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Substrate, in particular glass substrate, supporting a photocatalytic layer coated with a protective thin layer

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(54) Title: SUBSTRATE, IN PARTICULAR GLASS SUBSTRATE, SUPPORTING A PHOTOCATALYTIC LAYER COATED  
WITH A PROTECTIVE THIN LAYER

(54) Titre : SUBSTRAT, NOTAMMENT SUBSTRAT VERRIER, PORTANT UNE COUCHE A PROPRIÉTÉ PHOTOCATALY-  
TIQUE REVETUE D'UNE COUCHE MINCE PROTECTRICE

(57) Abstract: The invention relates to a structure, comprising a substrate supporting a layer with a photocatalytic and anti-soiling property, said layer being based on titanium dioxide (TiO<sub>2</sub>), on at least part of the surface thereof. Said structure is characterised in that the photocatalytic layer is coated with a non-porous thin layer, containing silicon and oxygen and having a coating capacity, providing a chemical and mechanical protection to the underlying photocatalytic layer, whilst maintaining the TiO<sub>2</sub> photocatalytic activity.

(57) Abrégé : Structure comprenant un substrat portant, sur au moins une partie de sa surface, une couche à propriété photocatalytique, anti-salissures, à base de dioxyde de titane (TiO<sub>2</sub>), caractérisée par le fait que ladite couche à propriété photocatalytique est revêtue par une couche mince à teneur en silicium et en oxygène, à pouvoir couvrant, non poruse, apte à assurer une protection mécanique et chimique de la couche photocatalytique sous-jacente en maintenant l'activité photocatalytique de TiO<sub>2</sub>.

WO 2005/040056 A3

5 SUBSTRATE, IN PARTICULAR GLASS SUBSTRATE, SUPPORTING A  
PHOTOCATALYTIC LAYER COATED WITH A PROTECTIVE THIN  
LAYER

The present invention relates to substrates, such as glass, glass-ceramic or plastic substrates, which have been provided with a photocatalytic coating in order to give them what is called an "antisoiling or self-cleaning" function.

One important application of these substrates relates to glazing, which may be applied in very many different situations - from utilitarian glazing to glazing used in domestic electrical appliances, from automotive glazing to architectural glazing.

20 It also applies to reflective glazing of the mirror type (domestic mirrors or driving mirrors) and to opacified glazing of the lightened type.

Similarly, the invention also applies to nontransparent substrates, such as ceramic substrates or any other substrate that may in particular be used as architectural material (metal, tiling, etc.). Preferably, it applies, irrespective of the nature of the substrate, to substantially flat or slightly curved substrates.

Photocatalytic coatings have already been studied, especially those based on titanium oxide crystallized in anatase form. Their capability of degrading any soiling of organic origin or microorganisms through the action of UV radiation is very beneficial. They also often have a hydrophilic character, allowing mineral

soiling to be removed by spraying it with water or, in the case of exterior glazing, by rain.

This type of coating exhibiting antisoiling, 5 bactericidal or algicidal properties has already been described, for example in patent WO 97/10186, which describes several embodiments thereof.

If it is not protected, the photocatalytic layer is 10 worn away over the course of time, this being manifested by a loss of its activity, loss of optical quality of the structure (appearance of haze or coloration), or even delamination of the layer.

15 If the thickness of the photocatalytic layer decreases, the coloration liable to appear when this layer is partially impaired will be less intense and the color change will be less over the course of time. However, this reduction in thickness will be to the detriment of 20 the performance of the layer.

It is therefore necessary to provide the layer with mechanical and chemical protection, the thickness of 25 the protective layer having to be small so that the photocatalytic layer fully retains its function.

European patent application EP-A-0 820 967 discloses an antifogging element comprising a transparent substrate, a transparent film of a photocatalyst formed on the 30 transparent substrate, and a transparent porous mineral oxide film formed on the photocatalyst film and having a surface exhibiting a hydrophilic property.

Japanese patent JP 2002 047 032 also discloses a 35 process for manufacturing a substrate coated with a photocatalytic membrane, which comprises the steps consisting in spraying nanoparticles of  $TiO_2$  of anatase crystalline structure with a size of 5-10 nm using a

spray gun, in heating and in depositing, by sputtering, an  $\text{SiO}_2$  membrane covering the  $\text{TiO}_2$  particles.

