated article of FIG. 1 (or alternatively, the coated article of FIG. 3 or FIG. 4) according to an example embodiment of this invention.

FIG. 3 is a cross sectional view of a coated article according to another example embodiment of this invention, similar to the FIG. 1 embodiment except that the tin oxide layer is not present.

FIG. 4 is a cross sectional view of a coated article according to another example embodiment of this invention, illustrating that a diamond-like carbon (DLC) layer may be provided over top of any of the coatings or layer systems herein.

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.

Certain embodiments of this invention provide a low-E coating or layer system that may be used in applications such as insulating glass (IG) window units, vehicle windows, skylights, glass doors, and the like. Coated articles (e.g., monolithic or IG units) according to certain embodiments of this invention preferably have high visible transmission of at least 70% (e.g., when using clear glass substrates from 1.0 to 3.5 mm thick). In the example context of IG units, this high visible transmission is coupled with at least one of: (a) SHGC no greater than about 0.45, more preferably no greater than about 0.40; (b) SC no greater than about 0.49, more preferably no greater than about 0.46; (c) chemical and/or mechanical durability; (d) neutral transmissive color such that transmissive a* is from −5.0 to 0 (more preferably from −3.5 to −1.5), and transmissive b* is from −2.0 to 4.0 (more preferably from 1.0 to 3.0); and (e) neutral reflective color from the exterior of the IG unit (i.e., Rg/R_{out}) such that reflective a* (i.e., a^*_g) is from −3.0 to 2.0 (more preferably from −2.0 to 0.5), and reflective b* (i.e., b^*_g) is from −5.0 to 1.0 (more preferably from −4.0 to −1.0).

FIG. **1** is a side cross sectional view of a coated article according to an example non-limiting 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 1.0 mm to 3.5 mm thick), and coating (or layer system) **27** provided on the substrate **1** either directly or indirectly. The coating (or layer system) **27** includes: first dielectric anti-reflection layer **3**, 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**), second dielectric layer **13** (which may be deposited in one or multiple steps in different embodiments of this invention), 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**), third dielectric layer **23**, and finally fourth protective dielectric layer **25**. The "contact" layers **7**, **11**, **17** and **21** each contact at least one IR reflecting layer (e.g., Ag layer). The aforesaid layers **3**–**25** make up low-E (i.e., low emissivity) coating **27** which is provided on glass or plastic substrate **1**.

In certain preferred embodiments of this invention, first dielectric layer **3** may be of or include titanium oxide (e.g., TiO_x where x is from 1.7 to 2.3, most preferably x is about 2.0). However, in other embodiments, layer **3** may be of or include silicon nitride (Si_xN_y 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), aluminum oxide, tin oxide, zinc oxide, BiO_x, SiZrN, or any other suitable dielectric material. Preferably, first dielectric layer **3** has an index of refraction "n" of at least 1.7, and preferably from 2.0 to 2.7, and most preferably from 2.2 to 2.6. First dielectric layer **3** functions as an antireflection layer in certain embodiments of this invention.

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 non-limiting embodiments of this invention. These IR reflecting layers help enable coating **27** to have low-E and/or good solar control characteristics.

The upper contact layers **11** and **21** (i.e., "upper" means the contact layers on top of the respective IR reflective layers **9**, **19**) are of or include nickel (Ni) oxide, chromium/chrome (Cr) oxide, or a nickel alloy oxide such as nickel chrome oxide ($NiCrO_x$), in preferred embodiments of this invention. The use of, for example, $NiCrO_x$ for/in these layers enables durability to be improved, compared to the use of certain other materials (e.g., compared to zinc oxide). $NiCrO_x$ layers **11** and/or **21** may be fully oxidized in certain embodiments of this invention (i.e., fully stoichiometric), or may be at least about 50% oxidized in other embodiments of this invention. While $NiCrO_x$ is a preferred material for upper contact layers **11** and **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 other suitable material) for one or more of these layers in alternative embodiments of this invention. It is noted that upper contact layers **11** and/or **21** may or may not be continuous in different embodiments of this invention, depending upon their respective thickness(es).

When upper contact layers **11** 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. In other embodiments, sputtering targets used in sputtering layer(s) **11** and/or **21** may be 50/50 Ni/Cr, 60/40 Ni/Cr, 70/30 Ni/Cr, or any other suitable ratio. 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 potentially Haynes 214 alloy as well (e.g., see U.S. Pat. No. 5,688,585). Upper contact layer(s) **11** and/or **21** (e.g., of or including $NiCrO_x$) may or may not be oxidation graded in different embodiments of this invention. Oxidation grading means that the degree of oxidation in the layer(s) changes throughout the thickness of the layer(s) so that for example a contact layer may be graded so as to be less oxidized at the contact interface with the immediately adjacent IR reflecting layer than at a portion of the contact layer(s) further or more/most distant from the immediately adjacent IR reflecting layer.

The lower contact layers **7** and **17** ("lower" means the contact layers on the underneath side of the IR reflecting layers **9**, **19**) are of or include zinc oxide (e.g., ZnO_x, where x if from 0.6 to 1.2 in different embodiments, more preferably x is from 0.7 to 1.0) in preferred, but non-limiting, embodiments of this invention. For example, lower contact layer(s) **7** and/or **11** may consist essentially of zinc oxide in certain embodiments of this invention, while in other embodiments of this invention lower contact layer(s) **7** and/or **11** may include or consist essentially of $ZnAlO_x$, where x is set to a value such that the % Al (by weight) in the layer is from about 0–15%, more preferably from about 0–6%, and most preferably from about 1–4%. The use of these materials (e.g., ZnO_x, $ZnAlO_x$, or the like) for lower contact layer(s) **7** and/or **17** enables visible transmission of the resulting coated article to be increased (compared to if $NiCrO_x$ was used for these layers), enables sheet resistance R_s and/or emissivity to be reduced, and overall enables solar performance to be improved. In ZnO_x inclusive contact layer(s) **7** and/or **17**, x may be set so that the layer is fully stoichiometric (e.g., ZnO), or alternatively may be set to a value from 0.4 to 0.99, more preferably from 0.7 to 0.99, and most preferably from 0.8 to 0.99 so that the layer(s) is more conductive (e.g., this can be done by reducing the amount of oxygen gas and increasing the amount of Ar gas used during a sputter coating process). Additionally, in certain embodiments of this invention, layer(s) **7** and/or **17** have an index of refraction of from 1.8 to 2.2, more preferably from about 1.9 to 2.1, so that for example layers **3** and **7** clearly represent separate and distinct films.

Surprisingly, it has been found that by using ZnO_x, $ZnAlO_x$, or the like for the lower contact layer(s) **7** and/or **17**, while using $NiCrO_x$ for the upper contact layer(s) **11** and/or **21**, the resulting coated article can achieve a combination of high visible transmission and reduced sheet resistance R_s, as well as acceptable durability (mechanical and/or chemical). The highly durable $NiCrO_x$ is used for the upper contact layers **11** and/or **21** for durability purposes, while the solar controlling ZnO_x, $ZnAlO_x$, or the like is used for the lower contact layer(s) **7** and/or **17** to improve visible transmission and/or other solar characteristics. In other words, the $NiCrO_x$ provides good durability, especially when on top of the Ag layers, and the zinc oxide inclusive contact layer(s) enable high visible transmission to be combined with low sheet resistance R_s and/or good solar performance.

Second dielectric layer **13** acts as a coupling layer between the two halves of the coating **27**, and is of or includes tin oxide (e.g., SnO_2 or some non-stoichiometric form thereof) 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.

Third and fourth dielectric layers **23** and **25** enable the environmental resistance of the coating **27** to be improved, and are also provided for color purposes. In certain example embodiments, dielectric layer **23** may be of or include tin oxide (e.g., SnO_2), although other materials may instead be used. Dielectric overcoat layer **25** may be of or include silicon nitride (e.g., Si_3N_4) in certain embodiments of this invention, although other materials may instead be used such as titanium dioxide, silicon oxynitride, tin oxide, zinc oxide, niobium oxide, 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. For example, in the FIG. **3** embodiment of this invention, a coating **27** is provided which is similar to the coating of FIG. **1** except that the upper SnO_2 inclusive layer **23** is not present in the FIG. **3** embodiment.

FIG. **2** illustrates the coating or layer system **27** being utilized on surface #**2** of an IG window unit. Coatings **27** according to any embodiment herein may be used in IG units as shown in FIG. **2**. In order to differentiate the "inside" of the IG unit from its "outside", the sun **29** is schematically presented on the outside. The IG unit includes outside glass pane or sheet (i.e., substrate **1** from FIG. **1**) and inside glass pane or sheet **31**. These two glass substrates (e.g. float glass 1–10 mm thick) are sealed at their peripheral edges by a conventional sealant and/or spacer **33** and may be provided with a conventional desiccant strip (not shown). The panes may then be retained in a conventional window or door retaining frame. By sealing the peripheral edges of the glass sheets and replacing the air in insulating space (or chamber) **30** with a gas such as argon, a typical, high insulating value IG unit is formed. Optionally, insulating space **30** may be at a pressure less than atmospheric pressure in certain alternative embodiments (with or without a gas in space **30**), although this of course is not necessary in all embodiments. While the inner side of substrate **1** is provided with coating **27** in FIG. **2**, this invention is not so limiting (e.g., coating **27** may instead be provided on the interior surface of substrate **31** in other embodiments of this invention).

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 FIGS. **1**-**2** embodiment are as follows:

TABLE 1

(Example Materials/Thicknesses: FIG. 1 Embodiment)

Layer	Preferred Range (Å)	More Preferred (Å)	Example (Å)
TiO_2 (layer 3)	0–700 Å	100–400 Å	200 Å
ZnO_x (layer 7)	25–200 Å	40–150 Å	90 Å
Ag (layer 9)	50–250 Å	80–200 Å	130 Å
$NiCrO_x$ (layer 11)	5–100 Å	15–60 Å	30 Å
SnO_2 (layer 13)	0–1,000 Å	500–900 Å	680 Å
ZnO_x (layer 17)	25–200 Å	40–150 Å	90 Å
Ag (layer 19)	50–250 Å	80–220 Å	168 Å
$NiCrO_x$ (layer 21)	5–100 Å	15–60 Å	30 Å
SnO_2 (layer 23)	0–500 Å	70–200 Å	125 Å
Si_3N_4 (layer 25)	0–500 Å	120–320 Å	220 Å

In certain exemplary embodiments of this invention, coating/layer systems **27** according to all embodiments above have the following low-E (low emissivity) characteristics set forth in Table 2 when provided in the context of an insulating glass (IG) window unit (see FIG. **2**), absent any significant heat treatment such as tempering or heat bending (although heat treatment may be performed in other embodiments of this invention). It is noted that in Table 2 the term E_n means normal emissivity/emittance.

TABLE 2

Low-E Characteristics (no heat treatment)

Characteristic	General	More Preferred	Most Preferred
R_s (ohms/sq.):	<=5.0	<=3.5	<=2.8
E_n:	<=0.07	<=0.04	<=0.03

Moreover, coated articles including coatings **27** according to certain exemplary embodiments of this invention have the following solar characteristics (e.g., when the coating(s) is provided on a clear soda lime silica glass substrate **1** from 2.0 to 3.2 mm thick) in monolithic form. In Table 3 below, R_gY is visible reflection from the glass (g) side of the monolithic article, while R_fY is visible reflection from the side of the monolithic article on which film (f) (i.e., coating **27**) is located.

TABLE 3

Monolithic Solar Characteristics

Characteristic	General	More Preferred
T_{vis} (or TY)(Ill. C, 2 deg.):	>=70%	>=75%
a^*_t (Ill. C, 2°):	−5.0 to 0.0	−4.0 to −1.5
b^*_t (Ill. C, 2°):	−4.0 to 4.0	1.0 to 3.0
R_gY (Ill. C, 2 deg.):	1 to 10%	3 to 6%

TABLE 3-continued

Monolithic Solar Characteristics		
Characteristic	General	More Preferred
a^*_g (Ill. C, 2°):	−2.0 to 4.0	0.0 to 2.5
b^*_g (Ill. C, 2°):	−7.0 to 1.0	−5.0 to 0.0
R_fY (Ill. C, 2 deg.):	1 to 7%	1 to 5%
a^*_f (Ill. C, 2°):	−2.0 to 5.0	−0.5 to 3.0
b^*_f (Ill. C, 2°):	−9.0 to 1.0	−7.0 to −0.0
SHGC:	<=0.49	<=0.45
SC:	<=0.56	<=0.53
$T_{ultraviolet}$:	<=0.43	<=0.39
$T_{UV\ damage\ weighted}$:	<=0.50	<=0.48

Meanwhile, IG window units utilizing coatings **27** according to certain embodiments of this invention as shown in FIG. **2**, have the following solar characteristics (e.g., where the coated glass substrate **1** is a clear soda lime silica glass substrate from 2 to 3.2 mm thick, and the other soda lime silica glass substrate **31** is clear and from 2 to 3.2 mm thick, absent any significant heat treatment). In Table 4 below, R_gY is visible reflection from the outside or exterior of the window (i.e., from where the sun is located in FIG. **2**), and R_fY is visible reflection from the interior side (e.g., from within the building interior), and the a*, b* values under these respective reflection parameters also correspond to glass (g) side (i.e., from outside the window in FIG. **2**) and film (f) side (i.e., from interior the window in FIG. **2**).

