



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p><b>(21) International Application Number:</b> PCT/EP99/10072</p> <p><b>(22) International Filing Date:</b> 15 December 1999 (15.12.99)</p> <p><b>(30) Priority Data:</b> 98204319.2      18 December 1998 (18.12.98)      EP</p> <p><b>(71) Applicant:</b> GLAVERBEL [BE/BE]; Chaussée de la Hulpe, 166, B-1170 Brussels (Watermael-Boitsfort) (BE).</p> <p><b>(72) Inventors:</b> AOMINE, Nobutaka; Asahi Glass Company Limited, 1150, Hazawa-Cho, Kanagawa-ku, Yokohama-shi, Kanagawa 221-8755 (JP). DECROUPET, Daniel; Glaverbel, Centre R &amp; D, rue de l'Aurore 2, B-6040 Jumet (BE). EBISAWA, Junichi; Asahi Glass Company Limited, 1150, Hazawa-Cho, Kanagawa-ku, Yokohama-shi, Kanagawa 221-8755 (JP). NODA, Kazuyoshi; Asahi Glass Company Limited, 426-1, Sumida, Aikawa-machi, Aiko-gun, Kanagawa 243-0301 (JP). TAKEDA, Satoshi; Asahi Glass Company Limited, 1150, Hazawa-cho, Kanagawa-ku, Yokohama-shi, Kanagawa 221-8755 (JP).</p> <p><b>(74) Agents:</b> FARMER, Guy et al.; Glaverbel, Intellectual Property Department, Center R. &amp; D., Rue de l'Aurore, 2, B-6040 Jumet (BE).</p> </td> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p><b>(81) Designated States:</b> AL, AM, AT, AZ, BA, BG, BY, CH, CZ, DE, DK, EE, ES, FI, GB, GE, HR, HU, IS, KG, KZ, LT, LU, LV, MD, MK, NO, PL, PT, RO, RU, SE, SI, SK, TJ, TM, TR, UA, UZ, YU, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p><b>Published</b> <i>With international search report.</i></p> </td> </tr> </table>			<p><b>(21) International Application Number:</b> PCT/EP99/10072</p> <p><b>(22) International Filing Date:</b> 15 December 1999 (15.12.99)</p> <p><b>(30) Priority Data:</b> 98204319.2      18 December 1998 (18.12.98)      EP</p> <p><b>(71) Applicant:</b> GLAVERBEL [BE/BE]; Chaussée de la Hulpe, 166, B-1170 Brussels (Watermael-Boitsfort) (BE).</p> <p><b>(72) Inventors:</b> AOMINE, Nobutaka; Asahi Glass Company Limited, 1150, Hazawa-Cho, Kanagawa-ku, Yokohama-shi, Kanagawa 221-8755 (JP). DECROUPET, Daniel; Glaverbel, Centre R &amp; D, rue de l'Aurore 2, B-6040 Jumet (BE). EBISAWA, Junichi; Asahi Glass Company Limited, 1150, Hazawa-Cho, Kanagawa-ku, Yokohama-shi, Kanagawa 221-8755 (JP). NODA, Kazuyoshi; Asahi Glass Company Limited, 426-1, Sumida, Aikawa-machi, Aiko-gun, Kanagawa 243-0301 (JP). TAKEDA, Satoshi; Asahi Glass Company Limited, 1150, Hazawa-cho, Kanagawa-ku, Yokohama-shi, Kanagawa 221-8755 (JP).</p> <p><b>(74) Agents:</b> FARMER, Guy et al.; Glaverbel, Intellectual Property Department, Center R. &amp; D., Rue de l'Aurore, 2, B-6040 Jumet (BE).</p>	<p><b>(81) Designated States:</b> AL, AM, AT, AZ, BA, BG, BY, CH, CZ, DE, DK, EE, ES, FI, GB, GE, HR, HU, IS, KG, KZ, LT, LU, LV, MD, MK, NO, PL, PT, RO, RU, SE, SI, SK, TJ, TM, TR, UA, UZ, YU, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p><b>Published</b> <i>With international search report.</i></p>
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<p><b>(54) Title:</b> GLAZING PANEL</p> <p><b>(57) Abstract</b></p> <p>A glazing panel carrying a solar control coating stack comprising in sequence at least: a glass substrate base antireflective layer comprises at least one layer comprising a nitride of aluminium an infra-red reflecting layer; and a top antireflective layer. The nitride of aluminium confers, inter alia, good thermal stability on the coating, particularly during heat treatment.</p>				
<div style="display: flex; justify-content: space-between; align-items: flex-start;"> <div style="width: 45%;"> </div> <div style="width: 50%;"> <p>23</p> <p>22</p> <p>20</p> <p>18</p> <p>16</p> <p>14</p> <p>13</p> <p>12</p> <p>10</p> </div> </div>				

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### Glazing Panel

This invention relates to glazing panels and particularly, but not exclusively, to solar control glazing panels which are intended to undergo heat treatment following application of a solar control filter.