None of these structures is satisfactory, the first because of  
5 the porous nature of the protective coating, which, because of  
the presence of pores, provides insufficient protection of the  
catalytic layer, and the second because of an insufficient  
amount of photocatalytic material, which does not form a  
continuous layer.

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According to the present invention there is provided a structure comprising a substrate bearing, on at least part of a surface of the substrate, a photocatalytic antisoiling layer based on titanium dioxide ( $\text{TiO}_2$ ), characterized in that said  
15 photocatalytic layer being coated with a thin nonporous layer, containing silicon and oxygen and having a covering power, capable of mechanically and chemically protecting the underlying photocatalytic layer, while maintaining the photocatalytic activity of the  $\text{TiO}_2$  and wherein there is located immediately  
20 below the  $\text{TiO}_2$ -based layer, an underlayer having a crystallographic structure for assisting in the crystallization, by heteroepitaxial growth, in the anatase form of the  $\text{TiO}_2$ -based upper layer.

25 According to the present invention there is provided a process for manufacturing a structure in which a doped  $\text{TiO}_2$  layer is deposited on a substrate made of glass or glass-ceramic or polycarbonate-type hard plastic, of the sheet type, or on glass or glass-ceramic fibers, said doped  $\text{TiO}_2$  layer being subjected  
30 to a heat treatment in order to provide a photocatalytic property if the photocatalytic property is not provided by conditions for depositing the doped  $\text{TiO}_2$  layer, and depositing a thin layer containing silicon and

3a

oxygen as defined in one of claims 1 to 15 on said photocatalytic layer.

The conditions for forming the titanium-dioxide-based layer -  
5 such as the nature and purity of the starting products, optional solvent, heat treatment - have to be adapted in a known manner for the purpose of obtaining the photocatalytic antisoiling property.

10 Preferably, said thin layer containing silicon and oxygen is present in the form of a continuous film. In particular, said thin layer is advantageously in the form of a film that conforms to the surface asperities of the underlying photocatalytic layer.

15 The thin layer containing silicon and oxygen is in particular a layer of at least one silicon-oxygen

compound chosen from  $\text{SiO}_2$ ,  $\text{SiOC}$ ,  $\text{SiON}$ ,  $\text{SiO}_x$ , where  $x < 2$ , and  $\text{SiOCH}$ ,  $\text{SiO}_2$  being particularly preferred.

According to an advantageous embodiment of the  
5 structure according to the present invention, the thin  
layer containing silicon and oxygen is a layer of at  
least one silicon-oxygen compound to which at least a  
compound chosen from  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  is associated, such  
a compound being chemically inert and enhancing the  
10 hydrolytic resistance. The role of  $\text{Al}_2\text{O}_3$ , a well-known  
inert oxide which increases the chemical resistance of  
the assembly may be emphasized.

The  $(\text{Al and/or Zr})/\text{Si}$  atomic ratio does not generally  
15 exceed 1, the  $\text{Al}/\text{Si}$  ratio being advantageously between  
0.03 and 0.5, in particular between 0.05 and 0.1, and  
the  $\text{Zr}/\text{Si}$  ratio being between 0.05 and 0.4.

The thin layer containing silicon and oxygen may have a  
20 thickness of at most 15 nm, especially at most 10 nm  
and in particular at most 8 nm, being preferably at  
most 5 nm, or about 5 nm, in particular 2 to 3 nm.

Said thin layer provides a lubricating effect and a  
25 mechanical role, by improving the scratch and abrasion  
resistance.

This greater mechanical resistance and this better  
chemical resistance are, however, not obtained to the  
30 detriment of a reduction in photocatalytic activity.  
This is because, although it might be expected that the  
photocatalytic activity of the  $\text{TiO}_2$ -based layer finally  
obtained would be reduced owing to the masking of the  
latter by the  $\text{SiO}_2$  overlayer, this photocatalytic  
35 activity is preserved, and even improved - any soiling,  
being diluted in a uniform film of  $\text{SiO}_2$ , owing to the  
hydrophilicity of the latter, is more easily destroyed  
by  $\text{TiO}_2$ .

The titanium dioxide-based layer consists of  $TiO_2$  alone or of  $TiO_2$  doped with at least one dopant chosen especially from: N; pentavalent cations such as Nb, Ta and V; Fe; and Zr. This  $TiO_2$ -based layer may have been deposited by a sol-gel method or by a 5 pyrolysis, especially chemical vapor deposition, method or by sputtering, at room temperature, where appropriate magnetron and/or ion-beam sputtering, using a metal or  $TiO_x$  target, where  $x < 2$ , and in an oxidizing atmosphere, or using a  $TiO_2$  target in an inert atmosphere, the  $TiO_2$  produced by the sputtering then 10 having possibly being subjected to a heat treatment so as to be in the crystallized state in a photocatalytically active form.