TABLE 4

IG Unit Solar Characteristics		
Characteristic	General	More Preferred
T_{vis} (or TY)(Ill. C, 2 deg.):	>=69%	>=70%
a^*_t (Ill. C, 2°):	−5.0 to 0.0	−3.5 to −1.5
b^*_t (Ill. C, 2°):	−2.0 to 4.0	1.0 to 3.0
R_gY (Ill. C, 2 deg.):	7 to 13%	9 to 11%
a^*_g (Ill. C, 2°):	−3.0 to 2.0	−2.0 to 0.5
b^*_g (Ill. C, 2°):	−5.0 to 1.0	−4.0 to −1.0
R_fY (Ill. C, 2 deg.):	7 to 14%	10 to 12%
a^*_f (Ill. C, 2°):	−3.0 to 2.0	−1.5 to 0.5
b^*_f (Ill. C, 2°):	−5.0 to 1.0	−4.0 to −1.5
SHGC:	<=0.45	<=0.40
SC:	<=0.49	<=0.46
U-value:	0.20 to 0.30	0.22 to 0.25
$T_{ultraviolet}$:	<=0.36	<=0.33
$T_{UV\ damage\ weighted}$:	<=0.45	<=0.39

It is noted that certain parameters can be tuned by adjusting layer thicknesses. For example, ultraviolet (UV) transmission ($T_{ultraviolet}$) can be reduced much further by adjusting dielectric thickness(es).

FIG. **4** is a cross sectional view of a coated article according to yet another embodiment of this invention. The FIG. **4** embodiment is the same as the FIG. **1** embodiment, except that a layer(s) of diamond-like carbon (DLC) **26** is provided as an overcoat over top of (and optionally contacting) silicon nitride layer **25** (note: the FIG. **3** embodiment may be modified in a similar manner). DLC inclusive layer **26** may be hydrophobic, hydrophillic, or neither in different embodiments of this invention. For example and without limitation, any of the DLC inclusive layers described and/or illustrated in any of U.S. Pat. Nos. 6,261,693, 6,277,480, 6,280,834, and/or 6,284,377 (all of which are hereby incorporated herein by reference) may be used as DLC inclusive layer **26** in different embodiments of this invention. DLC inclusive layer(s) **26** may be deposited on the substrate **1** as an overcoat via an ion beam deposition technique, or any other suitable deposition process.

EXAMPLES 1–2

The following example coated articles (Examples 1 and 2) were made in accordance with the FIG. **3** embodiment above (i.e., layer **23** was not present in the coating **27**). In Example 1, the FIG. **3** coating or layer system **27** was sputtered onto a 3 mm thick clear soda lime silica glass substrate, using a known Leybold sputter coater (**27** cathode system) at a line speed of 2.5 meters per minute. The sputter coater was set up/run as set forth below in Table 5 for Examples 1–2. Power (P) was measured in kW, current (I) in amps, and pressure (Press.) in mbar. The gas flow for Ar gas was measured in sccm, and included Ar gas flow from tuning gas segments. Thus, for example, for cathode **1**, there was 350 sccm of main Ar gas flow, and all three tuning gas segments were each adjusted to output 50 sccm each of Ar gas for that cathode, which adds up to 500 sccm of Ar gas flow for cathode **1**. For cathodes **1** and **2**, oxygen gas flow was controlled and determined by setting all three set points (SP) for plasma emission monitor to 18 (this is what is meant by S.P. in Table 5 below). Note: the NiCr target(s) was 80/20 Ni/Cr. The coater set-up was the same for Examples 1 and 2, and monolithically the only difference between the examples being that in Example 1 the coating **27** was sputtered onto a 3 mm thick clear glass substrate, while in Example 2 the coating **27** was sputtered onto a 4 mm thick clear glass substrate.

TABLE 5

Example Coater Set-up (Examples 1–2)								
Cathode	Target	Volts (V)	P (kW)	Ar (sccm)	O_2 (sccm)	N_2 (sccm)	Press. (mbar)	I (amp)
#1	Ti	704	75	500	SP	75	2.73×10^{-3}	90
#6	Ti	657	75	500	SP	75	4.87×10^{-3}	89
#7	ZnAl	600	22	350	530	0	4.83×10^{-3}	45
#9	Ag	438	5.5	150	0	0	2.35×10^{-3}	11.8
#10	NiCr	488	9	250	80	0	1.43×10^{-3}	18.7
#12	Sn	440	16	300	530	75	5.21×10^{-3}	34
#13	Sn	476	21	300	965	75	5.28×10^{-3}	50
#14	Sn	423	21	125	470	75	1.07×10^{-2}	50
#15	Sn	434	22.5	125	470	75	1.07×10^{-2}	50
#16	Sn	425	22	125	470	75	4.72×10^{-3}	55
#18	ZnAl	373	22	350	570	0	4.71×10^{-3}	72
#20	Ag	392	7.3	250	0	0	2.00×10^{-3}	18.8

TABLE 5-continued

Example Coater Set-up (Examples 1–2)

Cathode	Target	Volts (V)	P (kW)	Ar (sccm)	O_2 (sccm)	N_2 (sccm)	Press. (mbar)	I (amp)
#21	NiCr	495	8	250	75	0	1.99×10^{-3}	16.5
#25	Si	486	55	350	0	675	6.04×10^{-3}	134
#26	Si	444	55	350	0	1200	6.04×10^{-3}	140

Following the sputtering of the aforesaid coating **27** on substrate **1** (3 mm thick in Example 1, and 4 mm thick in Example 2), the coated articles were measured monolithically (see Tables 6–7 below). Thereafter, the coated substrate including coating **27** and substrate **1** of each example was attached to another clear soda lime silica glass substrate **31** (the another substrate **31** was 2.3 mm thick in Example 1, and 3 mm thick in Example 2) in order to form an IG unit for each example as shown in FIG. **2**. The IG units were also measured for solar properties. The measured solar properties of the monolithic units and the IG units are set forth in Tables 6–7 below:

TABLE 6

Monolithic & IG Unit Solar Characteristics (Example 1)

Characteristic	Monolithic (Ex. 1)	IG Unit (Ex. 1)
T_{vis} (or TY)(Ill. C, 2 deg.):	77.8%	71%
a^*_t (Ill. C, 2°):	−2.9	−2.9
b^*_t (Ill. C, 2°):	2.0	2.0
R_gY (Ill. C, 2 deg.):	4.85%	9.9%
a^*_g (Ill. C, 2°):	0.85	−1.0
b^*_g (Ill. C, 2°):	−2.75	2.0
R_fY (Ill. C, 2 deg.):	4%	11.5%
a^*_f (Ill. C, 2°):	2.5	−0.4
b^*_f (Ill. C, 2°):	−6.0	−3.0
SHGC:	0.448	0.394
SC:	0.52	0.45
$T_{ultraviolet}$:	0.38	0.32
$T_{UV\ damage\ weighted}$:	0.47	0.41

TABLE 7

Monolithic & IG Unit Solar Characteristics (Example 2)

Characteristic	Monolithic (Ex. 2)	IG Unit (Ex. 2)
T_{vis} (or TY)(Ill. C, 2 deg.):	76.2%	69.5%
a^*_t (Ill. C, 2°):	−1.8	−2.3
b^*_t (Ill. C, 2°):	2.05	2.09
R_gY (Ill. C, 2 deg.):	5%	9.8%
a^*_g (Ill. C, 2°):	1.65	−0.1
b^*_g (Ill. C, 2°):	−4.8	−2.4
R_fY (Ill. C, 2 deg.):	3.8%	11.2%
a^*_f (Ill. C, 2°):	0.6	−0.4
b^*_f (Ill. C, 2°):	−2.95	−1.1
SHGC:	0.448	0.397
SC:	0.52	0.46
$T_{ultraviolet}$:	0.38	0.32
$T_{UV\ damage\ weighted}$:	0.47	0.41

EXAMPLE 3

Example 3 is a theoretical example, and its characteristics are set forth below, including both coater set-up data and solar characteristic data. While Examples 1–2 dealt with the FIGS. 2–3 embodiment, Example 3 relates to the FIGS. 1–2 embodiment. Note that cathode #**23** is to be used in the sputter coater to form tin oxide layer **23** as shown in FIG. **1**.

TABLE 8

Example Coater Set-up (Example 3)

Cathode	Target	Volts (V)	P (kW)	Ar (sccm)	O_2 (sccm)	N_2 (sccm)	Press. (mbar)	I (amp)
#1	Ti	704	75	500	SP	75	2.73×10^{-3}	90
#6	Ti	657	75	500	SP	75	4.87×10^{-3}	89
#7	ZnAl	600	22	350	530	0	4.83×10^{-3}	45
#9	Ag	438	5.5	150	0	0	2.35×10^{-3}	11.8
#10	NiCr	488	9	250	80	0	1.43×10^{-3}	18.7
#12	Sn	440	16	300	530	75	5.21×10^{-3}	34
#13	Sn	476	21	300	965	75	5.28×10^{-3}	50
#14	Sn	423	21	125	470	75	1.07×10^{-2}	50
#15	Sn	434	22.5	125	470	75	1.07×10^{-2}	50
#16	Sn	425	22	125	470	75	4.72×10^{-3}	55
#18	ZnAl	373	22	350	570	0	4.71×10^{-3}	72
#20	Ag	392	7.3	250	0	0	2.00×10^{-3}	18.8
#21	NiCr	495	8	250	75	0	1.99×10^{-3}	16.5
#23	Sn	387	24	125	500	90	2.78×10^{-3}	60
#25	Si	486	35	350	0	675	6.04×10^{-3}	72
#26	Si	444	35	350	0	1200	6.04×10^{-3}	79

Following the sputtering of the aforesaid coating **27** on 2.3 mm thick substrate **1**, the coated article is theoretically measured monolithically. Thereafter, the coated substrate including coating **27** and substrate **1** is to be attached to another clear soda lime silica 2.3 mm thick glass substrate **31** in order to form an IG unit for Example 3. Solar properties are as follows:

TABLE 9

Monolithic & IG Unit Solar Characteristics (Example 3)

Characteristic	Monolithic (Ex. 3)	IG Unit (Ex. 3)
T_{vis} (or TY)(Ill. C, 2 deg.):	77%	70%
a^*_t (Ill. C, 2°):	−3.25	−2.5
b^*_t (Ill. C, 2°):	2.0	2.0
R_gY (Ill. C, 2 deg.):	5%	10%
a^*_g (Ill. C, 2°):	1.0	−0.5
b^*_g (Ill. C, 2°):	−3.0	−2.0
R_fY (Ill. C, 2 deg.):	4%	11.5%
a^*_f (Ill. C, 2°):	1.5	−0.5
b^*_f (Ill. C, 2°):	−4.0	−2.5

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_xY or R_x (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 a*, b* coordinates and scale (i.e. the CIE a*b* diagram, Ill. CIE-C, 2 degree observer). Other similar coordinates may be equivalently used such as by the subscript "h" to signify the conventional use of the Hunter Lab Scale, or Ill. CIE-C, 10° observer, or the CIE 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" 9/15/93 as augmented by ASTM E-308-85, 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 "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), infrared radiation transmittance, and ultraviolet radiation transmittance. Total solar energy transmittance (TS) is then usually characterized as a weighted average of these other values. With respect to these transmittances, visible transmittance, as reported herein, is characterized by the standard CIE Illuminant C, 2 degree observer, technique at 380–720 nm; near-infrared is 720–2500 nm; ultraviolet is 300–800 nm; and total solar is 300–2500 nm. For purposes of emittance, however, a particular infrared range (i.e. 2,500–40,000 nm) is employed.

