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Napfényvédő réteggel ellátott üveg

Az európai szabadalom ellen, megadásának az Európai Szabadalmi Közlönyben való meghirdetésétől számított kilenc hónapon belül, felszólalást lehet benyújtani az Európai Szabadalmi Hivatalnál. (Európai Szabadalmi Egyezmény 99. cikk(1))

A fordítást a szabadalmat az 1995. évi XXXIII. törvény 84/H. §-a szerint nyújtotta be. A fordítás tartalmi helyességét a Szellemi Tulajdon Nemzeti Hivatala nem vizsgálta.

Window comprising a solar control coating**I. Field of the invention.**

5 The field of the invention is that of solar-control glazing units consisting of a glazing substrate bearing a multilayer stack at least one thin layer of which confers said solar-control properties. With this functional layer are associated dielectric layers that have the role in particular of regulating reflective, transmissive, and hue properties and of protecting against mechanical or chemical degradation of the properties of the glazing unit.

10 More precisely, the invention relates to glazing units intended to adorn buildings but also motor vehicles. In these uses, certain required properties may differ as explained below.

The functionalities of solar-control glazing units are multiple. They relate in particular to the prevention of heating of the interior of the passenger compartment of a motor vehicle, in particular with respect to the solar radiation passing through a transparent roof, or of a building exposed to solar radiation when the latter is sufficiently intense. According to certain embodiments, this prevention of heating may be obtained while maintaining a suitable light transmission.

15 Glazing units, in particular automotive glazing units, must also participate in the establishment of conditions allowing temperature to be regulated during wintry periods by preventing energy loss to the exterior of the passenger compartment or building. The glazing units must thus have low-E properties. They oppose the emission of energetic radiation from the passenger compartment or building.

In the case of glazing units for buildings, it is in addition required that they be able to withstand heat treatments without their colour, in particular in reflection, being substantially modified. The objective is to be able to place side-by-side heat-treated glazing units and others that have not been, without differences in colour being obvious.

25 In the rest of the description, the optical properties are defined for glazing units the substrate of which is made of ordinary clear "float" glass of 4 mm thickness. The choice of the substrate obviously influences these properties. For ordinary clear glass the light transmission under 4 mm, in the absence of any layers, is located at approximately 90% and the reflection at approximately 8%, as measured with a source according to the "daylight" illuminant standardized D65 by the CIE, and under a solid angle of 30 2°. The energy measurements, for their part, are carried out according to standard EN 410.

The term "glass" is understood to designate an inorganic glass. By that, what is meant is a glass of thickness at least larger than or equal to 0.5 mm and at most smaller than or equal to 20.0 mm, preferably at least larger than or equal to 1.5 mm and at most smaller than or equal to 10.0 mm, comprising silicon as one of the indispensable constituents of the glass material. For certain applications, the thickness may for example be 1.5 or 1.6 mm, or 2 or 2.1 mm. For other applications, it will for example be about 4 or 6 mm. Soda-lime-silica glasses that are clear, extra clear or tinted in their bulk or on their surface are preferred.

40 The presence of a multilayer stack may cause colour-related problems. Most often, the market requires that glazing units have, both in transmission and in reflection, a tint that is as neutral as possible



and therefore of grey appearance. Slightly green or bluish tints are also possible. Multilayer stacks, and in particular the natures, indices and thicknesses of the dielectric layers flanking the functional layers, are in particular chosen to control these tints.

Automotive glazing units may in theory be multiple glazing units in order to provide them with better in particular thermal insulation properties. In fact, such multiple glazing units are exceptional. The vast majority of these glazing units consist of single glazing units, i.e. either of monolithic or laminated glazing units. In these two cases, if the low-E character is to be suitably expressed, the multilayer stack must be on a face that is not sheltered from mechanical or chemical stresses. The stacks in question must therefore be very resistant to these possible aggressions.

In practice, to limit the risk of degradation, multilayer stacks are normally placed on that face of the glazing unit which is turned towards the passenger compartment. However, even in this position they must have a very good mechanical strength.

The systems of layers according to the invention must also lend themselves to the forming of the glazing units. Those used in vehicles are in particular subjected to heat treatments during the forming and in particular the bending of the glass sheets, or even during the tempering intended to provide them in particular with strengthened mechanical properties. The layers used according to the invention must withstand these treatments without their properties being degraded. Treatments of this type require temperatures that exceed 600°C for a few tens of minutes. Subjected to these temperatures the layers must preserve their qualities.

In many applications requiring high-light-transmittance glazing units to be provided, the choice of the functional layers requires that the latter be particularly transparent. Most commonly, one or more metal layers of very small thickness are selected: for example, one or more silver layers placed between dielectric layers that protect them and minimize both reflection and adjust neutrality. On the whole, the obtained systems of layers are limited by a certain in particular mechanical fragility, even in the presence of specific protective layers.