The thin layer containing silicon and oxygen has in particular been deposited by room-temperature vacuum sputtering, at, where 15 appropriate magnetron and/or ion-beam sputtering, using a target of Al (8 at%)-doped Si in an  $Ar/O_2$  atmosphere at a pressure of 0.2 Pa.

The structure according to the present invention includes, 20 immediately below the  $TiO_2$ -based layer, an underlayer having a crystallographic structure for assisting in the crystallization, by heteroepitaxial growth, in the anatase form of the  $TiO_2$ -based upper layer, especially an underlayer consisting of  $ATiO$ , where A denotes barium or strontium. The thickness of this underlayer 25 is not critical - for example, it may be between 10 nm and 100 nm.

The substrate consists for example of a sheet, whether plane or having curved faces, of monolithic or laminated glass, glass- 30 ceramic or a hard thermoplastic, such as polycarbonate, or else of glass or glass-ceramic fibers, said sheets or said fibers having, where appropriate, received at least one other functional layer before application of the  $TiO_2$ -based layer or

of a layer for assisting in the crystallization of the latter by heteroepitaxial growth. (In the case of more than one layer, this may also be referred to as a stack or multilayer).

5 The applications of the sheets were mentioned above. As regards applications of the fibers, mention may be made of air or water filtration, and also bactericidal applications.

10 The functional layer or the other functional layers are chosen from layers having an optical functionality, thermal control layers or conducting layers, and also, if the substrate is made of glass or glass-ceramic, layers acting as a barrier to the migration of alkali metals from the glass or from the glass-ceramic.

15 The layers having an optical functionality are especially antireflection layers, light radiation filtration layers, coloration filtration layers, scattering layers, etc.  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{TiO}_2$ ,  $\text{SnO}_2$ ,  $\text{ZnO}$  layers may be mentioned.

20 The thermal control layers are especially solar control layers or what are called "low-e" (low-emissivity) layers.

25 The conducting layers are especially heating layers, antenna layers or antistatic layers - arrays of conducting wires may be included in these layers.

30 If the substrate is made of glass or glass-ceramic, at least one functional layer acting as a barrier to the migration of alkali metals from the glass or glass-ceramic may be placed beneath the photocatalytic layer or beneath the underlayer for assisting in the crystallization of the latter, if such an underlayer is provided. The other functional layers (having an optical

functionality, thermal control or conducting layers) when they are present are on top of the barrier layer or layers.

Alkali metals are liable to migrate as a result of applying 5 temperatures in excess of 600°C. Such layers forming a barrier to alkali metals during subsequent heat treatments are known, and mention may be made of SiO<sub>2</sub>, SiOC, SiO<sub>x</sub>N<sub>y</sub> and Si<sub>3</sub>N<sub>4</sub> layers, having a thickness for example of at least 5 or 10 nm, and in many cases of at least 50 nm, as described in PCT international 10 application WO 02/24971.

As an example, mention may be made of glass or glass-ceramic substrates, especially of the sheet type, that have received a 15 layer forming a barrier to the migration of alkali metals from the glass or glass-ceramic, followed by a monolayer, bilayer or trilayer of optical functionality.

The subject of the present invention is also a process for manufacturing such a structure as defined above, characterized 20 in that in one form an optionally doped TiO<sub>2</sub> layer is deposited on a substrate made of glass or glass-ceramic or polycarbonate-type hard plastic, of the sheet type, or on glass or glass-ceramic fibers, said optionally doped TiO<sub>2</sub> layer being subjected to a heat treatment in order to give it a photocatalytic 25 property if this is not provided by the conditions used for depositing it, and then a thin layer containing silicon and oxygen as defined above is deposited on said photocatalytic layer.