Visible transmittance can be measured using known, conventional techniques. For example, by using a spectrophotometer, such as a Perkin Elmer Lambda 900 or Hitachi U4001, a spectral curve of transmission is obtained. Visible transmission is then calculated using the aforesaid ASTM 308/2244-93 methodology. A lesser number of wavelength points may be employed than prescribed, if desired. Another technique for measuring visible transmittance is to employ a spectrometer such as a commercially available Spectrogard spectrophotometer manufactured by Pacific Scientific Corporation. This device measures and reports visible transmittance directly. As reported and measured herein, visible transmittance (i.e. the Y value in the CIE tristimulus system, ASTM E-308–85) uses the Ill. C, 2 degree observer.

"Emittance" (E) is a measure, or characteristic of both absorption and reflectance of light at given wavelengths. When transmittance is zero, which is approximately the case for float glass with wavelengths longer than 2500 nm, the emittance may be represented by the formula:

$$E=1-\text{Reflectance}_{film}$$

For architectural purposes, emittance 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 "emittance" as used herein, is thus used to refer to emittance values measured in this infrared range as specified by ASTM Standard E 1585–93 for measuring infrared energy to calculate emittance, 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, emittance is reported as hemispherical emittance/emissivity (E_h) and normal emittance/emissivity (E_n).

The actual accumulation of data for measurement of such emittance 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, emittance is calculated using the aforesaid ASTM E 1585–93 which has been incorporated herein by reference.

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 emittance 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"×5" sample of a coated glass substrate in about 500 cc of 5% HCl for one hour (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") if the sample's layer system shows no visible discoloration or visible peeling, and no pinholes greater than about 0.003" in diameter after this one hour boil.

"Mechanical durabilility" as used herein is defined by the following tests. The test uses a Pacific Scientific Abrasion Tester (or equivalent) wherein a 2"×4"×1" nylon brush is cyclically passed over the layer system in 500 cycles employing 150 gm of weight, applied to a 6"×17" 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.

The term "U-value" or "U-Factor" (synonymous with "thermal transmittance") is a term well understood in the art and is used herein according to this well known meaning. "U-value" herein is reported in terms of BTU/hr/ft^2/degrees F., and may be determined according to the guarded hot box method as reported in, and according to ASTM designation: C1199–91.

The term "shading coefficient" (SC) is a term well understood in the art and is used herein according to its well known meaning. It is determined according to ASHRAE Standard 142 "Standard Method for Determining and Expressing the Heat Transfer and Total Optical Properties of Fenestration Products" by ASHRAE Standards Project Committee, SPC 142, September 1995. SC may be obtained by dividing solar heat gain coefficient (SHGC) by about 0.87. Thus, the following formula may be used: SC=SHGC/0.87.

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 coated article comprising:

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

a) a titanium oxide inclusive layer;

b) a zinc oxide inclusive contact layer;

c) a silver inclusive layer contacting the zinc oxide inclusive layer b);

d) a nickel chrome oxide inclusive layer contacting the silver inclusive layer c);

e) a tin oxide inclusive layer;

f) a zinc oxide inclusive layer;

g) a silver inclusive layer;

h) a nickel chrome oxide inclusive layer; and

i) a silicon nitride inclusive layer;

wherein the coated article has a visible transmission of at least about 70% and the coating or layer system has a sheet resistance (R_s) of no greater than 5.0 ohms/square.

wherein the coated article is not tempered or heat bent.

2. The coated article of claim 1, wherein the coated article comprises an insulating glass (IG) window unit.

3. The coated article of claim 1, further comprising a tin oxide inclusive layer located between layers h) and i), and wherein the layers have the following thicknesses:

a) titanium oxide inclusive layer:	100–400 Å
b) zinc oxide inclusive contact layer:	40–150 Å
c) silver inclusive layer:	50–250 Å
d) nickel chrome oxide inclusive layer:	15–60 Å
e) tin oxide inclusive layer:	<=1,000 Å
f) zinc oxide inclusive layer:	40–150 Å
g) silver inclusive layer:	50–250 Å
h) nickel chrome oxide inclusive layer:	15–60 Å
i) silicon nitride inclusive layer:	<=500 Å.

4. The coated article of claim 1, wherein the coated article comprises an IG window unit and has the following characteristics:

a^*_T (transmissive):	−5.0 to 0.0
b^*_T (transmissive):	−2.0 to 4.0
R_gY (outside reflectance):	7 to 13%
a^*_g (outside reflective):	−3.0 to 2.0
b^*_g (outside reflective):	−5.0 to 1.0
SHGC:	<=0.45
SC:	<=0.49
$T_{ultraviolet}$:	<=0.36.

5. The coated article of claim 4, wherein the coated article comprises an IG window unit and has the following characteristics:

a^*_T (transmissive):	−3.5 to 1.5
b^*_T (transmissive):	1.0 to 3.0
R_gY (outside reflectance):	9 to 11%
a^*_g (outside reflective):	−2.0 to 0.5
b^*_g (outside reflective):	−4.0 to −1.0
SHGC:	<=0.40
SC:	<=0.46
$T_{ultraviolet}$:	<=0.33.

6. The coated article of claim 1, wherein at least one of the zinc oxide inclusive layers b) and f) comprises zinc-aluminum-oxide, and where the coated article further comprises a tin oxide inclusive layer located between layers h) and i).

7. A non-heat-treated coated article comprising:

a substrate;

a first dielectric layer supported by the substrate;

a lower contact layer comprising zinc oxide;

an infrared(IR) reflecting layer comprising silver contacting the lower contact layer comprising zinc oxide;

an upper contact layer comprising at least one of an oxide of nickel, an oxide of chromium, and nickel chrome oxide which contacts the IR reflecting layer comprising silver;

wherein the IR reflecting layer comprising silver is located between and in contact with the lower and upper contact layers;

wherein the coated article is not heat treated;

a second dielectric layer provided over top of and in contact with the upper contact layer;

another lower contact layer comprising zinc oxide;

another infrared (IR) reflecting layer comprising silver which contacts the another lower contact layer;

another upper contact layer comprising nickel chrome oxide, the another IR reflecting layer being sandwiched between and contacting the another lower contact layer and the another upper contact layer; and

a third dielectric layer provided over top of and in contact with the another upper contact layer.

8. The coated article of claim **7**, wherein the lower contact layer comprises zinc aluminum oxide.

9. The coated article of claim **7**, wherein the coated article has a visible transmission of at least 70% and a sheet resistance (R_s) of no greater than 5.0 ohms/square.

10. The coated article of claim **7**, wherein the coated article comprises an insulating glass (IG) window unit.

11. The coated article of claim **7**, wherein the first dielectric layer comprises titanium oxide.

12. The coated article of claim **7**, wherein the first dielectric layer comprises tin oxide.

13. The coated article of claim **7**, wherein the third dielectric layer comprises one of silicon nitride and tin oxide, and wherein the coated article further comprises a diamond-like carbon (DLC) inclusive layer provided as an overcoat.

14. The coated article of claim **7**, wherein the coated article comprises an IG window unit and has the following characteristics:

a^*_T (transmissive):	−5.0 to 0.0
b^*_T (transmissive):	−2.0 to 4.0
R_gY (outside reflectance):	7 to 13%
a^*_g (outside reflective):	−3.0 to 2.0
b^*_g (outside reflective):	−5.0 to 1.0
SHGC:	<=0.45
SC:	<=0.49
$T_{ultraviolet}$:	<=0.36.

15. The coated article of claim **14**, wherein the coated article comprises an IG window unit and has the following characteristics:

a^*_T (transmissive):	−3.5 to 1.5
b^*_T (transmissive):	1.0 to 3.0
R_gY (outside reflectance):	9 to 11%
a^*_g (outside reflective):	−2.0 to 0.5
b^*_g (outside reflective):	−4.0 to −1.0
SHGC:	<=0.40
SC:	<=0.46
$T_{ultraviolet}$:	<=0.33.

16. An insulating glass (IG) window unit comprising:

first and second substrates spaced from one another,

a coating supported by the first substrate, the coating including first and second IR reflecting layers, each of the IR reflecting layers being sandwiched between and contacting a respective pair of contact layers;

wherein the coating has a sheet resistance (R_s) no greater than 3.5 ohms/square;

wherein the IG window unit has a visible transmission of at least 70%, a solar heat gain coefficient (SHGC) no greater than 0.45, and outside reflective color characterized by $a^*_{outside\ reflective}$ from −3.0 to 2.0 and $b^*_{outside\ reflective}$ from −5.0 to 1.0;

wherein the pair of contact layers sandwiching the first IR reflecting layer therebetween includes a lower contact layer and an upper contact layer, and wherein the first IR reflecting layer includes Ag, wherein the lower contact layer comprises zinc aluminum oxide and is located between the first IR reflecting layer and the substrate, and the upper contact layer comprises an oxide of NiCr.

17. The IG window unit of claim **16**, wherein the IG window unit has a SHGC no greater than 0.40 and a shading coefficient (SC) no greater than 0.46.

18. A non-heat-treated coated article comprising:

a coating supported by a glass substrate, the coating comprising an infrared (IR) reflecting layer sandwiched between and contacting first and second contact layers; and

wherein the first contact layer includes zinc oxide and the second contact layer comprises nickel-chrome oxide.

19. The coated article of claim **18**, wherein the first contact layer comprises an oxide of ZnAl.

20. The coated article of claim **18**, wherein the coating is durable, and the coated article has a visible transmission of at least 70% and the coating has a sheet resistance (R_s) no greater than 3.5 ohms/square, and wherein the first contact layer is located between the IR reflecting layer and the glass substrate.

21. The coated article of claim **18**, wherein the coated article comprises an IG window unit and has the following characteristics:

a^*_T (transmissive):	−5.0 to 0.0
b^*_T (transmissive):	−2.0 to 4.0
R_gY (outside reflectance):	7 to 13%
a^*_g (outside reflective):	−3.0 to 2.0
b^*_g (outside reflective):	−5.0 to 1.0
SHGC:	<=0.45
SC:	<=0.49
$T_{ultraviolet}$:	<=0.36.

22. The coated article of claim **21**, wherein the coated article has the following characteristics:

a^*_T (transmissive):	−3.5 to 1.5
b^*_T (transmissive):	1.0 to 3.0
R_gY (outside reflectance):	9 to 11%
a^*_g (outside reflective):	−2.0 to 0.5
b^*_g (outside reflective):	−4.0 to −1.0
SHGC:	<=0.40
SC:	<=0.46
$T_{ultraviolet}$:	<=0.33.

23. A coated article comprising:

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

a) at least one dielectric layer;

b) a zinc oxide inclusive contact layer;

c) a silver inclusive layer contacting the zinc oxide inclusive layer b);

d) a contact layer including at least one of nickel oxide and chrome oxide that is located over and contacts the silver inclusive layer c);

e) a dielectric layer;

f) a zinc oxide inclusive contact layer;

g) a silver inclusive layer;

h) a contact layer; and

i) at least one dielectric layer;

wherein the coated article has a visible transmission of at least about 70% and the coating or layer system has a sheet resistance (R_s) no greater than 5.0 ohms/square;

wherein the coated article is not thermally tempered or heat bent; and

wherein the e) dielectric layer(s) comprises tin oxide, and wherein the contact layer d) comprises an oxide of NiCr.

24. The coated article of claim **23**, wherein the at least one dielectric layer a) comprises titanium oxide.

25. The coated article of claim **23**, wherein the dielectric layer i) comprises at least one of silicon nitride and tin oxide.

26. A coated article comprising:

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

a) a dielectric layer;
b) a zinc oxide inclusive contact layer;
c) a silver inclusive layer contacting the zinc oxide inclusive layer b);
d) a contact layer including at least one of nickel oxide and chrome oxide that is located over and contacts the silver inclusive layer c);
e) a dielectric layer;
f) a zinc oxide inclusive contact layer;
g) a silver inclusive layer;
h) a contact layer; and
i) a dielectric layer;

wherein the coated article has a visible transmission of at least about 70% and the coating or layer system has a sheet resistance (R_s) no greater than 5.0 ohms/square;

wherein the coated article is not thermally tempered or heat bent; and

wherein the contact layers d) and h) each comprise an oxide of NiCr.

27. The coated article of claim **23**, wherein at least one of the zinc oxide inclusive contact layers b) and f) comprises an oxide of ZnAl.

28. The coated article of claim **23**, wherein the coated article comprises an IG window unit.

29. A non-heat-treated coated article comprising:

a coating supported by a glass substrate, the coating comprising from the glass substrate outwardly:

a) a layer comprising an oxide of titanium;
b) a layer comprising zinc oxide;
c) a layer comprising silver located over and contacting the layer b) comprising zinc oxide;
d) a layer comprising an oxide of nickel chrome located over and contacting the layer c) comprising silver;
e) a dielectric layer;
f) a layer comprising zinc oxide;
g) a layer comprising silver;
h) a contact layer; and
i) a dielectric layer.