For glazing units that do not require a high light transmittance, and even possibly for glazing units the transmission of which must remain low, a more diverse choice of systems of layers is available.

2. Solutions of the prior art.

The prior art proposes glazing units including layers that are made of metals or metal alloys that absorb solar radiation, nitrides or oxynitrides of various metals and in particular of NiCr, Mo, W, Ta, CoCr, Al, Nb or Zr. To ensure these metal layers have a good in particular mechanical resistance, it is also proposed to provide dielectric layers that are known to be relatively hard. In this field, the most usual layers are layers of silica, SiO₂, and of silicon nitride, Si₃N₄.

The previous propositions meet some at least of the requirements of the envisioned use of glazing units according to the invention. There nevertheless remains a need for improvement in particular from the point of view of the resistance to heat treatments.

Documents US 2012/0225316, US 2012/0225316 and US 2012/0225304 disclose solar-control glazing units with a nickel-chromium-based barrier possibly incorporating zirconium.

3. Objectives of the invention.

The objective of the invention is in particular to mitigate these drawbacks of the prior art.

More precisely, one objective of the invention, in at least one of its embodiments, is to provide a glazing unit equipped with a multilayer stack that is able to undergo a high-temperature heat treatment, such as a tempering and/or bending heat treatment, preferably without significant modification of its hue, in particular in reflection substrate side, such that a non-heat-treated glazing unit can be juxtaposed with its heat-treated version without an observer being able to detect a significant difference in overall aesthetic appearance.

Yet another objective of the invention, in at least one of its embodiments, is to provide a glazing unit equipped with a multilayer stack having a good stability from the thermal, chemical and mechanical point of view.

Yet another objective of the invention, in at least one of its embodiments, is to provide a glazing unit the multilayer stack of which can be placed in external position without necessarily having to be protected from the external environment by another substrate.

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4. Summary of the invention.

The invention relates to a solar-control glazing unit including on at least one of the faces of a glazing substrate a multilayer stack comprising at least one solar-radiation-absorbing layer and dielectric coatings flanking said solar-radiation-absorbing layer, characterized in that the solar-radiation-absorbing layer is a layer of a metal alloy based on zirconium and chromium, comprising at least 25% by weight chromium and at least 20% by weight zirconium, the multilayer stack comprising, between the substrate and the solar-radiation-absorbing layer, and above the solar-radiation-absorbing layer, at least one coating made of a dielectric material based on a compound selected from silicon oxide, aluminium oxide, silicon nitride, aluminium nitride, mixed aluminium-silicon nitrides, silicon oxynitride and aluminium oxynitride.

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The general principle of the invention is based on the presence of a metal solar-radiation-absorbing layer, namely a layer of a metal alloy based on zirconium and chromium, said layer being encased between at least two layers based on at least one dielectric material listed in Claim 1. The inventors have determined that, surprisingly, such a multilayer stack has a good chemical, thermal and mechanical durability. Specifically, the metal solar-radiation-absorbing layer based on chromium and zirconium causes a decrease in the transmission of solar energy, said layer preserving its absorption properties more particularly after a heat treatment.

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By "layer of a metal alloy" for the solar-radiation-absorbing layer, what is meant is a layer having an essentially metal character. However, it is not excluded that this layer possibly contain a few traces of nitrogen or oxygen. Specifically, the atmosphere during the deposition of this metal layer may consist of a pure noble gas, for example 100% argon, or the atmosphere may contain a little nitrogen or oxygen originating from neighbouring zones of deposition. In the case where the dielectric layers that surround the absorbing layer are silicon nitrides, the metal target intended to form the absorbing layer may even be placed in the same deposition chamber, without hard isolation from the zones of deposition of the silicon nitrides, because the nitrogen will principally be attracted by the silicon. In this case, the

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surrounding atmosphere may contain a relatively high percentage of nitrogen, and therefore, even though the nitrogen will associate principally with the silicon, the absorbing metal layer will possibly contain a little nitrogen, without however losing its metal character. In the case where the dielectric layers that surround the absorbing layer are oxides or oxynitrides, there may even also be therein a little oxygen originating from the neighbouring zones of deposition of the deposition atmosphere.

Preferably, the layer comprises at least 35%, and advantageously at least 40% and even at least 45% by weight zirconium. Preferably, the layer comprises between 20 and 75% by weight zirconium, advantageously between 25 and 75% or between 30 and 75% by weight zirconium, and favourably between 45 and 65% by weight zirconium.