EP 233003A describes a glazing panel carrying a sputter coated optical  
5 filter having the structure: glass substrate/  $\text{SnO}_2$  base dielectric/ first metallic barrier of Al, Ti, Zn, Zr or Ta / Ag / second metallic barrier of Al, Ti, Zn, Zr or Ta /  $\text{SnO}_2$  top dielectric. The optical filter is designed to block a significant portion of the incident radiation in the infra red portion of the spectrum whilst allowing passage of a  
10 significant portion of the incident radiation in the visible portion of the spectrum. In this way, the filter acts to reduce the heating effect of incident sunlight whilst allowing good visibility through the glazing and is particularly suitable for car windscreens.

In this type of structure, the Ag layer acts to reflect incident infra red radiation; in order to fulfil this role it must be maintained as silver metal rather than silver oxide and must not be contaminated by adjacent layers. The dielectric layers  
15 which sandwich the Ag layer serve to reduce the reflection of the visible portion of the spectrum which the Ag layer would otherwise provoke. The second barrier serves to prevent oxidation of the Ag layer during sputtering of the overlying  $\text{SnO}_2$  dielectric layer in an oxidising atmosphere; this barrier is at least partially oxidised during this process. The main role of the first barrier is to prevent oxidation of the  
20 silver layer during heat treatment of the coating (e.g. during bending and/or tempering) of the glazing panel by being oxidised itself rather than allowing passage of oxygen to the Ag layer. This oxidation of the barrier during heat treatment provokes an increase in TL of the glazing panel.

EP 792847A discloses a heat treatable solar control glazing panel  
25 which is based on the same principle and has the structure: glass substrate/ ZnO dielectric/ Zn barrier/ Ag / Zn barrier/ ZnO dielectric/ Zn barrier/ Ag / Zn barrier/ ZnO dielectric. The Zn barriers positioned below each of the Ag layers are intended to be oxidised completely during heat treatment and serve to protect the Ag layers from oxidation. As well known in the art, the structure of having two, spaced Ag layers  
30 rather than a single layer Ag layer increases the selectivity of the filter.

EP 718250A discloses the use of a layer which provides a barrier to oxygen diffusion as at least part of the outermost dielectric layer in this type of filter stack. Such a layer must have a thickness of at least 100 Å and preferably at least 200 Å in order to form an effective barrier and may comprise a silicon compound  
35  $\text{SiO}_2$ ,  $\text{SiOxCy}$ ,  $\text{SiOxNy}$ , nitrides like  $\text{Si}_3\text{N}_4$  or  $\text{AlN}$ , carbides like  $\text{SiC}$ ,  $\text{TiC}$ ,  $\text{CrC}$  and  $\text{TaC}$ .

According to one aspect, the present invention provides a glazing panel as defined in Claim 1.

The term "heat treatable glazing panel" as used herein means that the glazing panel carrying the coating stack is adapted to undergo a bending and/or thermal tempering and/or thermal hardening operation and/or other heat treatment process without the haze of the so treated glazing panel exceeding 0.5, and preferably without the haze exceeding 0.3. The term "substantially haze free heat treated glazing panel" as used herein means a glazing panel carrying a coating stack which has been bent and/or thermally tempered and/or thermally hardened and/or subject to another heat treatment process after deposition of the coating stack and has a haze that does not exceed 0.5 and which preferably does not exceed 0.3. Such heat treatment processes may involve heating or exposing the glazing carrying the coating stack or to a temperature greater than about 560 °C, for example, between 560 °C and 700°C in the atmosphere. Other such heat treatment processes may be sintering of a ceramic or enamel material, vacuum sealing of a double glazing unit and calcination of a wet-coated low reflective coating or anti-glare coating. The heat treatment process, especially when this is a bending and/or thermal tempering and/or thermal hardening operation, may be carried out at a temperature of at least, 600 °C for at least 10 minutes, 12 minutes, or 15 minutes, at least 620 °C for at least 10 minutes, 12 minutes, or 15 minutes, or at least 640 °C for at least 10 minutes, 12 minutes, or 15 minutes.

Any suitable method or combination of methods may be used to deposit the coating layers. For example, evaporation (thermal or electron beam), liquid pyrolysis, chemical vapour deposition, vacuum deposition and sputtering, particularly magnetron sputtering, the latter being particularly preferred. Different layers of the coating stack may be deposited using different techniques.

The nitride of aluminium may be pure AlN, substantially pure AlN, AlN containing impurities or AlN containing one or more dopants, for example, chromium and/or silicon and/or titanium, which may improve chemical durability of the material. The nitride of aluminium may contain about 97% pure AlN by weight. Alternatively, it may contain an oxynitride, a carbonitride or an oxycarbonitride. The nitride of aluminium may be deposited by sputtering a target in a nitrogen atmosphere. Alternatively, it may be deposited by sputtering a target in an atmosphere which is a mixture of argon and nitrogen. The target may be, for example, 6061 alloy, 6066 alloy or 4032 alloy.