30. The coated article of claim **29**, wherein the coated article has a visible transmission of at least about 70% and the coating or layer system has a sheet resistance (R_s) of no greater than 5.0 ohms/square.

31. The coated article of claim **29**, wherein said contact layer h) comprises an oxide of NiCr.

32. The coated article of claim **29**, wherein at least one of the layers b) and g) comprising zinc aluminum oxide.

33. The coated article of claim **29**, wherein the dielectric layer e) comprises tin oxide, and wherein another dielectric layer is provided between layers h) and i).

34. The coated article of claim **29**, wherein the dielectric layer i) comprises at least one of tin oxide and silicon nitride.

35. The coated article of claim **29**, wherein the coated article is part of an IG window unit.

36. A non-heat-treated coated article comprising:

a coating supported by a glass substrate, the coating comprising from the glass substrate outwardly:

a) a dielectric layer;
b) a layer comprising zinc oxide;
c) a layer comprising silver located over and contacting the layer b) comprising zinc oxide;
d) a layer comprising an oxide of at least one of Ni and Cr located over and contacting the layer c) comprising silver;
e) a dielectric layer;
f) a layer comprising zinc oxide;
g) a layer comprising silver;
h) a layer comprising an oxide of NiCr; and
i) a dielectric layer.

37. The coated article of claim **36**, wherein said dielectric layer a) comprises an oxide of Ti.

38. A coated article comprising:

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

a) a dielectric layer;
b) a zinc oxide inclusive contact layer;
c) a silver inclusive layer contacting the zinc oxide inclusive layer b);
d) a layer comprising an oxide of NiCr contacting the silver inclusive layer c);
e) a layer comprising tin oxide;
f) a layer comprising zinc oxide;
g) a silver inclusive layer;
h) a layer comprising an oxide of NiCr; and
i) at least one dielectric layer.

39. The coated article of claim **38**, wherein the coated article has a visible transmission of at least about 70% and the coating or layer system has a sheet resistance (R_s) of no greater than 5.0 ohms/square.

40. The coated article of claim **38**, wherein the coated article is not tempered or heat bent.

41. The coated article of claim **38**, wherein the layer i) comprises at least a layer comprising tin oxide.

42. The coated article of claim **38**, wherein the zinc oxide inclusive layer b) further comprises aluminum.

43. A coated article comprising:

a coating supported by a glass substrate, the coating comprising an infrared (IR) reflecting layer comprising silver sandwiched between and contacting first and second contact layers; and

wherein the first contact layer is under the layer comprising silver and comprises zinc oxide, and the second contact layer is over the layer comprising silver and comprises nickel-chrome oxide.

44. The coated article of claim **43**, wherein the coated article has a visible transmission of at least about 70% and the coating or layer system has a sheet resistance (R_s) of no greater than 5.0 ohms/square.

45. The coated article of claim **43**, wherein the coated article is not tempered or heat bent.

46. The coated article of claim **43**, wherein the first contact layer comprises an oxide of ZnAl.

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(12) United States Patent
Veerasamy

(10) **Patent No.: US 7,067,175 B2**

(45) **Date of Patent: *Jun. 27, 2006**

(54) **METHOD OF MAKING HEAT TREATABLE COATED ARTICLE WITH DIAMOND-LIKE CARBON (DLC) INCLUSIVE LAYER**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 166 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **10/682,823**

(22) Filed: **Oct. 10, 2003**

(65) **Prior Publication Data**

US 2004/0074260 A1 Apr. 22, 2004

Related U.S. Application Data

(62) Division of application No. 09/915,552, filed on Jul. 27, 2001, now Pat. No. 6,713,178, which is a division of application No. 09/808,345, filed on Mar. 15, 2001, now Pat. No. 6,303,226, which is a division of application No. 09/303,548, filed on May 3, 1999, now Pat. No. 6,261,693.

(51) **Int. Cl.**
C23C 16/26 (2006.01)

(52) **U.S. Cl.** **427/249.7**; 427/255.7; 427/372.2

(58) **Field of Classification Search** 427/249.7, 427/255.7, 372.2
See application file for complete search history.

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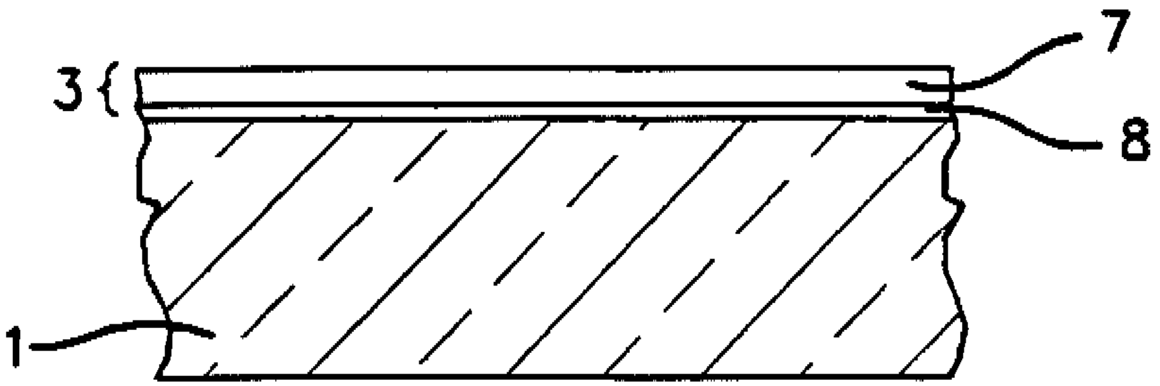
(57) **ABSTRACT**

A method of making a coated article includes providing a protective layer on a substrate over a coating in order to protect the coating. The protective layer may protect the coating before or during heat treatment in certain example embodiments of this invention.

11 Claims, 4 Drawing Sheets



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US 4,960,645, 10/1990, Lingle et al. (withdrawn)