By "layer based on a dielectric material", what is also meant is layers doped with at least one other element and containing up to about at most 10% by weight of this other element, such layers having dielectric properties that in practice do not differ from layers consisting of said dielectric material. Thus, for example, when the layer is made of silicon oxide or nitride, said layer may contain up to 10% by weight aluminium (for example, layers deposited by the cathode sputtering process from a silicon target containing up to 10% by weight aluminium). The dielectric layers according to the invention may furthermore consist of a plurality of individual layers comprising or consisting essentially of the above materials. The dielectric layers may also be deposited by the well-known plasma-enhanced chemical vapour deposition (PECVD) technique.

Thus, the invention is based on a completely novel and inventive approach based on the selection of a metal solar-radiation-absorbing layer that is based on an alloy of chromium and zirconium.

Advantageously, the glazing unit according to the invention is such that the metal solar-radiation-absorbing layer based on chromium and zirconium also comprises a supplementary metal selected from Ti, Nb, Ta, Ni, Sn and W.

Preferably, the solar-radiation-absorbing layer has a geometric thickness comprised between 0.5 and 30 nm, advantageously comprised between 1 and 30 nm and preferably comprised between 2 and 25 nm.

A metal layer based on chromium and zirconium having such thicknesses possesses infrared absorption properties that are most particularly required for it to be used in architectural or automotive glazing-unit multilayer stacks, or as a glazed element of a household electrical appliance, such as an oven door.

According to one embodiment of the invention, the solar-radiation-absorbing layer preferably has a geometric thickness comprised between 10 and 25 nm, and advantageously comprised between 12 and 22 nm. This embodiment of the invention is most particularly appropriate when the solar-radiation-absorbing layer forms the or at least one functional layer of the multilayer stack, i.e. it constitutes the or one of the layers that are fundamental to the obtainment of the solar-control properties.

According to another embodiment of the invention, the solar-radiation-absorbing layer preferably has a geometric thickness comprised between 0.5 and 30 nm, advantageously comprised between 1 and 10 nm, and preferably comprised between 2 and 5 nm. This other embodiment of the invention is most particularly appropriate when the solar-radiation-absorbing layer is a layer complementary to the functional layer of the multilayer stack, i.e. it is a layer intended to improve the

solar-control properties already obtained with the one or more functional layers.

According to one advantageous embodiment, the glazing unit according to the invention is such that the layer made of dielectric material between the substrate and the solar-radiation-absorbing layer has an optical thickness of at least 10 nm and of at most 200 nm, preferably of at least 20 nm and of at most 180 nm.

The optical thickness of a layer of dielectric material is obtained by multiplying the geometric (physical) thickness of the layer in question by the refractive index of the material from which it is made.

According to one preferred embodiment, the glazing unit according to the invention is such that the layer made of dielectric material located above the solar-radiation-absorbing layer has an optical thickness of at least 15 nm and of at most 200 nm.

According to a first preferred embodiment, the metal solar-radiation-absorbing layer is the basic functional layer of the multilayer stack. The advantage of this multilayer stack is that it is extremely simple and very resistant.

Preferably, the multilayer stack comprises at least two solar-radiation-absorbing layers. This feature allows the optical and thermal properties of the multilayer stack to be more easily adapted to the desiderata. Advantageously, these two solar-radiation-absorbing layers are separated by a dielectric layer, for example one made of silicon nitride. The following is a particularly appropriate structure:
substrate/Si₃N₄/CrZr/Si₃N₄/CrZr/Si₃N₄.

According to a second preferred embodiment, the glazing unit according to the invention is such that the multilayer stack comprises at least one supplementary silver-based metal layer, such that the or each silver-based layer is surrounded by a dielectric coating. This dielectric coating may be formed from a material such as described above in relation to the other embodiments of the invention. It may also be a question of any dielectric material that is well known in the field, such as for example zinc stannate or optionally doped ZnO.

In this second embodiment, the basic functional layer of the multilayer stack is the silver-based layer, which reflects infrared radiation, thereby allowing more effective solar control while preserving a higher light transmittance and therefore allowing a significant improvement in selectivity to be obtained. The addition of a supplementary silver-based layer is surprising because this type of layer generally resists poorly high-temperature heat treatment, and in addition weakens the multilayer stack assembly from the mechanical and chemical point of view. In general, the presence of a silver-based layer prevents the multilayer stack from being positioned in contact with the external environment and requires the multilayer stack to be protected using an additional substrate. The inventors have discovered that, surprisingly, the invention allows these drawbacks to be mitigated.

The combination of a silver-based layer with the solar-radiation-absorbing layer allows on the one hand properties of reflection of infrared radiation, which properties are procured by the silver-based-layer, and properties of absorption of energetic solar radiation to be obtained simultaneously.