30 In particular, the deposition of a TiO<sub>2</sub> layer and that of the thin layer containing silicon and oxygen are carried out in succession at room temperature, by vacuum sputtering, where

appropriate magnetron and/or ion-beam sputtering, in the same chamber, the conditions being the following:

- for depositing the  $TiO_2$ -based layer, supply in AC or DC mode, at a pressure of 1-3 mbar and in an oxygen/inert gas
- 5 (argon) atmosphere, using a Ti or  $TiO_x$  target, where  $x = 1.5$  to 2; and
- for depositing the layer containing silicon and oxygen, supply in AC mode at a pressure of 0.1 to 1.0 Pa and in an  $Ar/O_2$  atmosphere using a target having a high silicon content,
- 10 the deposition of the  $TiO_2$  layer being optionally preceded by the deposition of an underlayer for assisting in the crystallization by epitaxial growth in the anatase form of the  $TiO_2$  layer.
- 15 The conditions for depositing a nonporous layer containing silicon and oxygen are known to those skilled in the art, being especially low-pressure and high-power conditions (Thornton diagram).
- 20 In the case in which the coating is applied to a glass or glass-ceramic substrate, provision may be made, before application of the  $TiO_2$  layer or of the underlayer associated therewith, for at least one layer forming a barrier to the migration of alkali metals present in the glass or glass-ceramic to be deposited on
- 25 the substrate, an annealing or toughening operation then possibly being carried out, after the  $TiO_2$  layer and the thin silicon-based layer covering the latter have been deposited, at a temperature of between 250°C and 550°C, preferably between 350°C and 500°C, in the case of the annealing operation and at a
- 30 temperature of at least 600°C in the case of the toughening operation.

2004283938 07 Jun 2010

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It is also possible according to the invention to provide, after the optional application of at least one layer forming a barrier to the migration of alkali metals and before application of the  
5 TiO<sub>2</sub> layer or the underlayer associated with the latter, for at least one functional layer chosen from layers having an optical functionality, thermal control layers or conducting layers to be deposited, said functional layers being

2281776\_1 (GHNMatters) 7/06/10

advantageously deposited by vacuum sputtering, where appropriate magnetron and/or ion-beam sputtering.

The present invention also relates to single or 5 multiple glazing, in particular for motor vehicles or buildings, comprising, on at least one face, a structure according to the invention as defined above, said face being especially that facing the outside, or possibly also that facing the inside.

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Those faces of this glazing that do not have the structure of the present invention may include at least one other functional layer.

15 Such glazing is applicable as "self-cleaning" glazing, especially antifogging, anticondensation and antisoiling glazing, especially as architectural glazing of the double-glazing type, automotive glazing of the windshield, rear window and side windows of 20 automobiles, driving mirrors, glazing for trains, airplanes and ships, utilitarian glazing, such as glass for aquariums, shop windows, greenhouses, interior furnishing, urban furniture (bus shelters, advertising panels, etc.), mirrors, screens for display systems of 25 the computing, television or telephone type, electrically controllable glazing, such as electrochromic or liquid-crystal glazing, electroluminescent glazing and photovoltaic glazing.

30 The following examples illustrate the present invention without however limiting the scope thereof.

Examples 1a and 1b (according to the invention):  
Glass/Al:SiO<sub>2</sub>/TiO<sub>2</sub>/Al:SiO<sub>2</sub> stack

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The following successive layers were deposited on a sheet of glass 4 mm in thickness:

- an Al-doped SiO<sub>2</sub> underlayer 150 nm in thickness;

- a  $\text{TiO}_2$  layer 100 nm in thickness (Example 1a) or 20 nm in thickness (Example 1b); and
- an Al-doped  $\text{SiO}_2$  overlayer 2 nm in thickness.

5 The  $\text{Al:SiO}_2$  underlayer was deposited using an  $\text{Al:Si}$  target (containing 8 at% aluminum) with a power of 2000 W, with the following gas flow rates : 15 sccm Ar and 15 sccm  $\text{O}_2$ , and at a pressure of  $2 \times 10^{-3}$  mbar.

10 The  $\text{TiO}_2$  layer was deposited using a  $\text{TiO}_x$  target with a power of 2000 W, with the following gas flowrates: 200 sccm Ar and 2 sccm  $\text{O}_2$  and at a pressure of  $23 \times 10^{-3}$  mbar.

15 The  $\text{Al:SiO}_2$  overlayer was deposited using an  $\text{Al:Si}$  target (containing 8 at% Al) with a power of 1000 W, with the following gas flowrates: 15 sccm Ar and 15 sccm  $\text{O}_2$  and at a pressure of  $2 \times 10^{-3}$  mbar.