* cited by examiner

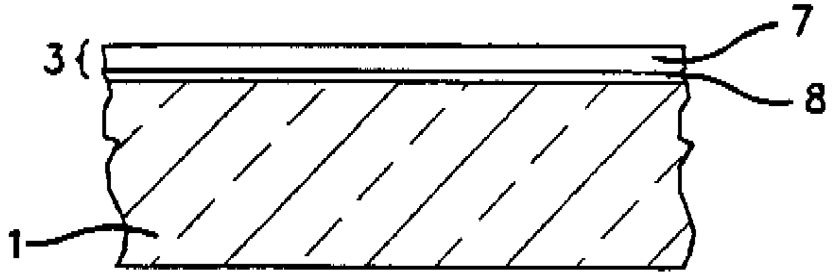

FIG. 1

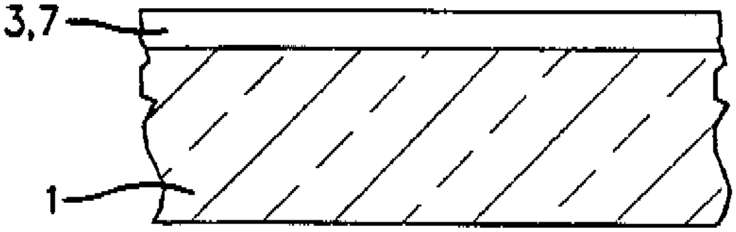

FIG. 2

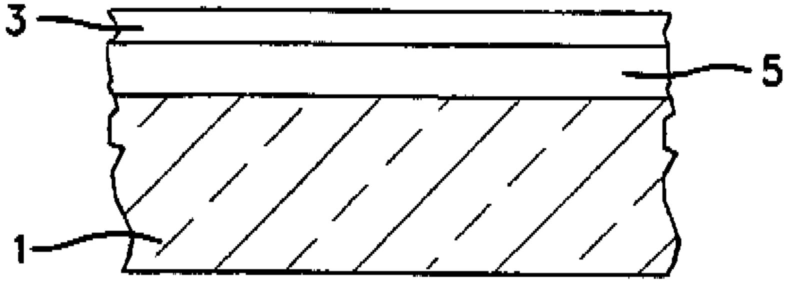

FIG. 3

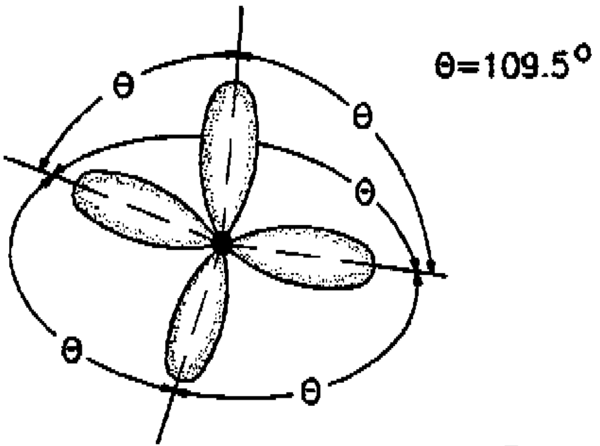

FIG. 4

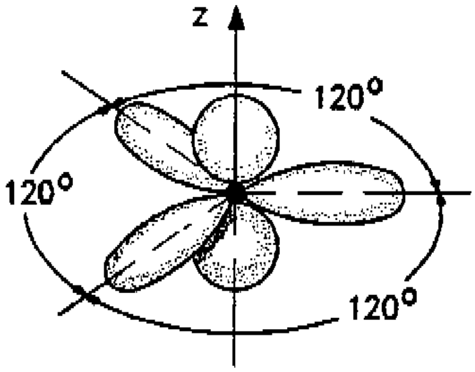

FIG. 5

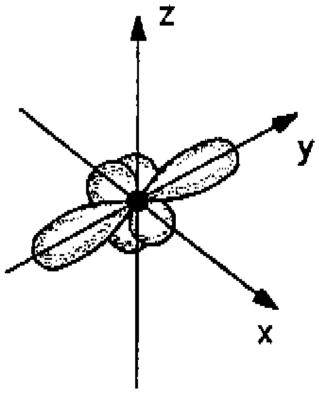

FIG. 6

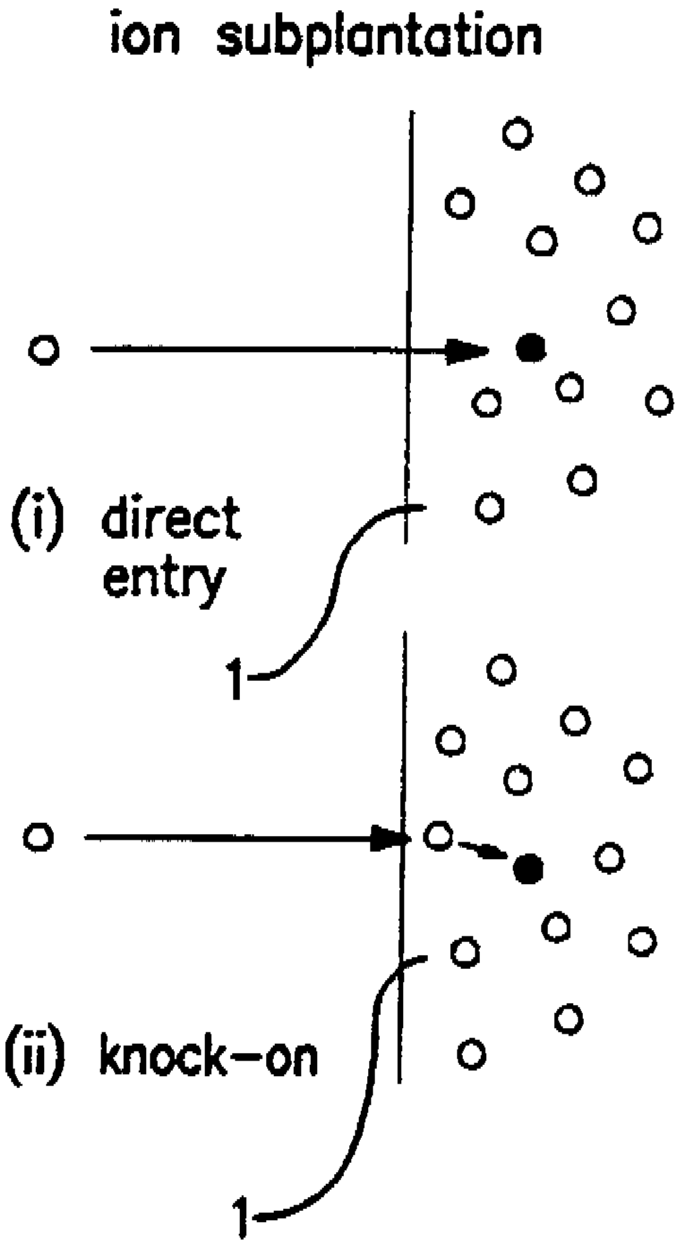

FIG. 7

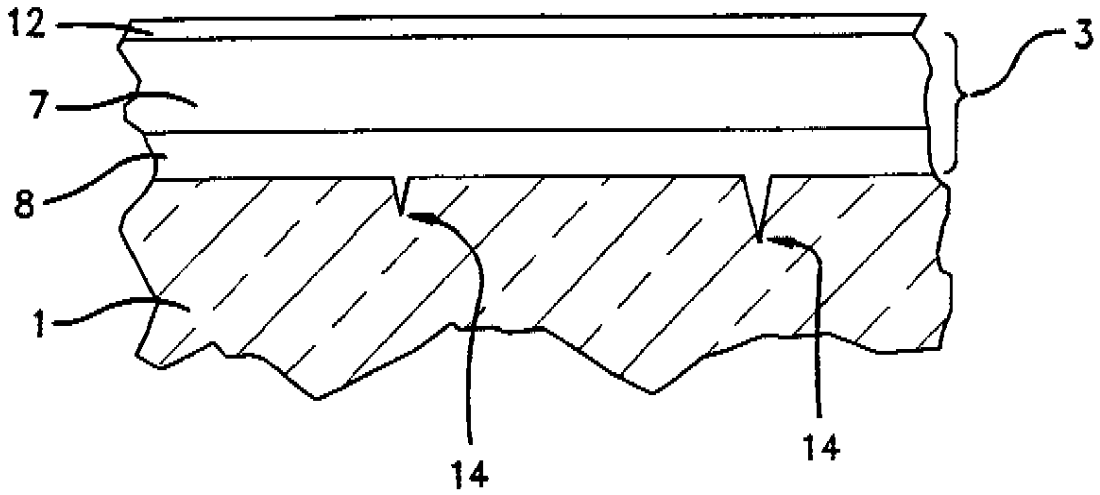

FIG. 8

METHOD OF MAKING HEAT TREATABLE COATED ARTICLE WITH DIAMOND-LIKE CARBON (DLC) INCLUSIVE LAYER

This application is a division of Ser. No. 09/915,552, filed Jul. 27, 2001 (now U.S. Pat. No. 6,713,178), which is a division of Ser. No. 09/808,345, filed Mar. 15, 2001 (now U.S. Pat. No. 6,303,226), which is a division of Ser. No. 09/303,548, filed May 3, 1999 (now U.S. Pat. No. 6,261,693), the disclosures of which are all hereby incorporated herein by reference.

This invention relates to a diamond-like carbon (DLC) coating provided on (directly or indirectly) a glass or other substrate. More particularly, in certain preferred embodiments, this invention relates to a highly tetrahedral amorphous diamond like carbon coating on a soda inclusive glass substrate (e.g. on a soda lime silica glass substrate) for purposes of repelling water and/or reducing corrosion on the coated article. Ion beam and filtered carbon cathodic arc deposition are preferred methods of deposition for the coating.

BACKGROUND OF THE INVENTION

Soda inclusive glasses are known in the art. For is example, see U.S. Pat. No. 5,214,008, which is hereby incorporated herein by reference.

Soda lime silica glass, for example, is used for architectural glass, automotive windshields, and the like. The aforesaid '008 patent discloses one type of soda lime silica glass known in the art.

Unfortunately, conventional soda inclusive glasses are susceptible to environmental corrosion which occurs when sodium (Na) diffuses from or leaves the glass interior. This sodium, upon reaching the surface of the glass, may react with water to produce visible stains or smears (e.g. stains of sodium hydroxide) on the glass surface. Such glasses are also susceptible to retaining water on their surfaces in many different environments, including when used as automotive windows (e.g. backlites, side windows, and/or windshields). These glasses are also susceptible to fogging up on the interior surface thereof in automotive and other environments.

In view of the above, it is apparent that there exists a need in the art to prevent and/or minimize visible is stains/corrosion on soda inclusive coated glass surfaces. There also exists a need in the art to provide a strong protective coating on window substrates. Other needs in the art include the need for a coating on glass that reduces the coated article's susceptibility to fogging up in automotive and other environments, and the need for a coated glass article that can repel water and/or dirt.

It is known to provide diamond like carbon (DLC) coatings on glass. U.S. Pat. No. 5,637,353, for example, states that DLC may be applied on glass. The '353 patent teaches that because there is a bonding problem between glass and that type of DLC, an intermediate layer is provided therebetween. Moreover, the '353 patent does not disclose or mention the highly tetrahedral amorphous type of DLC used in many embodiments set forth below. The DLC of the '353 patent would not be an efficient corrosion minimizer on glass in many instances due to its low density (likely less than 2.0 gm/cm^3). Still further, the DLC of the '353 patent is deposited in a less than efficient manner for certain embodiments of this invention.

It is known that many glass substrates have small is cracks defined in their surface. The stress needed to crack glass

typically decreases with increasing exposure to water. When water enters such a crack, it causes interatomic bonds at the tip of the crack to rupture. This weakens glass. Water can accelerate the rate of crack growth more than a thousand times by attacking the structure of the glass at the root or tip of the crack. Strength of glass is in part controlled by the growth of cracks that penetrate the glass. Water, in these cracks, reacts with glass and causes it to crack more easily as described in "The Fracturing of Glass," by T. A. Michalske and Bruce C. Bunker, hereby incorporated herein by reference. Water molecules cause a concerted chemical reaction in which a silicon-oxygen bond (of the glass) at the crack tip and on oxygen-hydrogen bond in the water molecule are both cleaved, producing two silanol groups. The length of the crack thus increases by one bond rupture, thereby weakening the glass. Reaction with water lowers the energy needed to break the silicon-oxygen bonds by a factor of about 20, and so the bond-rupture allows glass cracks to grow faster.

Thus, there also exists a need in the art for preventing water from reaching silicon-oxygen bonds at tips of cracks in a glass substrate, so as to strengthen the glass.

It is a purpose of different embodiments of this invention to fulfill any or all of the above described needs in the art, and/or other needs which will become apparent to the skilled artisan once given the following disclosure.

SUMMARY OF THE INVENTION

An object of this invention is to provide a coated article that can shed water (e.g. automotive windshield, automotive backlite, automotive side window, architectural window, etc.).

Another object of this invention is to provide a system or means for reducing or minimizing corrosion on soda inclusive coated glass articles.

Another object of this invention is to provide a coated glass article wherein a DLC coating protects the glass from acids such as HF, nitric, and sodium hydroxide (the coating may be chemically inert).

Another object of this invention is to provide a coated glass article that is not readily susceptible to fogging up.

Another object is to provide a barrier layer with no pin holes on a glass substrate.

Another object of this invention is to provide a coated glass article that is abrasion resistant, and/or can repel dirt and the like.

Another object of this invention is to provide a glass substrate with a DLC coating inclusive of a highly tetrahedral dense amorphous carbon layer, either in direct or indirect contact with the substrate.

Another object of this invention is to provide a DLC coating on a substrate, wherein the coating includes different portions or layers with different densities and different sp^3 carbon-carbon bond percentages. The ratio of sp^3 to sp^2 carbon-carbon bonds may be different in different layers or portions of the coating. Such a coating with varying compositions therein may be continuously formed by varying the ion energy used in the deposition process so that stresses in the coating are reduced in the interfacial portion/layer of the DLC coating immediately adjacent the underlying substrate. Thus, a DLC coating may have therein an interfacial layer with a given density and sp^3 carbon-carbon bond percentage, and another layer with a higher density and higher sp^3 carbon-carbon bond percentage.

Generally speaking, this invention fulfills certain of the above described needs/objects in the art by providing a coated glass comprising:

a glass substrate including at least about 5% by weight soda/Na_2O;

an amorphous carbon layer provided on the glass substrate in order to reduce corrosion or stains on the coated glass, wherein said amorphous carbon layer includes sp^2 and sp^3 carbon-carbon bonds; and

wherein the amorphous carbon layer has more sp^3 carbon-carbon bonds than sp^2 carbon-carbon bonds.

In other embodiments, this invention fulfills certain of the above described needs in the art by providing a coated glass comprising:

a soda inclusive glass substrate comprising, on a weight basis, from about 60–80% SiO_2, from about 10–20% Na_2O, from about 0–16% CaO, from about 0–10% K_2O, from about 0–10% MgO, and from about 0–5% Al_2O_3; and

a non-crystalline diamond-like carbon (DLC) coating provided on the glass substrate, wherein the DLC coating includes at least one highly tetrahedral amorphous carbon layer having at least about 35% sp^3 carbon-carbon bonds.

In certain embodiments, the glass substrate is a soda lime silica float glass substrate.

In preferred embodiments, the entire DLC coating or alternatively only a layer within the DLC coating, has a density of from about 2.4 to 3.4 gm/cm^3, most preferably from about 2.7 to 3.0 gm/cm^3.

In certain embodiments, the tetrahedral amorphous carbon layer has the aforesaid density range and includes at least about 70% sp^3 carbon-carbon bonds, and most preferably at least about 80% sp^3 carbon-carbon bonds.

In certain embodiments, the DLC coating includes a top layer (e.g. from about 2 to 8 atomic layers, or less than about 20 Å) that is less dense than other portions of the DLC coating, thereby providing a solid lubricant portion at the top surface of the DLC coating. Layered graphene connected carbon atoms are provided in this thin layer portion. The coefficient of friction is less than about 0.1 for this thin layer portion.

Another advantage of this invention is that the temperature of the glass substrate is less than about 200° C., preferably less than about 150° C., most preferably from about 60–80° C., during the deposition of DLC material. This is to minimize graphitization during the deposition process.

This invention further fulfills the above described needs in the art by providing a window having a substrate and a highly tetrahedral amorphous carbon layer thereon, wherein the substrate is or includes at least one of borosilicate glass, soda lime silica glass, and plastic.

This invention will now be described with respect to certain embodiments thereof, along with reference to the accompanying illustrations.

IN THE DRAWINGS

FIG. 1 is a side cross sectional view of a coated article according to an embodiment of this invention, wherein a substrate is provided with a DLC coating including at least two layers therein.

FIG. 2 is a side cross sectional view of a coated article according to another embodiment of this invention, wherein a highly tetrahedral amorphous carbon DLC coating is provided on and in contact with a substrate.

FIG. 3 is a side cross sectional view of a coated article according to yet another embodiment of this invention wherein a low-E or other coating is provided on a substrate, with the DLC coating of either of the FIG. 1 or FIG. 2 embodiments also on the substrate but over top of the intermediate low-E or other coating.

FIG. 4 illustrates an exemplar sp^3 carbon atom hybridization bond.

FIG. 5 illustrates an exemplar sp^2 carbon atom hybridization bond.

FIG. 6 illustrates exemplar sp hybridizations of a carbon atom.

FIG. 7 is a side cross sectional view of carbon ions penetrating the substrate or DLC surface so as to strongly bond a DLC layer according to any embodiment herein.

FIG. 8 is a side cross sectional view of a coated glass substrate according to an embodiment of this invention, illustrating DLC bonds penetrating cracks in the surface of a glass substrate.

DETAILED DESCRIPTION OF CERTAIN EMBODIMENTS OF THIS INVENTION

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

FIG. 1 is a side cross sectional view of a coated glass article according to an embodiment of this invention, wherein at least one diamond-like carbon (DLC) protective coating(s) **3** is provided directly on soda-inclusive glass substrate **1**. DLC coating **3** in the FIG. **1** embodiment includes at least one highly tetrahedral amorphous carbon (ta-C) layer **7** that has a high density (e.g. greater than about 2.4 grams per cubic centimeter) and functions to repel water and seal soda within the soda inclusive glass substrate. Coating **3** further includes at least one interfacing layer **8** directly adjacent substrate **1**, where layer **8** has a lesser density and a lesser percentage of sp^3 carbon-carbon bonds than ta-C layer **7**. Even though layer **8** differs from layer **7** in these manner(s), interfacing layer **8** may or may not qualify as ta-C with a density of at least about 2.4 gm/cm^3, as described below. It is noted that in certain embodiments, coating **3** may include multiple ta-C layers **7** and/or multiple layers **8**. Layers **7** and **8** of the coating may be formed in a continuous or non-continuous deposition process in different embodiments of this invention.