A nitride of aluminium in the base antireflective layer is believed effective in blocking not only oxygen but also sodium ions and other ions that can

diffuse from the glass into the coating stack and cause a deterioration of optical and electrical properties, particularly if the glazing panel is subjected to heat treatment.

SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are known to be effective barriers to diffusion of sodium ions in sputtered coating stacks. In addition to being easier, quicker and more cost effective to deposit by sputtering, it is believed that a nitride of aluminium as part of the base dielectric layer provides an effective barrier to both sodium ions and oxygen diffusion. Furthermore, it is believed that a nitride of aluminium may provide an effective diffusion barrier at smaller geometrical thicknesses than that required using known materials. For example, good thermal resistance with respect to ion and oxygen diffusion from the glass substrate may be conferred on the coating stack by arranging a nitride of aluminium having a geometrical thickness of greater than 40 Å, for example, about 50 Å as at least part of the base antireflective layer particularly if the coating stack also includes a barrier layer, for example a metal or sub-oxide barrier layer, underlying the infra-red reflecting layer. In the absence of such a barrier layer underlying the infra-red reflecting layer, good thermal resistance with respect to ion and oxygen diffusion from the glass substrate may be conferred on the coating stack by arranging a nitride of aluminium having a geometrical thickness of greater than 50 Å, preferably greater than 80 Å or 90 Å, for example, about 100 Å as at least part of the base antireflective layer. A layer of a nitride of aluminium may confer advantageous properties even if it is less than 195 Å thick.

The coating stack may comprise a barrier layer overlying the infra red reflecting layer and/or a barrier layer underlying the infra red reflecting layer. Such barriers may contain one or more metals and may be deposited, for example, as metal oxides, as metal sub-oxides or as metals.

The ability to block ion and oxygen diffusion from the glass substrate with a relatively thin layer provides great flexibility in the materials and thickness that may be used for the other layers in the coating stack.

Providing a layer of a metal oxide between the nitride of aluminium and the infra-red reflecting material (particularly when this is silver or a silver alloy) may combine the thermal stability properties of the nitride of aluminium with an interposed material which favours crystallisation of the infra-red reflecting material so as to balance the infra red reflecting properties with the haze of the coating stack, particularly when it is subjected to heat treatment. One preferred such oxide is a mixed oxide of zinc and aluminium, preferably with a Al/Zn atomic ratio of about 0.1 to 0.2, especially 0.1 to 0.15. One possible explanation for this may be that the presence of the Al in the zinc oxide structure may reduce the crystal grain growth in the mixed oxide layer.

Heat treatment may provoke an increase in the TL of the glazing panel. A controlled increase in TL may be advantageous in ensuring that TL is sufficiently high for the glazing panel to be used, for example, in a vehicle windscreen. TL may increase in absolute terms during heat treatment by , for example, greater than about 2.5%, greater than about 3%, greater than about 5% , greater than about 8% or greater than about 10%. Heat treatment may also provoke a decrease in the emissivity of the glazing panel.

The effectiveness of a relatively thin layer of the nitride of aluminium in conferring thermal stability allows use of a relatively thick layer of such an oxide.

Both  $\text{Si}_3\text{N}_4$  and  $\text{AlN}$  take longer to deposit by common sputtering techniques than oxides traditionally used in such coatings e.g.  $\text{ZnO}$ ,  $\text{SnO}_2$ . The ability to provide good thermal stability with a relatively thin layer of a nitride of aluminium thus alleviates the deposition of such a layer as a limiting factor in a deposition process.

A nitride of aluminium is also more cost effective to deposit by sputtering than, for example,  $\text{Si}_3\text{N}_4$  and does not require the doping or control precautions required for depositing  $\text{Si}_3\text{N}_4$ .

The optical thickness of the antireflective layers and particularly that of the top antireflective layer is critical in determining the colour of the glazing panel. If a portion of an antireflective layer is oxidised, for example during heat treatment of the glazing panel then, particularly with  $\text{Si}_3\text{N}_4$  (refractive index about 2) the optical thickness can be modified as  $\text{Si}_3\text{N}_4$  may be oxidised to  $\text{SiO}_2$  (refractive index about 1.45). Where the antireflective layer comprises a nitride of aluminium having a refractive index of about 1.7, oxidation of a part of this to  $\text{Al}_2\text{O}_3$  (refractive index about 1.7) will have negligible effect upon the optical thickness of the layer.

The infra red reflecting material may be silver or a silver alloy, for example an alloy of silver containing one or more of Pd, Au, and Cu as an additional material. Such an additional material may be present in the silver alloy in an atomic ratio based on the total amount of silver and additional metal of 0.3 to 10%, preferably 0.3 to 5% and more particularly, especially where the additional material is Pd 0.3 to 2%.

One or more of the antireflective layers may comprise an oxide, a nitride, a carbide or a mixture thereof. For example, the antireflective layer may comprise:

- an oxide of one or more of Zn, Ti, Sn, Si, Al, Ta or Zr; an oxide of zinc containing Al, Ga, Si or Sn or an oxide of indium containing Sn;

- a nitride of one or more of Si, Al and B or a mixture (including a double nitride) of a nitride of Zr or Ti with one of the aforementioned nitrides;
- a double compound, for example, SiOxCy, SiOxNy, SiAlxNy or SiAlxOyNz.