20 Examples 2 and 2b (comparative examples): Glass/ $\text{Al:SiO}_2$ / $\text{TiO}_2$  stack

The same stacks as in Examples 1a and 1b were manufactured except that the  $\text{Al:SiO}_2$  overlayer was omitted.

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Example 3 (comparative example): Glass/ $\text{Al:SiO}_2$ / $\text{TiO}_2$ / $\text{Al:Si}_3\text{N}_4$  stack

30 The same stack as in Example 1a was manufactured, except that instead of the  $\text{Al:SiO}_2$  overlayer, an  $\text{Al:Si}_3\text{N}_4$  overlayer was deposited, again with a thickness of 2 nm, using an  $\text{Al:Si}$  target (containing 8 at% Al) with a power of 1000 W, with the following gas flow

35 rates: 18 sccm Ar and 12 sccm  $\text{N}_2$  and at a pressure of  $2 \times 10^{-3}$  mbar.

Example 4 : Resistance to the Opel test

Considerable improvement in the resistance to the Opel test (dry rubbing of the surface of the stack using a felt pad) was observed when going from the stack of Example 2a to the stack of Example 1a.

5.

No change was observed ongoing from the stack of Example 2a to the stack of Example 3.

Moreover, before and after the above Opel test, the 10 photocatalytic activity of the  $\text{TiO}_2$  layer was evaluated for each of the stacks of Examples 1a, 2a and 3 according to the stearic acid photodegradation test (SAT) followed by infrared transmission, described in PCT international application WO 00/75087.

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The results are given in Table I. Also shown in this table are the colorimetric change in reflection on the layer side due to the Opel test ( $\Delta E$ ), the haze induced by the Opel test and the observation regarding the 20 delamination of the layer after the Opel test.

TABLE I

Example	SAT ( $\text{cm}^{-1} \cdot \text{min}^{-1}$ )		$\Delta E$	Haze (%)	Delamination
	Before Opel test	After Opel test			
1a (invention)	$59 \times 10^{-3}$	$41 \times 10^{-3}$	2.0	0.5	no
2a (comparative)	$54 \times 10^{-3}$	$25 \times 10^{-3}$	9.3	9.3	yes
3 (comparative)	$40 \times 10^{-3}$	$15 \times 10^{-3}$	10.0	12	yes

Example 5 : Taber Test

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An improvement in the resistance to the Taber test (abrasion resistance = resistance to the passage of an abrasive wheel) was observed on going from the stack of Example 2b to the stack of Example 1b.

The layer of Example 2b delaminated after 500 revolutions in the Taber test. For the stack of Example 1b, a 0.8% haze was observed after 200 revolutions in the Taber test and 2% haze after 500 revolutions in the Taber test.

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Example 6 : NSF Test

An improvement in the resistance to the NSF (neutral salt fog) test was observed on going from the stack of Example 2a to the 10 stack of Example 1a.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word

15 "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

20 It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

2004283938 07 Jun 2010

13

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A structure comprising a substrate bearing, on at least part of a surface of the substrate, a photocatalytic antisoiling 5 layer based on titanium dioxide ( $TiO_2$ ), said photocatalytic layer being coated with a thin nonporous layer, containing silicon and oxygen and having a covering power, capable of mechanically and chemically protecting the underlying photocatalytic layer, while maintaining the photocatalytic 10 activity of the  $TiO_2$  and wherein there is located immediately below the  $TiO_2$ -based layer, an underlayer having a crystallographic structure for assisting in the crystallization, by heteroepitaxial growth, in the anatase form of the  $TiO_2$ -based upper layer.
- 15 2. The structure as claimed in claim 1, in which said thin layer containing silicon and oxygen is present in the form of a continuous film.
- 20 3. The structure as claimed in claim 1 or 2, in which the thin layer containing silicon and oxygen is a layer of at least one silicon-oxygen compound chosen from  $SiO_2$ ,  $SiOC$ ,  $SiON$ ,  $SiO_x$ , where  $x < 2$ , or  $SiOCH$ .
- 25 4. The structure as claimed in any one of claims 1 to 3, in which the thin layer containing silicon and oxygen is a layer of at least one silicon-oxygen compound with which at least one compound chosen from  $Al_2O_3$  or  $ZrO_2$  is associated.
- 30 5. The structure as claimed in claim 4, in which the  $Al/Si$  ratio is between 0.03 and 0.5.

2281776\_1 (GRHMatters) 7/06/10

6. A structure as claimed in any one claims 1 to 5 in which the thin layer containing silicon and oxygen has a thickness of at most 5nm.