FIG. 2 is a side cross sectional view of a coated glass article according to another embodiment of this invention, wherein at least one DLC coating(s) **3** is provided on glass substrate **1**. In the FIG. 2 embodiment, substantially the entire DLC coating **3** is made up of highly tetrahedral amorphous carbon (ta-C), similar to layer **7**, having a density of at least about 2.4 grams per cubic centimeter and a high percentage (e.g. at least about 35%, more preferably at least about 70%, and most preferably at least about 80%) of sp^3 carbon-carbon bonds. In other words, ta-C layer **7** from the FIG. **1** embodiment forms the entirety of DLC coating **3** in the FIG. 2 embodiment. DLC coating **3** in the FIG. 2 embodiment may or may not have equal densities and/or the same percentages of sp^3 carbon-carbon bonds throughout the thickness of coating **3**, as these parameters may be varied throughout layers **3**, **7** and **8** in the FIGS. **1** and **2** embodiments by changing the ion energy used during the deposition process of coating **3**.

In the FIG. **3** embodiment, a low-E or other coating S is provided between substrate **1** and DLC coating **3** (i.e. the DLC coating of either the FIG. **1** or FIG. **2** embodiment).

However, DLC coating **3** is still on substrate **1** in the FIG. **3** embodiment, along with a ta-C portion **7** of coating **3**. Thus, the term "on" herein means that substrate **1** supports DLC coating **3** or any layer (e.g. 7, **8**) thereof, regardless of whether or not other layer(s) **5** are provided therebetween. Thus, protective coating 3 may be provided directly on substrate **1** as shown in FIGS. **1 2** , or may be provided on substrate **1** with a low-E or other coating(s) **5** therebetween as shown in FIG. 3. Coating **5**, instead of its illustrated position in FIG. **3**, may also be provided on top of DLC coating **3** so that coating **3** (of either the FIG. 1 or FIG. **2** embodiment) is located between coating(s) **5** and substrate 1. In still other embodiments, a DLC coating **3** may be provided on both sides of a low-E coating **5**.

Exemplar coatings (in full or any portion of these coatings) that may be used as low-E or other coating(s) **5**, either on top of or below DLC coating **3**, are shown and/or described in any of U.S. Pat. Nos. 5,837,108, 5,800,933, 5,770,321, 5,557,462, 5,514,476, 5,425,861, 5,344,718, 5,376,455, 5,298,048, 5,242,560, 5,229,194, 5,188,887 and 4,960,645, which are all hereby incorporated herein by reference. Simple silicon oxide and/or silicon nitride coating(s) may also be used as coating(s) **5**.

As will be discussed in more detail below, highly tetrahedral amorphous carbon (ta-C) layer(s) **7** is a special form of diamond-like carbon (DLC), and includes at least about 35% sp^3 carbon-carbon bonds (i.e. it is highly tetrahedral). In certain embodiments of this invention, ta-C layer(s) 7 has at least about 35% sp^3 carbon-carbon bonds of the total sp bonds in the layer, more preferably at least about 70%, and most preferably at least about 80% sp^3 carbon-carbon bonds so as to increase the density of layer **7** and its bonding strength. The amounts of sp^3 bonds may be measured using Raman finger-printing and/or electron energy loss spectroscopy. The high amount of sp^3 bonds increases the density of layer thereby allowing it to prevent soda diffusion to the surface of the coated article.

Ta C layer **7** forms the entirety of DLC coating **3** in the FIG. **2** embodiment, and ta-C layer **7** forms only a portion of DLC coating **3** in the FIG. **1** embodiment. This is because interfacial amorphous carbon layer **8** in the FIG. **1** is embodiment sometimes has a density less than about 2.4 grams per cubic centimeter and/or less than about 35% sp^3 carboncarbon bonds. However, it is noted that DLC coating **3** has an interfacial layer immediately adjacent substrate **1** in each of the FIG. **1** and FIG. 2 embodiments, with the difference being that the interfacial layer in the FIG. 2 embodiment has a density of at least about 2.4 grams per cubic centimeter and at least about 35% sp^3 (more preferably at least about 70%, and most preferably at least about 80%) carbon-carbon bonds. Thus, layer **7** herein refers to both layer 7 as illustrated in the FIG. 1 embodiment as well as DLC coating 3 in the FIG. 2 embodiment.

At least some carbon atoms of DLC coating 3, and/or some sp^2 and/or sp^3 carbon-carbon bonds, are provided in fissures or cracks in a surface (e.g. top surface) of the glass substrate, or may penetrate the glass surface of substrate **1** itself or the surface of growing DLC, so as to strongly bond coating 3 to substrate 1. Subimplantation of carbon atoms into the surface of substrate **1** enables coating **3** to be strongly bonded to substrate **1**.

For purposes of simplicity, FIG. **4** illustrates an exemplar sp^3 carbon-carbon or C—C bond (i.e. carbon to carbon diamond like bond) in coating **3**, FIG. **4** an exemplar sp^2 C C bond in coating **3**, and FIG. **5** an exemplar sp.

The provision of dense (density of at least about 2.4 gm/cm^3) ta-C layer **7** on soda inclusive glass substrate **1** reduces the amount of soda which can exit the substrate or reach the surface of the substrate or coated article (i.e. ta-C limits sodium diffusion from the substrate). Thus, less soda is allowed to react with water or other material(s) on the surface of the article. The end result is that the provision of ta-C layer **7** on the substrate reduces stains and/or corrosion on the glass article which can form over time. The large number of sp^3 carbon-carbon bonds increases the density of layer **7** and allows the layer to repel water and minimize soda diffusion from soda inclusive glass.

Coating(s) **3**, and layer(s) **7**, **8**, also strengthen the glass article, reduce stress at the bonding surfaces between coating **3** and substrate **1**, and provide a solid lubricant surface on the article when coating **3** is located at a surface of the article. Coating(s) **3** and/or layer **7** may includes a top layer portion (e.g. the top 3 to 15 Å) that is less dense than central areas of coating 3, thereby providing a solid lubricant at the top surface of coating **3** furthest from the substrate so that the article is resistant to scratching. Ta C layer **7** also provides resistance to water/moisture entering or coming into substrate **1**. Coating 3, and thus ta-C layer **7**, are preferably formed/deposited continuously across glass substrate **1**, absent any pinholes or apertures.

In certain embodiments, layer **7** and/or **8** adjacent the glass substrate is deposited at an ion energy that allows significant numbers of carbon atoms to penetrate cracks in the glass surface as shown in FIG. **8**. The small size of carbon atoms and the ion energy utilized prevent substantial water from reaching the tip of the crack(s). This strengthens the glass in the long term by slowing down and/or stopping the rupture of silicon-oxygen bonds at crack tips caused by water exposure.

Advantages associated with certain embodiments of this invention include: (i) coated window articles that can shed water in different environments (e.g. automotive windows such as backlites and windshields, or commercial and residential windows); (ii) anti-fog coated articles that are resistant to fogging up; (iii) strengthened coated windows; (iv) abrasion resistant coated windows; (v) coated articles that can repel dirt; and (vi) coated glass articles less susceptible to visible corrosion on surfaces thereof. For example, in automotive window embodiments, the outer surface of substrate **1** exposed to the environment is coated with coating **3** in accordance with any of the FIG. **1–3** embodiments. In anti-fog automotive embodiments, the inner surface of automotive window substrates **1** may be coated with coating **3** in accordance with any of the FIG. **1 3** embodiments.

In certain embodiments, coating **3** is at least about 70% transparent to or transmissive of visible light rays, preferably at least about 80%, and most preferably at least about 90% transparent to visible light rays.

In certain embodiments, DLC coating 3 (and thus layer 7 in the FIG. **2** embodiment) may be from about 30 to 3,000 Å thick, most preferably from about 50 to 300 Å thick. As for glass substrate **1**, it may be from about 1.5 to 5.0 mm thick, preferably from about 2.3 to 4.8 mm thick, and most preferably from about 3.7 to 4.8 mm thick. Ta C layer **7**, in certain embodiments, has a density of at least about 2.4 grams per cubic centimeter, more preferably from about 2.4 to 3.4 gm/cm^3, and most preferably from about 2.7 to 3.0 gm/cm^3.

Substrate 1 includes soda or Na_2O in certain embodiments of this invention. Thus, ta-C layer(s) 7 minimize the amount of soda that can reach the surface of the coated article and cause stains/corrosion. In certain embodiments, substrate **1** includes, on a weight basis, from about 60 80% SiO_2, from about 10–20% Na_2O, from about 0 16% CaO, from about

0–10% K_2O, from about 0–10% MgO, and from about 0–5% Al_2O_3. In certain other embodiments, substrate **1** may be soda lime silica glass including, on a weight basis, from about 66–75% SiO_2, from-about 10–20% Na_2O, from about 5–15% CaO, from about 0–5% MgO, from about 0–5% Al_2O_3, and from about 0–5% K_2O. Most preferably, substrate **1** is soda lime silica glass including, by weight, from about 70–74% SiO_2, from about 12–16% Na_2O, from about 7–12% CaO, from about 3.5 to 4.5% MgO, from about 0 to 2.0% Al_2O_3, from about 0–5% K_2O, and from about 0.08 to 0.15% iron oxide. Soda lime silica glass according to any of the above embodiments may have a density of from about 150 to 160 pounds per cubic foot (preferably about 156), an average short term bending strength of from about 6,500 to 7,500 psi (preferably about 7,000 psi), a specific heat (0–100 degrees C.) of about 0.20 Btu/lbF, a softening point of from about 1330 to 1345 degrees F., a thermal conductivity of from about 0.52 to 0.57 Btu/hrftF, and a coefficient of linear expansion (room temperature to 350 degrees C.) of from about 4.7 to 5.0×10^{-6} degrees F. In certain embodiments, any glass disclosed in U.S. Pat. No. 5,214,008 or U.S. Pat. No. 5,877,103, each incorporated herein by reference, may be used as substrate **1**. Also, soda lime silica float glass available from Guardian Industries Corp., Auburn Hills, Mich., may be used as substrate **1**.

S Any such aforesaid glass substrate **1** may be, for example, green, blue or grey in color when appropriate colorant(s) are provided in the glass.

In certain other embodiments of this invention, substrate **1** may be of borosilicate glass, or of substantially transparent plastic. In certain borosilicate embodiments, the substrate **1** may include from about 75–85% SiO_2, from about 0–5% Na_2O, from about 0 to 4% Al_2O_3, from about 0–5% K_2O, from about 8–15% B_2O_3, and from about 0–5% Li_2O.

In still further embodiments, an automotive window (e.g. windshield or side window) including any of the above glass substrates laminated to a plastic substrate may combine to make up substrate **1**, with the coating **3** of any of the FIGS. 1–3 embodiments provided on either or both sides of such a window. Other embodiments would have substrate **1** made up of a sheet of soda lime silica glass laminated to a plastic sheet for automotive window purpose, with coating(s) **3** of any of the FIG. 1–3 embodiments on the inner side of the substrate bonded to the plastic. In other embodiments, substrate **1** may include first and second glass sheets of any of the above mentioned glass materials laminated to one another, for use in window (e.g. automotive windshield, residential window, commercial window, automotive side window, automotive backlite or back window, etc.) and other similar environments.

In certain embodiments, coating **3** and/or ta-C layer **7** may have an average hardness of from about 30–80 GPa (most preferably from about 40–75 GPa), and a bandgap of from about 1.8 to 2.2 eV. It is noted that the hardness and density of coating **3** and/or layers **7**, **8** thereof may be adjusted by varying the ion energy of the depositing apparatus or process described below.

When substrate **1** of any of the aforesaid materials is coated with at least DLC coating **3** according to any of the FIGS. 1–3 embodiments, the resulting coated article has the following characteristics in certain embodiments: visible transmittance (Ill. A) greater than about 60% (preferably greater than about 70%), UV (ultraviolet) transmittance less than about 38%, total solar transmittance less than about 45%, and IR (infrared) transmittance less than about 35% (preferably less than about 25%, and most preferably less than about 21%). Visible, "total solar", UV, and IR transmittance measuring techniques are set forth in U.S. Pat. No. 5,800,933, as well as the '008 patent, incorporated herein by reference.

Diamond-like carbon (DLC) and the special tetrahedral amorphous carbon (ta-C) form **7** of DLC utilized in certain embodiments herein will now be described in detail. All DLC **3** shown in drawings herein is amorphous. Ta–C **7** is amorphous and yet has substantial C—C tetrahedral (sp^3-type) bonding and hence is termed tetrahedral amorphous carbon (ta-C) [or highly ta-C] as it has at least 35% sp^3 C—C bonds, preferably at least about 70% and most preferably at least about 80% sp^3 C—C bonds. Diamond-like bonding gives this ta-C material gross physical properties approaching those of diamond such as high hardness, high density and chemical inertness. However, ta-C also includes sp^2 C—C trigonal bonding and its optical and electronic properties are largely determined by this bonding component. The fraction of sp^2 bonding, and thus the density, in a ta-C layer depends for example on the carbon ion energy used during deposition of coating **3** and/or layers **7** and **8**. Properties of a given DLC coating are a function of the fraction of sp^3 to sp^2 bonding throughout the coating and thus throughout layers **7** and **8**.