The antireflective layer may be a single layer or it may comprise two or  
 5 more layers having different compositions. An oxide of zinc, preferably a zinc oxide containing at least one of Sn, Cr, Si, B, Mg, In, Ga and preferably Al and/or Ti is particularly preferred as use of these materials may facilitate stable formation of an adjacent infra red reflecting layer with a high crystallinity.

According to another aspect, the present invention provides a glazing  
 10 panel as defined in Claim 5.

The ability to use a layer of a nitride of aluminium which is less than 100 Å in thickness to provide an effective thermal barrier provides significant flexibility in the choice of the overall structure of the top antireflective layer. The layer comprising a nitride of aluminium may be about 85 Å in thickness; this  
 15 provides a compromise between good thermal resistance and thickness. The layer comprising a nitride of aluminium may have a thickness of greater than or equal to about 50 Å, 60 Å or 80 Å; its thickness may be less than or equal to about 85 Å, 90 Å or 95 Å.

According to a further aspect, the present invention provides a method  
 20 of manufacturing a glazing panel as defined in Claim 16. This provides a heat treated glazing panel having a haze of less than about 0.5 and preferably less than about 0.3 suitable for use, for example, in architectural, vehicle and industrial applications.

Examples of the present invention will now be described with  
 25 reference to Fig 1 which is a cross-section through a glazing panel prior to a bending and tempering operation (for ease of representation, the relative thicknesses of the glazing panel and coating layers are not shown to scale).

### Example 1

30 Fig 1 shows a double Ag layer, heat treatable, coating layer deposited on a glass substrate by magnetron sputtering and having the following sequential structure:

	Reference number	Geometrical thickness	Atomic ratios
Glass substrate	10	2 mm	
Base dielectric comprising: AlN	11 12	60 Å	

ZnAlO <sub>x</sub>	13	250 Å	Al/Zn=0.1
ZnAlO <sub>y</sub> underlying barrier	14	10 Å	Al/Zn=0.1
Ag	15	100 Å	
ZnAlO <sub>y</sub> overlying barrier	16	12 Å	Al/Zn=0.1
Central dielectric comprising ZnAlO <sub>x</sub>	17	750 Å	Al/Zn=0.1
ZnAlO <sub>y</sub> underlying barrier	18	7 Å	Al/Zn=0.1
Ag	19	100 Å	
ZnAlO <sub>y</sub> overlying barrier	20	17 Å	Al/Zn=0.1
Top dielectric comprising: ZnAlO <sub>x</sub>	22	185 Å	Al/Zn=0.1
AlN	23	85 Å	

in which ZnAlO<sub>x</sub> is a mixed oxide containing Zn and Al deposited in this example by reactively sputtering a target which is an alloy or mixture of Zn and Al in the presence of oxygen. The ZnAlO<sub>y</sub> barriers are similarly deposited by sputtering a target which is an alloy or mixture of Zn and Al in an argon rich oxygen containing atmosphere to deposit a barrier that is not fully oxidised.

Alternatively, the mixed oxide layer ZnAlO<sub>x</sub> may be formed by sputtering a target which is a mixture of zinc oxide and an oxide of Al, particularly in an argon gas or argon rich oxygen containing atmosphere.

Where the barrier layers comprise the same materials as the mixed oxide layer, particularly the adjacent mixed oxide layer, this may facilitate management of targets and control of deposition conditions and may provide good adhesion between the layers and thus good mechanical durability of the coating stack.

The oxidation state in each of the base, central and top ZnAlO<sub>x</sub> dielectric layers need not necessarily be the same. Similarly, the oxidation state in each of the ZnAlO<sub>y</sub> barriers need not be the same. Equally, the Al/Zn ratio need not be the same for all of the layers; for example, the barrier layers may have a different Al/Zn ratio to the antireflective dielectric layers and the antireflective dielectric layers may have different Al/Zn ratios from each other.

Each overlying barrier protects its underlying silver layer from oxidation during sputter deposition of its overlying ZnAlO<sub>x</sub> oxide layer. Whilst further oxidation of these barrier layers may occur during deposition of their overlying oxide layers a portion of these barriers preferably remains in the form of an



oxide that is not fully oxidised to provide a barrier for subsequent heat treatment of the glazing panel.