5 7. A structure as claimed in claim 6 in which the thin layer containing silicon and oxygen has a thickness of about 2 to 3nm.

8. The structure as claimed in any one of claims 1 to 7, in which the titanium dioxide-based layer consists of  $TiO_2$  alone or 10 of  $TiO_2$  doped with at least one dopant chosen from: N pentavalent cations, Fe and Zr.

9. The structure as claimed in claim 8 in which the pentavalent cation is Nb, Ta or V.

15 10. The structure as claimed in any one of claims 1 to 9, in which the  $TiO_2$ -based layer has been deposited by a sol-gel method or by a pyrolysis method or by room-temperature vacuum sputtering.

20 11. The structure as claimed in claim 10 in which the  $TiO_2$ -based layer has been deposited by chemical vapour deposition.

12. The structure as claimed in claim 10 or 11 in which the 25  $TiO_2$  produced by sputtering is subjected to a heat treatment so as to be in the crystallised state in a photocatalytically active form.

13. The structure as claimed in any one of claims 1 to 12 in which the under layer consists of  $ATiO_3$ , where A denotes barium or strontium.

5 14. The structure as claimed in any one of claims 1 to 13, in which the substrate consists of a sheet, whether plane or having curved faces, of monolithic or laminated glass, glass-ceramic or a hard thermoplastic.

10 15. A structure as claimed in claim 14 in which the said sheets or said fibers have received at least one other functional layer before application of the  $TiO_2$ -based layer or of a layer for assisting in the crystallization of the  $TiO_2$ -based layer.

15

16. The structure as claimed in claim 14 or 15, in which the functional layer or the other functional layers are chosen from layers having an optical functionality, thermal control layers and conducting layers.

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17. A structure as claimed in claim 16 in which if the substrate is made of glass-ceramic, layers acting as a barrier to the migration of alkali metals from the glass or from the glass-ceramic are included as a functional layer.

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18. A process for manufacturing a structure as defined in any one of claims 1 to 17, in which a doped  $TiO_2$  layer is deposited on a substrate made of glass or glass-ceramic or polycarbonate-type hard plastic, of the sheet type, or on glass or glass-ceramic fibers, said doped  $TiO_2$  layer being subjected to a heat treatment in order to provide a photocatalytic property if the

photocatalytic property is not provided by conditions for depositing the doped TiO<sub>2</sub> layer, and depositing a thin layer containing silicon and oxygen as defined in one of claims 1 to 15 on said photocatalytic layer.

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19. The process as claimed in claim 18, in which the deposition of the TiO<sub>2</sub> layer and of the thin layer containing silicon and oxygen are carried out in succession at room temperature, by vacuum sputtering.

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20. A process as claimed in claim 19 in which the deposition of the TiO<sub>2</sub> layer is preceded by the deposition of an underlayer for assisting in the crystallization by epitaxial growth in the anatase form of the TiO<sub>2</sub> layer.

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21. The process as claimed in any one of claims 18 to 20, in which the coating of a glass or glass-ceramic substrate is carried out before application of the TiO<sub>2</sub> layer or of the underlayer associated therewith depositing, at least one layer 20 forming a barrier to the migration of alkali metals present in the glass or glass-ceramic on the substrate.

22. The process as claimed in claim 21 further including the step of annealing or toughening after the TiO<sub>2</sub> layer and the 25 thin-silicon base layer covering the TiO<sub>2</sub> layer have been deposited.

23. The process as claimed in any one of claims 18 to 22, in which, after the optional application of at least one layer 30 forming a barrier to the migration of alkali metals and before application of the TiO<sub>2</sub> layer or the underlayer associated with

2004283938 07 Jun 2010

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the latter, at least one functional layer chosen from layers having an optical functionality, thermal control layers or conducting layers is deposited, said functional layers are advantageously deposited by vacuum sputtering.

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24. Single or multiple glazing, comprising, on at least one face respectively, a structure as defined in one of claims 1 to 17.

10 25. Single or multiple glazing according to claim 24 for motor vehicles or buildings.

26. Single or multiple glazing according to claim 24 or 25 in which said face faces the outside of the structure.

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27. A structure comprising a substrate bearing substantially as herein described with reference to the accompanying examples.

28. A process for manufacturing a structure substantially as 20 herein described with reference to the accompanying examples.

29. Single or multiple glazing substantially as herein described with reference to the accompanying examples.

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