It is noted that the sp^3 bonds discussed herein are sp^3 carbon-carbon bonds which result in a high density coating **3** and/or **7** and are not sp^3 carbon-hydrogen bonds which do not provide as high of density.

Depending on the technique of deposition, many ta-C layers **7** herein contain amounts of H (up to about 4%) which either include the C atom to take either a tetrahedral configuration or an sp^2 planar configuration or to be sp-hybridised within a linear polymeric-like form. In other words C—C, C—H and H—H correlations all contribute to the average structure of layers **7** in some embodiments.

In the case of ta-C which is fully or at least about 90% hydrogen-free, C—C bonding describes the local structure. Ta—C films also have some fraction of sp^2 or graphic bonding. The spatial distribution of trigonal (sp^2) and tetrahedral carbon atoms may determine the bonding strength of layer(s) **3** to glass, as well as the layer's density, strength, stress, etc. Tetrahedral amorphous carbon (ta-C) and its hydrogenated form ta-C:H (which contains no more than about 10 at % or so H) have the highest percentage of carbon-carbon (C—C) sp^3 bonding, and are used as layer **7** in the FIG. **1** embodiment and coating **3** in the FIG. **2** embodiment, and either of these in the FIG. **3** embodiment. This diamond-like bonding confers upon ta-C **7** properties which are unrivaled by other forms of so called DLC which have lower densities and/or greater proportion of graphitic sp^2 and polymeric sp C—C and C—H bonding.

Ta–C **7** has high density (at least about 2.4 grams per cubic centimeter), hardness, Young's modulus (700–800), as well as a low coefficient of friction (see Table 1 below).

TABLE 1

Properties	c-Diamond	ta-C	ta-C:H (10% at H)
Bandgap (eV)	5.45	2.0	2.2–2.5
Breakdown voltage (V cm-1) 10^5	100	25–35	30
Dielectric Constant	5.5	4.5	4.7
Resistivity (ohm - cm)	10^{18}	10^{11}	10^{12}
Thermal Conductivity (Wcm $^{-1}$K $^{-1}$)	20	0.1	0.1
Young's modulus Gpa	1000	700–800	500
Hardness (Gpa)	100	30–80	5–80

TABLE 1-continued

Properties	c-Diamond	ta-C	ta-C:H (10% at H)
Refractive index	2.4	2.0	1.6–1.9
Structure	crystalline	amorphous	amorphous
Deposition condition/rate	high temp CVD 0.1 um/hr	low temp <200 C. 20 A/s	low temp
wetability		contact angle 5 to 50	
Max thickness	>1 um	<200 nm stress limited	<200 nm
Coefficient of Friction	<0.2 single crystal	<0.1	<0.1

Methods of depositing coating **3** on substrate **1** are described below for certain embodiments of this invention.

Prior to coating **3** being formed on the glass substrate, the top surface of substrate **1** is preferably cleaned by way of an ion beam utilizing oxygen gas in each of the FIG. **1** and **2** embodiments. Oxygen gas physically cleans the surface due to its atomic weight of from about 28–40 amu, most preferably about 32. Substrate **1** may also be cleaned by, for example, sputter cleaning the substrate prior to actual deposition of ta-C or other DLC material. This cleaning may utilize oxygen and/or carbon atoms, and can be at an ion energy of from about 800 to 1200 eV, most preferably about 1,000 eV.

In plasma ion beam embodiments for depositing coatings **3**, **7** and/or **8**, carbon ions may be energized to form a stream from plasma toward substrate **1** so that carbon from the ions is deposited on substrate **1**. An ion beam from gas phase produces a beam of C+, CH+, C_2H, and/or C_2H_2+ ions (i.e. carbon or carbon based radicals). Preferably, acetylene feedstock gas (C_2H_2) is used to prevent or minimize polymerization and to obtain an appropriate energy to allow the ions to penetrate the substrate **1** surface and subimplant therein, thereby causing coating **3** atoms to intermix with the surface of substrate **1** a few atom layers thereinto. Impact energy of ions for the bulk of coating **3** (e.g. layer **7** in the FIGS. **1** and **2** embodiments) may be from about 100 to 200 eV per carbon atom, preferably from about 100–150 eV, to cause dense sp^3 C—C bonds to form in the DLC layer. The ions impact the substrate with this energy which promotes formation of sp^3 carbon-carbon bonds. The impact energy of the energetic carbon ions may be within a range to promote formation of the desired lattice structure, such bonds in an interfacing portion (e.g. layer **8** in the FIG. **1** embodiment) of coating **3** apparently being formed at least in part by subimplantation into the substrate as shown in FIG. **7**. The stream may be optionally composed of ions having approximately uniform weight, so that impact energy will be approximately uniform. Effectively, the energetic ions impact on the growing film surface and/or substrate **1** and are driven into the growing film and/or substrate **1** to cause densification. Coating **3**, and especially layer **7**, are preferably free of pinholes, to achieve satisfactory water repulsion and suppression of soda diffusion.

Thus, the C—C sp^3 bonding is preferably formed by having a predetermined range of ion energy prior to reaching substrate **1**, or prior to reaching ta-C growing on the substrate. The optimal ion energy window for ta-C layer **7** formation in the FIGS. **1** and **2** embodiments is from about 100–200 eV (preferably from about 100–150 eV, and most preferably from about 100–140 eV) per carbon ion. At these energies, films **7** (i.e. layer **3** in the FIG. **2** embodiment) emulate diamond.

However, compressive stresses can develop in ta-C when being deposited at 100–150 eV. Such stress can reach as high as 10 Gpa and can potentially cause delamination from many substrates. It has been found that these stresses can be controlled and decreased by increasing the ion energy the deposition process to a range of from about 200–1,000 eV. The plasma ion beam source enables ion energy to be controlled within different ranges in an industrial process for large area deposition utilized herein. The compressive stress in amorphous carbon is thus decreased significantly at this higher ion energy range of 200–1,000 eV.

High stress is undesirable in the thin interfacing portion **8** of coating **3** that directly contacts the surface of a glass substrate **1**. Thus, for example, the first 1–40% thickness (preferably the first 1–20% and most preferably the first 5–10% thickness) **8** of coating **3** is deposited on substrate **1** using high anti-stress energy levels of from about 200–1,000 eV, preferably from about 400–500 eV. Then, after this initial interfacing portion **8** of coating **3** has been grown, the ion energy in the ion deposition process is decreased (either quickly or gradually while deposition continues) to about 100–200 eV, preferably from about 100–150 eV, to grow the remainder ta-C layer **7** of coating **3**.

For example, assume for exemplary purposes only with reference to FIG. **1** that DLC coating **3** is 100 Å thick. The first 10 Å layer **8** of coating **3** (i.e. interfacing portion **8**) may be deposited using an ion energy of from about 400 to 500 eV so that layer **8** of coating **3** that contacts the surface of substrate **1** has reduced compressive stresses relative to the remainder **7** of coating **3**. Interfacing portion **8** of coating **3** at least partially subimplants into the surface of substrate **1** to allow intermixing with the glass surface. In certain embodiments, only C ions are used in the deposition of interfacing layer **8**, with the graded is composition interface being mainly SiC. This interface **8** between substrate **1** and coating **3** improves adhesion of coating **3** to substrate **1** and the gradual composition change distributes strain in the interfacial region instead of narrowly concentrating it. Layer **8** of DLC coating **3** may or may not have a density of at least about 2.4 grams per cubic centimeter in different embodiments, and may or may not have at least about 35%, 70%, or 80% sp^3 carbon-carbon bonds in different embodiments. After the first 10 Å (i.e. layer **8**) of coating **3** has been deposited, then the ion energy is gradually or quickly decreased to 100 to 150 eV for the remainder [may be either ta-C or ta-C:H] **7** of coating **3** so that layer **7** has a higher density and a higher percentage of sp^3 C—C bonds than layer **8**.

Thus, in certain embodiments, because of the adjustment in ion energy during the deposition process, ta-C coating **3** in FIGS. **1**–**3** has different densities and different percentages of sp^3 C—C bonds at different areas therein. However, at least a portion of coating **3** is a highly tetrahedral ta-C layer **7** having a density of at least about 2.4 grams per cubic centimeter and at least about 35% sp^3. The highly tetrahedral ta-C portion is the portion furthest from substrate **1** in FIG. **1**, but may optionally be at other areas of coating **3**. In a similar manner, the portion of coating **3** having a lesser percentage of sp^3 C—C bonds is preferably the portion immediately adjacent substrate **1** (e.g. interfacing layer **8**).

In certain embodiments, CH_4 may be used as a feedstock gas during the deposition process instead of or in combination with the aforesaid C_2H_2 gas.

Referring to FIG. **8**, it is noted that the surface of a glass substrate has tiny cracks or microcracks defined therein. These cracks may weaken glass by orders of magnitude, especially when water seeps therein and ruptures further bonds. Thus, another advantage of this invention is that in certain embodiments amorphous carbon atoms and/or networks of layer 7 or **8** fill in or collect in these small cracks because of the small size of carbon atoms (e.g. less than about 100 pm radius atomic, most preferably less than about 80 pm, and most preferably about 76.7 pm) and because of the ion energy of 200 to 1,000 eV, preferably about 400–500 eV, and momentum. This increases the mechanical strength of the glass. The nano cracks in the glass surface shown in FIG. **8** may sometimes be from about 0.4 nm to 1 nm is in width. The inert nature and size of the carbon atoms in these nonocracks will prevent water from attacking bonds at the crack tip **14** and weakening the glass. The carbon atoms make their way to positions adjacent the tips **14** of these cracks, due to their size and energy. Tips **14** of these cracks are, typically, from about 0.5 to 50 nm below the glass substrate surface. The top surface of layers **7** and/or **8** remains smooth and/or approximately flat within about less than 1.0 nm even above the cracks.

Carbon is now described generally, in many of its forms, to aid in the understanding of this invention.

Carbon has the ability to form structures based on directed covalent bonds in all three spatial dimensions. Two out of the six electrons of a carbon atom lie in the **1***s* core and hence do not participate in bonding, while the four remaining **2***s* and **2***p* electrons take part in chemical bonding to neighboring atoms. The carbon atom's one **2***s* and three **2***p* electron orbitals can hybridise in three different ways. This enables carbon to exist as several allotropes. In nature, three allotropic crystalline phase exists, namely diamond, graphite and the fullerenes and a plethora of non-crystalline forms.

For the diamond crystalline allotrope, in tetrahedral or sp^3 bonding all the four bonding electrons form σ bonds. The space lattice in diamond is shown in FIG. **4** where each carbon atom is tetrahedrally bonded to four other carbon atoms by σ bonds of length 0.154 nm and bond angle of 109° 53". The strength of such a bond coupled with the fact that diamond is a macromolecule (with entirely covalent bonds) give diamond unique physical properties: high atomic density, transparency, extreme hardness, exceptionally high thermal conductivity and extremely high electrical resistivity (10^{16} Ω-cm)

The properties of graphite are governed by its trigonal bonding. The outer $2s$, $2p_x$ and $2p_y$ orbitals hybridise in a manner to give three co-planar sp^2 orbitals which form σ bonds and a p-type **π** orbital $2p_z$ perpendicular to the sp^2 orbital plane, as shown in FIG. **5**. Graphite consists of hexagonal layers separated from each other by a distance of 0.34 nm. Each carbon atom is bonded to three others by 0.142 nm long σ bonds within an hexagonal plane. These planes are held together by weak van der Waals bonding which explains why graphite is soft along the sp^2 plane.

As for fullerenes, it is known that C_{60} and C_{70} are the most accessible members of the family of closed-cage molecules called fullerenes, formed entirely of carbon in the sp^2 hybridised state. Each fullerenes C_n consists of 12 pentagonal rings and m hexagonal rings such that m=(n−20)/2 (satisfying Euler's Theorem). The σ bonds are wrapped such that the fullerene has a highly strained structure and the molecule is rigid.

As for amorphous carbon, there exists a class of carbon in the metastable state without any long range order.

Material properties change when using different deposition techniques or even by varying the deposition parameters within a single technique. In this category of materials on one extreme we have ta-C (e.g. layer **7**) which is the most diamond-like with up to 90% C—C sp^3 bonding in certain preferred embodiments and on the other a-C (amorphous carbon), produced by thermal evaporation of carbon, in which more than 95% graphitic bonds are prevalent. In this respect, these two materials reflect the intrinsic diversity of non-crystalline forms of carbon.