This particular glazing panel is intended for incorporation in a laminated vehicle windscreen and displays the following properties:

Property	Prior to heat treatment <small>see Note 1 below</small>	Following heat treatment <small>see Note 2 below</small>
TL(Illuminant A)	63%	76%
TE (System Moon 2)	38%	42%
haze	0.1	0.25
a*	-20 (coated side)	-6 (external)
b*	+3 (coated side)	-12 (external)
RE (System Moon 2)	31% (coated side)	33% (external)

5 Note 1: Measured for monolithic glazing panel with coating prior to heat treatment

Note 2: Measured following heat treatment at 650° C for 10 minutes followed by bending and tempering, and lamination with clear 2mm glass sheet and 0.76mm clear pvb

10 Heat treatment preferably causes substantially complete oxidation of all of the barrier layers such that the structure of the coating stack after heat treatment is:

	Reference number	Geometrical thickness	Atomic ratios
Glass substrate	10	2 mm	
Base dielectric comprising: AlN (partially oxidised)	11		
ZnAlOx	12	60 Å	
	13	250 Å	Al/Zn=0.1
ZnAlOx (oxidised underlying barrier )	14	10 Å - 16 Å	Al/Zn=0.1
Ag	15	100 Å	
ZnAlOx (oxidised overlying barrier)	16	12 Å - 20 Å	Al/Zn=0.1
Central dielectric comprising ZnAlOx	17	750 Å	Al/Zn=0.1
ZnAlOx (oxidised underlying barrier )	18	7 Å - 12 Å	Al/Zn=0.1
Ag	19	100 Å	
ZnAlOx (oxidised overlying barrier)	20	17 Å - 28 Å	Al/Zn=0.1

barrier)			
Top dielectric comprising: ZnAlOx	22	185 Å	Al/Zn=0.1
AlN (partially oxidised)	23	85 Å	

The AlN (partially oxidised) layers may comprise a mixture of AlN and Al<sub>2</sub>O<sub>3</sub>, the AlN being partially oxidised during the heat treatment process. The barrier layers are not necessarily completely oxidised and their thickness will depend to a certain extent upon their degree of oxidation.

5

### Example 2

Example 2 is similar to Example 1, save that the underlying barriers of the coating stack were omitted. The coating stacks and properties of the Example are set out below:

	Reference number	Geometrical thickness	Atomic ratios
Glass substrate	10	2 mm	
Base dielectric comprising: AlN ZnAlOx	11		
	12	100 Å	
	13	200 Å	Al/Zn=0.1
Ag	15	100 Å	
ZnAl overlying barrier	16	10 Å	Al/Zn=0.1
Central dielectric comprising ZnAlOx			
	17	750 Å	Al/Zn=0.1
Ag	19	100 Å	
ZnAl overlying barrier	20	15 Å	Al/Zn=0.1
Top dielectric comprising: ZnAlOx AlN			
	22	185 Å	Al/Zn=0.1
	23	85 Å	

10

in which ZnAlOx is a mixed oxide containing Zn and Al deposited in this example by reactively sputtering a target which is an alloy or mixture of Zn and Al in the presence of oxygen. The ZnAl barriers are similarly deposited by sputtering a target which is an alloy or mixture of Zn and Al in a substantially inert, oxygen free atmosphere.

15

At least a portion of the overlying barriers 16, 20 is oxidised during deposition of their overlying oxide layers. Nevertheless, a portion of these barriers

preferably remains in metallic form, or at least in the form of an oxide that is not fully oxidised to provide a barrier for subsequent heat treatment of the glazing panel.

This particular glazing panel is intended for incorporation in a laminated vehicle windscreen and displays the following properties:

Property	Prior to heat treatment see Note 1 below	Following heat treatment see Note 2 below
TL (Illuminant A)	70%	77%
TE (System Moon 2)	41%	43%
haze	0.1	0.2
a*	-17 (coated side)	-5 (external)
b*	+8 (coated side)	-9 (external)
RE (System Moon 2)	33% (coated side)	34% (external)

5 Note 1: Measured for monolithic glazing panel with coating prior to heat treatment

Note 2: Measured following heat treatment at 625° C for 14 minutes followed by bending and tempering, and lamination with clear 2 mm glass sheet and 0.76mm clear pvb

10 Heat treatment preferably causes substantially complete oxidation of all of the barrier layers such that the structure of the coating stack after heat treatment is:

Coating stack following heat treatment

	Reference number	Geometrical thickness	Atomic ratios
Glass substrate	10	2 mm	
Base dielectric comprising: AlN (partially oxidised)	11		
ZnAlOx	12	100 Å	
	13	200 Å	Al/Zn=0.1
Ag	15	100 Å	
ZnAlOx (oxidised overlying barrier)	16	12 - 20 Å	Al/Zn=0.1
Central dielectric comprising ZnAlOx	17	750 Å	Al/Zn=0.1
Ag	19	100 Å	
ZnAlOx (oxidised overlying barrier)	20	17 - 30 Å	Al/Zn=0.1

Top dielectric comprising: ZnAlO <sub>x</sub>	22	185 Å	Al/Zn=0.1
AlN (partially oxidised)	23	85 Å	

### Example 3

Example 3 is similar to Example 2. The coating stacks and properties of the Example are set out below:

	Reference number	Geometrical thickness	Atomic ratios
Glass substrate	10	2 mm	
Base dielectric comprising: AlN <sub>x</sub> ZnAlO <sub>x</sub>	11		Al/Zn=0.14
	12	110 Å	
	13	240 Å	
Ag	15	100 Å	
ZnAl overlying barrier	16	12 Å	Al/Zn=0.14
Central dielectric comprising ZnAlO <sub>x</sub>			Al/Zn=0.14
	17	750 Å	
Ag	19	100 Å	
ZnAl overlying barrier	20	18 Å	Al/Zn=0.14
Top dielectric comprising: ZnAlO <sub>x</sub> AlN <sub>x</sub>	22	180 Å	Al/Zn=0.14
	23	85 Å	

5 At least a portion of the overlying barriers 16, 20 is oxidised during deposition of their overlying oxide layers. Nevertheless, a portion of these barriers preferably remains in metallic form, or at least in the form of an oxide that is not fully oxidised to provide a barrier for subsequent heat treatment of the glazing panel.

10 This particular glazing panel is intended for incorporation in a laminated vehicle windscreen and displays the following properties:

Property	Prior to heat treatment <sup>see</sup> Note 1 below	Following heat treatment <sup>see</sup> Note 2 below
TL (Illuminant A)		76%
TE (System Moon 2)		43%
haze		0.23
a*	-10 (coated side)	
b*		
RE (System Moon 2)		32% (external)

Note 1: Measured for monolithic glazing panel with coating prior to heat treatment

Note 2: Measured following heat treatment at 645° C for 14 minutes with bending and tempering, and lamination with clear 2 mm glass sheet and 0.76 mm clear pvb

5

#### Examples 4

Example 4 is similar to Example 2. The coating stacks and properties of the Example are set out below:

	Reference number	Geometrical thickness	Atomic ratios
Glass substrate	10	2 mm	
Base dielectric comprising: AlN <sub>x</sub>	11		
	12	100 Å	
ZnAlO <sub>x</sub>	13	220 Å	Al/Zn=0.14
Ag	15	100 Å	
ZnAl overlying barrier	16	12 Å	Al/Zn=0.14
Central dielectric comprising ZnAlO <sub>x</sub>	17	800 Å	Al/Zn=0.14
Ag	19	100 Å	
ZnAl overlying barrier	20	18 Å	Al/Zn=0.14
Top dielectric comprising: ZnAlO <sub>x</sub>	22	180 Å	Al/Zn=0.14
AlN <sub>x</sub>	23	85 Å	

At least a portion of the overlying barriers 16, 20 is oxidised during deposition of their overlying oxide layers. Nevertheless, a portion of these barriers preferably remains in metallic form, or at least in the form of an oxide that is not fully oxidised to provide a barrier for subsequent heat treatment of the glazing panel.

This particular glazing panel is intended for incorporation in a laminated vehicle windscreen and displays the following properties:

Property	Following heat treatment <small>see Note 2 below</small>
TL (Illuminant A)	75.5 %
TE (System Moon 2)	43.4 %
haze	0.21
a*	
b*	
RE (System Moon 2)	31.5 % (external)

Note 2: Measured following heat treatment at 645° C for 14 minutes with bending and tempering, and lamination with clear 2 mm glass sheet and 0.76 mm clear pvb

### Examples 5

5 Example 5 is similar to Example 2. The coating stacks and properties of the Example are set out below:

	Reference number	Geometrical thickness	Atomic ratios
Glass substrate	10	2 mm	
Base dielectric	11		
Comprising: AlN <sub>x</sub>	12	100 Å	
ZnAlO <sub>x</sub>	13	220 Å	Al/Zn=0.05
Ag-Pd	15	100 Å	Pd/Ag=0.005
ZnAl overlying barrier	16	12 Å	Al/Zn=0.05
Central dielectric			
Comprising ZnAlO <sub>x</sub>	17	800 Å	Al/Zn=0.05
Ag-Pd	19	100 Å	Pd/Ag=0.005
ZnAl overlying barrier	20	18 Å	Al/Zn=0.05
Top dielectric comprising:			
ZnAlO <sub>x</sub>	22	180 Å	Al/Zn=0.05
AlN <sub>x</sub>	23	85 Å	

At least a portion of the overlying barriers 16, 20 is oxidised during deposition of their overlying oxide layers. Nevertheless, a portion of these barriers preferably remains in metallic form, or at least in the form of an oxide that is not fully oxidised to provide a barrier for subsequent heat treatment of the glazing panel.

10 This particular glazing panel is intended for incorporation in a laminated vehicle windscreen and displays the following properties:

Property	Following heat treatment <sup>see Note 2 below</sup>
TL (Illuminant A)	75.2 %
TE (System Moon 2)	42.9 %
haze	0.24
a*	
b*	
RE (System Moon 2)	31.4 % (external)

Note 2: Measured following heat treatment at 645° C for 14 minutes with bending and tempering, and lamination with clear 2 mm glass sheet and 0.76 mm clear pvb

Additional layers may be introduced above, below or between the film stacking arrangement if desired without departing from the invention.