Amorphous materials, such as layer(s) **3**, **7** and **8**, are metastable solids. In an amorphous solid there exists a set of equilibrium positions about which atoms oscillate. The atoms in an amorphous material are often extended into a three dimensional network with the absence of order beyond the second nearest neighbor distance.

Referring again to ta-C layer 7, the sp^3/sp^2 C—C bonded fraction or percentage (%), e.g. in a vacuum arc deposition technique or techniques used in the '477 patent or deposition techniques discussed above, can be controlled by changing the energy of the incident C^+ ions. The films deposited being metastable in nature are under high compressive stress. The sp^2 hybridised carbon atoms are clustered and embedded within a sp^3 matrix. The extent of the latter bonding confers onto ta-C its diamond-like physical properties. The fraction of the sp^2 hybridised atoms determines the extent of clustering. The degree of clustering, which is seen as a strain relief mechanism, implies that the π and π* states become delocalised to such an extent that they control the electronic and optical properties of the films. At high density of states, the π bands merge with the σ states to form the conduction and valence mobility band-edges. Their lower density tail states are localised giving a pseudo-gap. The term "tetrahedral amorphous carbon (ta-C)" is thus used to distinguish this highly tetrahedral material from other "diamond-like carbon" which have C—C correlations mostly of the sp^2 type.

The sp^3 bonding in coatings **3** is believed to arise from a densification process under energetic ion bombardment conditions. Hybridisation of the carbon atom is expected to adjust to the local density, becoming more sp^3 if the density is high and more sp^2 if low. This can occur if an incident ion penetrates the first atomic layer and then enters an interstitial subsurface position. The local bonding then reforms around this atom and its neighbours to adopt the most appropriate hybridisation. High energy ions in principle can penetrate the surface layer of the substrate or growing DLC, increase the density of deeper layers which then forces sp^3 bonding. Ions of lower energy than the penetration threshold only append to the surface forming sp^2 bonded a-C.

Coated articles according to any of the aforesaid embodiments may be used, for example, in the context of automotive windshields, automotive back windows, automotive side windows, architectural glass, IG glass units, residential or commercial windows, and the like.

In any of the aforesaid embodiments, a layer of non-porous tungsten disulfide (WS_2) **12** may be provided on top of layer **7** to prevent the DLC from burning off upon exposure to air if taken to high temperatures after the coating deposition. Layer **12** (e.g. see FIG. **8**) may be applied by plasma spraying to a thickness of from about 300 to 10,000 Å. WS_2 layer **12** is removeable in certain embodiments. Other suitable materials may instead be used for layer **12**.

Once given the above disclosure, many other features, modifications, and improvements will become apparent to the skilled artisan. 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.

I claim:

1. A method of making a heat treated coated article for use in a window comprising diamond-like carbon (DLC), the method comprising:
   providing a glass substrate that supports at least a layer comprising diamond-like carbon (DLC);
   forming a protective layer over at least the layer comprising DLC, the protective layer for protecting the layer comprising DLC from significantly burning off during heat treatment;
   heat treating the glass substrate together with the layer comprising DLC and the protective layer; and
   using the heat treated glass substrate in a window.

2. The method of claim 1, wherein the protective layer comprises WS2.

3. The method of claim 1, wherein the layer comprising DLC has an average density of at least 2.4 gm/cm3.

4. The method of claim 1, wherein at least 35% of carbon-carbon bonds in the layer comprising DLC are of the sp3 type.

5. The method of claim 1, wherein at least 70% of carbon-carbon bonds in the layer comprising DLC are of the sp3 type.

6. The method of claim 1, further comprising causing the protective layer to be removed after the heat treating.

7. A method of making a coated article, the method comprising:
   providing a low-E coating on a glass substrate; and
   forming a layer comprising carbon over the low-E coating, the layer comprising carbon for protecting the low-E coating, and wherein the layer comprising carbon burns off during heating of the coated article.

8. The method of claim 7, wherein the layer comprising carbon comprises DLC.

9. The method of claim 7, wherein the layer comprising carbon comprises DLC and has an average density of at least 2.4 gm/cm3.

10. The method of claim 8, wherein the DLC further includes hydrogen.

11. The method of claim 7, further comprising using the coated article in a window unit after said heating.

* * * * *

JS 44 (Rev. 11/04)

CIVIL COVER SHEET

The JS 44 civil cover sheet and the information contained herein neither replace nor supplement the filing and service of pleadings or other papers as required by law, except as provided by local rules of court. This form, approved by the Judicial Conference of the United States in September 1974, is required for the use of the Clerk of Court for the purpose of initiating the civil docket sheet. (SEE INSTRUCTIONS ON THE REVERSE OF THE FORM.)

I. (a) PLAINTIFFS

Guardian Industries Corp.

(b) County of Residence of First Listed Plaintiff Oakland, Michigan

(EXCEPT IN U.S. PLAINTIFF CASES)

26125

(c) Attorney's (Firm Name, Address, and Telephone Number)

Andrew M. Grove, Reising, Barnes, Kisselle, P.C., P.O. Box 4390, Troy, MI 48099-4390, ph. (248) 689-3500

DEFENDANTS

AFG Industries

County of Residence of First Listed Defendant

(IN U.S. PLAINTIFF CASES ONLY)

NOTE: IN LAND CONDEMNATION CASES, USE THE LOCATION OF THE LAND INVOLVED.

Attorneys (If Known)

II. BASIS OF JURISDICTION (Place an "X" in One Box Only)

☐ 1 U.S. Government Plaintiff

☒ 3 Federal Question (U.S. Government Not a Party)

☐ 2 U.S. Government Defendant

☐ 4 Diversity (Indicate Citizenship of Parties in Item III)

III. CITIZENSHIP OF PRINCIPAL PARTIES (Place an "X" in One Box for Plaintiff

(For Diversity Cases Only) fendant)

DEF

Ci 4 ☐ 4

Ci 5 ☐ 5

Ci 6 ☐ 6

Case: 2:06-cv-15728
Assigned To: Roberts, Victoria A
Referral Judge: Pepe, Steven D
Filed: 12-26-2006 At 01:40 PM
CMP GUARDIAN IND CORP V. AFG INDUST
RIES (TAM)

IV. NATURE OF SUIT (Place an "X" in One Box Only)

CONTRACT

- ☐ 110 Insurance
- ☐ 120 Marine
- ☐ 130 Miller Act
- ☐ 140 Negotiable Instrument
- ☐ 150 Recovery of Overpayment & Enforcement of Judgment
- ☐ 151 Medicare Act
- ☐ 152 Recovery of Defaulted Student Loans (Excl. Veterans)
- ☐ 153 Recovery of Overpayment of Veteran's Benefits
- ☐ 160 Stockholders' Suits
- ☐ 190 Other Contract
- ☐ 195 Contract Product Liability
- ☐ 196 Franchise

REAL PROPERTY

- ☐ 210 Land Condemnation
- ☐ 220 Foreclosure
- ☐ 230 Rent Lease & Ejectment
- ☐ 240 Torts to Land
- ☐ 245 Tort Product Liability
- ☐ 290 All Other Real Property

TORTS

PERSONAL INJURY

- ☐ 310 Airplane
- ☐ 315 Airplane Product Liability
- ☐ 320 Assault, Libel & Slander
- ☐ 330 Federal Employers' Liability
- ☐ 340 Marine
- ☐ 345 Marine Product Liability
- ☐ 350 Motor Vehicle
- ☐ 355 Motor Vehicle Product Liability
- ☐ 360 Other Personal Injury

PERSONAL INJURY

- ☐ 362 Personal Injury - Med. Malpractice
- ☐ 365 Personal Injury - Product Liability
- ☐ 368 Asbestos Personal Injury Product Liability

PERSONAL PROPERTY

- ☐ 370 Other Fraud
- ☐ 371 Truth in Lending
- ☐ 380 Other Personal Property Damage
- ☐ 385 Property Damage Product Liability

CIVIL RIGHTS

- ☐ 441 Voting
- ☐ 442 Employment
- ☐ 443 Housing/ Accommodations
- ☐ 444 Welfare
- ☐ 445 Amer. w/Disabilities - Employment
- ☐ 446 Amer. w/Disabilities - Other
- ☐ 440 Other Civil Rights

PRISONER PETITIONS

- ☐ 510 Motions to Vacate Sentence
- Habeas Corpus:
- ☐ 530 General
- ☐ 535 Death Penalty
- ☐ 540 Mandamus & Other
- ☐ 550 Civil Rights
- ☐ 555 Prison Condition

FO

- ☐ 610 Agriculture
- ☐ 620 Other Food & Drug
- ☐ 625 Drug Related Seizure of Property 21 USC 881
- ☐ 630 Liquor Laws
- ☐ 640 R.R. & Truck
- ☐ 650 Airline Regs.
- ☐ 660 Occupational Safety/Health
- ☐ 690 Other

LABOR

- ☐ 710 Fair Labor Standards Act
- ☐ 720 Labor/Mgmt. Relations
- ☐ 730 Labor/Mgmt.Reporting & Disclosure Act
- ☐ 740 Railway Labor Act
- ☐ 790 Other Labor Litigation
- ☐ 791 Empl. Ret. Inc. Security Act

- ☐ 422 Appeal 28 USC 158
- ☐ 423 Withdrawal 28 USC 157

PROPERTY RIGHTS

- ☐ 820 Copyrights
- ☒ 830 Patent
- ☐ 840 Trademark

SOCIAL SECURITY

- ☐ 861 HIA (1395ff)
- ☐ 862 Black Lung (923)
- ☐ 863 DIWC/DIWW (405(g))
- ☐ 864 SSID Title XVI
- ☐ 865 RSI (405(g))

FEDERAL TAX SUITS

- ☐ 870 Taxes (U.S. Plaintiff or Defendant)
- ☐ 871 IRS—Third Party 26 USC 7609

TUTES

- ☐ 400 State Reapportionment
- ☐ 410 Antitrust
- ☐ 430 Banks and Banking
- ☐ 450 Commerce
- ☐ 460 Deportation
- ☐ 470 Racketeer Influenced and Corrupt Organizations
- ☐ 480 Consumer Credit
- ☐ 490 Cable/Sat TV
- ☐ 810 Selective Service
- ☐ 850 Securities/Commodities/ Exchange
- ☐ 875 Customer Challenge 12 USC 3410
- ☐ 890 Other Statutory Actions
- ☐ 891 Agricultural Acts
- ☐ 892 Economic Stabilization Act
- ☐ 893 Environmental Matters
- ☐ 894 Energy Allocation Act
- ☐ 895 Freedom of Information Act
- ☐ 900Appeal of Fee Determination Under Equal Access to Justice
- ☐ 950 Constitutionality of State Statutes

V. ORIGIN (Place an "X" in One Box Only)

☒ 1 Original Proceeding
☐ 2 Removed from State Court
☐ 3 Remanded from Appellate Court
☐ 4 Reinstated or Reopened
☐ 5 Transferred from another district (specify)
☐ 6 Multidistrict Litigation
☐ 7 Appeal to District Judge from Magistrate Judgment

VI. CAUSE OF ACTION

Cite the U.S. Civil Statute under which you are filing **(Do not cite jurisdictional statutes unless diversity)**:
35 U.S.C. - The Patent Statutue

Brief description of cause:
Patent Infringement

VII. REQUESTED IN COMPLAINT:

☐ CHECK IF THIS IS A CLASS ACTION UNDER F.R.C.P. 23

DEMAND $

CHECK YES only if demanded in complaint:
JURY DEMAND: ☑ Yes ☐ No

VIII. RELATED CASE(S) IF ANY

(See instructions): JUDGE Tarnow DOCKET NUMBER 03-73722

DATE
12/26/2006

SIGNATURE OF ATTORNEY OF RECORD
(P48868)

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RECEIPT # ______ AMOUNT ______ APPLYING IFP ______ JUDGE ______ MAG. JUDGE ______

PURSUANT TO LOCAL RULE 83.11

1. Is this a case that has been previously dismissed? ☐ Yes ☑ No

If yes, give the following information:

Court: ______________________________

Case No.: ______________________________

Judge: ______________________________

2. Other than stated above, are there any pending or previously discontinued or dismissed companion cases in this or any other court, including state court? (Companion cases are matters in which it appears substantially similar evidence will be offered or the same or related parties are present and the cases arise out of the same transaction or occurrence.) ☐ Yes ☑ No

If yes, give the following information:

Court: ______________________________

Case No.: ______________________________

Judge: ______________________________

Notes :