5 In addition to the advantageous optical properties that may be obtained, each of the examples provides a coating layer which may be electrically heated, for example, in an electrically heated car windscreen to provide a de-misting and/or de-frosting function with the addition of suitably placed electrical connectors.

10 The colour co-ordinates of the examples are particularly suited to car windscreens as they give a neutral or slightly blue or slightly green appearance in reflection when the windscreen is mounted at an angle in the car body. For other applications, for example architectural applications, the colour in reflection may be adjusted as is known in the art by adjusting the thicknesses of the dielectric layers and/or silver layer(s).

15 The TL of the glazing panel may be adjusted to suit the desired application. For example

- if the glazing panel is to be used as a windscreen for the European market, TL may be selected to be greater than 75% (as required by European regulations).
- 20 • if the glazing panel is to be used as a windscreen for the US market, TL may be selected to be greater than 70% (as required by US regulations).
- if the glazing panel is to be used as a vehicle front sidelight, TL may be adjusted to be greater than 70% (as required by European regulations).
- 25 • if the glazing panel is to be used as a vehicle rear sidelight or a rear window for a vehicle, TL may be selected to be between about 30% and 70%.

Such adjustment of TL may be achieved, for example,

- 30 • by adapting the thicknesses of the layers of the coating stack, in particular the thicknesses of the dielectric layers and/or the infra-red reflecting layer(s).
- by combining the coating stack with a tinted glass substrate.
- by combining the coating stack with a tinted pvb or other laminating materials.

35

### Glossary

Unless otherwise indicated by the context, the terms listed below have the following meanings in this specification:

a*		colour co-ordinate measured on the CIELab scale at normal incidence
Ag	silver	
Al	aluminium	
Al <sub>2</sub> O <sub>3</sub>	aluminium oxide	
AlN	aluminium nitride	
b*		colour co-ordinate measured on the CIELab scale at normal incidence
Bi	bismuth	
Cr	chromium	
haze		the percentage of transmitted light which in passing through the specimen deviates from the incident beam by forward scattering, as measured in accordance with the ASTM Designation D 1003-61 (Reapproved 1988).
Hf	hafnium	
infra red reflecting material		a material that has a reflectance higher than the reflectance of sodalime glass in the band of wavelengths between 780 nm and 50 microns
Na	sodium	
Nb	niobium	
NiCr		an alloy or mixture comprising nickel and chromium
NiTl		an alloy or mixture comprising nickel and titanium
RE	energetic reflection	the solar flux (luminous and non-luminous) reflected from a substrate as a percentage of the incident solar flux
Sb	antimony	
selectivity		the ratio of the luminous transmittance to the solar factor i.e. TL/TE
SiO <sub>2</sub>	silicon oxide	
Si <sub>3</sub> N <sub>4</sub>	silicon nitride	
SnO <sub>2</sub>	tin oxide	
Ta	tantalum	
TE	energetic transmittance	the solar flux (luminous and non-luminous) transmitted through a substrate as a percentage of the incident solar flux
Ti	titanium	
TL	luminous transmittance	the luminous flux transmitted through a substrate as a percentage of the incident luminous flux
Zn	zinc	
ZnAl		an alloy or mixture comprising zinc and aluminium
ZnAlOx		a mixed oxide containing zinc and aluminium
ZnAlOy		a partially oxidised mixture comprising zinc and aluminium
ZnO	zinc oxide	
ZnTi		an alloy or mixture comprising zinc and titanium
ZnTiOx		a mixed oxide containing zinc and titanium
ZnTiOy		a partially oxidised mixture comprising zinc and titanium
Zr	zirconium	

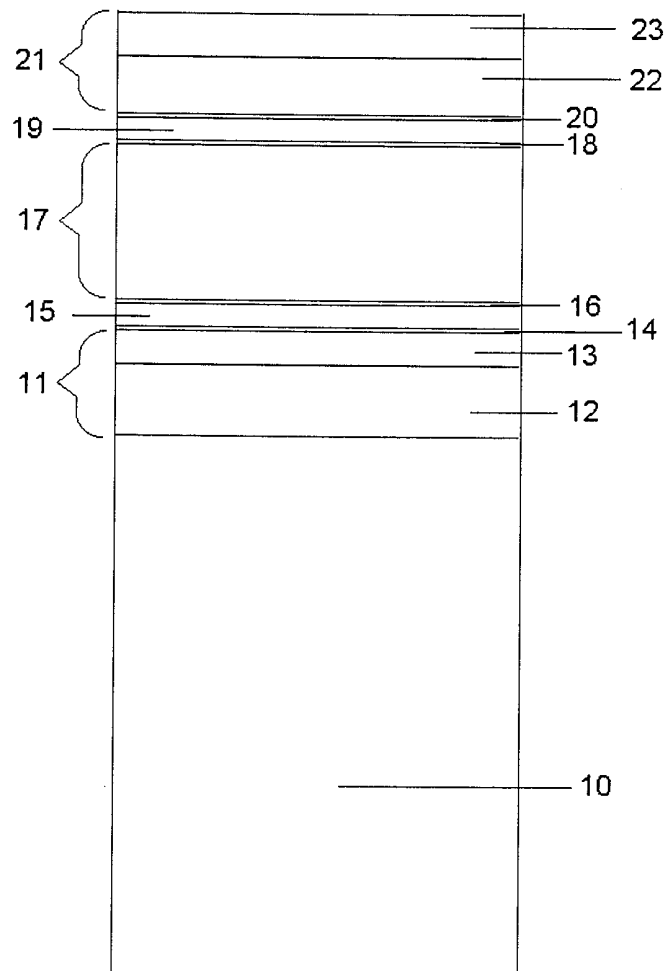


Claims

1. A heat treatable or substantially haze free heat treated glazing panel carrying a coating stack comprising in sequence at least :  
5 a glass substrate  
a base antireflective layer comprising at least one layer comprising a nitride of aluminium  
an infra-red reflecting layer, and  
a top antireflective layer  
10 characterised in that heat treatment of the heat treatable glazing panel to form a substantially haze free heat treated glazing panel provokes an increase of the value of TL of the glazing panel of at least 2.5%..
2. A heat treatable or substantially haze free heat treated glazing panel in  
15 accordance with Claim 1 comprising in sequence at least:  
a glass substrate  
a base antireflective layer comprising at least one layer comprising a nitride of aluminium  
an infra-red reflecting layer  
20 a central antireflective layer  
an infra-red reflecting layer  
a top antireflective layer  
characterised in that heat treatment of the heat treatable glazing panel to form a substantially haze free heat treated glazing panel provokes an  
25 increase of the value of TL of the glazing panel of at least 2.5%..
3. A heat treatable or substantially haze free heat treated glazing panel in  
accordance with Claim 1 or Claim 2, in which the at least one layer  
comprising a nitride of aluminium has a geometrical thickness greater than  
30 40 Å.
4. A heat treatable or substantially haze free heat treated glazing panel in  
accordance with any preceding claim, in which the at least one layer  
comprising a nitride of aluminium has a geometrical thickness less than 195  
35 Å.

5. A heat treatable or substantially haze free heat treated glazing panel carrying a solar control coating stack comprising in sequence at least :  
a glass substrate  
a base antireflective layer  
5 an infra-red reflecting layer, and  
a top antireflective layer  
characterised in that the top antireflective layer comprises at least one layer comprising a nitride of aluminium having a geometrical thickness of less than 100 Å.
- 10 6. A heat treatable or substantially haze free heat treated glazing panel in accordance with any preceding claim, in which the base antireflective layer and the top antireflective layer each comprises at least one layer comprising a nitride of aluminium.
- 15 7. A heat treatable or substantially haze free heat treated glazing panel in accordance with any preceding claim, in which each antireflective layer comprises at least one layer comprising a nitride of aluminium.
- 20 8. A heat treatable or substantially haze free heat treated glazing panel in accordance with any preceding claim, in which the base antireflective layer comprises a first layer adjacent to the substrate comprising a nitride of aluminium and an overlying layer comprising a metal oxide.
- 25 9. A heat treatable or substantially haze free heat treated glazing panel in accordance with any preceding claim, in which the top antireflective layer comprises a first layer of a metal oxide and an overlying layer comprising a nitride of aluminium.
- 30 10. A heat treatable or substantially haze free heat treated glazing panel in accordance with Claim 8 or Claim 9, in which the layer of a metal oxide is a layer of a mixed oxide of zinc and aluminium.
- 35 11. A heat treatable or substantially haze free heat treated glazing panel in accordance with claim 10, in which the mixed oxide of zinc and aluminium has an atomic ratio Al/Zn of greater than or equal to 0.05 and less than or equal to 0.25.

12. A heat treatable or substantially haze free heat treated glazing panel in accordance with any preceding claim, in which heat treatment of the heat treatable glazing panel to form the substantially haze free heat treated glazing panel provokes an increase of the value of TL of the glazing panel of at least 2.5%.
13. A heat treatable or substantially haze free heat treated glazing panel in accordance with any preceding claim, in which heat treatment of the heat treatable glazing panel to form the substantially haze free heat treated glazing panel provokes an increase of the value of TL of the glazing panel of at least 7%.
14. A heat treatable or substantially haze free heat treated glazing panel in accordance with any preceding claim, in which the nitride of aluminium is substantially pure AlN.
15. A heat treatable or substantially haze free heat treated glazing panel in accordance with any one of claims 1 to 13, in which the nitride of aluminium contains at least 90% and preferably at least 95% pure AlN by weight.
16. A method of manufacturing a glazing panel having a haze of less than about 0.5 comprising the step of subjecting a glazing panel in accordance with any preceding claim to a heat treatment process at at least 570 °C.

Fig 1

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 99/10072

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C03C17/36

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 718 250 A (SAINT GOBAIN VITRAGE) 26 June 1996 (1996-06-26) cited in the application claims	1-8, 14-16
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

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- "O" document referring to an oral disclosure, use, exhibition or other means
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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/10072

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Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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