According to a first preferred form of this second embodiment, at least one of the dielectric coatings comprises at least two dielectric layers and the metal solar-radiation-absorbing layer is inserted between these two dielectric layers of this dielectric coating. The inventors have observed that this

configuration effectively separates the infrared-reflection function from the solar-radiation-absorption function, thereby allowing the two functions to be more easily optimized, in particular when it is desired to improve the crystal quality of the silver to obtain a lower emissivity, for example using a ZnO-based layer under the silver, namely what is often called a wetting layer, and/or above the silver, without loss of the absorption function of the metal solar-radiation-absorbing layer. In addition, this arrangement allows the metal solar-radiation-absorbing layer to be better protected during the heat treatment, in order that it integrally preserve as far as possible its absorption function.

Preferably, the first dielectric layer, of the first dielectric coating, i.e. the layer that is deposited on the glazing substrate and that makes contact therewith, is a layer of mixed zinc-tin oxide advantageously containing at least 20% tin, and even more preferably a layer of mixed zinc-tin oxide in which the zinc-tin proportion is close to 50-50% by weight (Zn_2SnO_4). This arrangement is advantageous for the resistance to high-temperature heat treatment. The mixed zinc-tin oxide forms an excellent barrier to the alkali ions that migrate from the glazing substrate at the high temperature of the in particular tempering heat treatment. It also has and preserves a good adhesion with respect to the glazing substrate. It furthermore has a good deposition rate, compared, for example, to SiO_2 or Al_2O_3 and it has a good durability, compared, for example, to pure ZnO or to bismuth oxide. It may, furthermore, be advantageous in that it has less tendency to generate haze after heat treatment of the stack, compared, for example, to oxides of Ti or Zr. The oxide layer in direct contact with the substrate advantageously has a thickness of at least 5 nm, preferably of at least 8 nm, and more preferably of at least 10 nm. These minimum thickness values allow, *inter-alia*, the chemical durability of the non-heat-treated product to be ensured, but also the resistance to the heat treatment to be ensured.

Preferably, said two dielectric layers enclosing the metal solar-radiation-absorbing layer based on chromium and zirconium are based on silicon nitride or aluminium nitride. This ensures a very good protection of the metal solar-radiation-absorbing layer during the high-temperature heat treatment.

Preferred, but nonlimiting, examples of this embodiment may be schematically represented as follows:

- G/Si₃N₄/CrZr/Si₃N₄/D/ZnO/Ag/AZO/Si₃N₄/ZnO/Ag/AZO/Si₃N₄/CrZr/Si₃N₄;
- G/D/ZnO/Ag/AZO/D/ZnO/Ag/AZO/D/Si₃N₄/CrZr/Si₃N₄;
- G/Si₃N₄/CrZr/Si₃N₄/D/ZnO/Ag/AZO/D/ZnO/Ag/AZO/D/Si₃N₄[/TOP];
- G/Si₃N₄/CrZr/Si₃N₄/D/ZnO/Ag/B/D/ZnO/Ag/B/D/TOP;
- G/Si₃N₄/CrZr/Si₃N₄/D/ZnO/Ag/AZO/D/Si₃N₄/D/ZnO/Ag/AZO/D/Si₃N₄[/TOP];
- G/D/ZnO/Ag/AZO/D/Si₃N₄/CrZr/Si₃N₄/D/ZnO/Ag/AZO/D/Si₃N₄[/TOP];
- G/D/ZnO/Ag/B/D/Si₃N₄/CrZr/Si₃N₄/D/ZnO/Ag/B/D/Si₃N₄[/TOP];

G representing the substrate, preferably a sheet of ordinary soda-lime glass; B representing a layer presenting a barrier to the oxidation of the silver, i.e. a layer such as well known in the field; AZO representing a barrier layer based on optionally aluminium-doped zinc oxide, said layer being deposited from a ceramic (optionally aluminium-doped) zinc oxide (cathode) target sputtered in an argon-based atmosphere containing a little or no oxygen; D representing one or more dielectric layers, in particular based on zinc stannate, optionally doped ZnO or another material known in the field and suitable for this type of layer stack, for example TiO_2 , ZrO_2 or a mixture thereof, or a nitride such as AlN. The term

"TOP" represents a protective top layer containing Ti and/or Zr in metal, oxidized or nitrided form. The expression "[/TOP]" means that this protective top layer is optional. As a variant, AZO may be replaced by other barriers well known in the field and suitable for the properties desired for the formed layer system, such as, for example, an oxide of Ti, optionally doped with niobium or zirconium, said oxide preferably being obtained from a ceramic target formed from the oxide to be deposited; or pure ZnO. The examples given above use CrZr as solar-radiation-absorbing layer by way of concrete examples, but CrZr may also be replaced by another material based on zirconium and chromium, such as CrZrNb, CrZrW, CrZrNi, etc. in pure metal form or with traces of nitrogen or oxygen.

Preferably, in this first form of the second embodiment of the invention, the system of layers comprises, at least once, the succession of following layers: "aluminium or silicon nitride or a mixture thereof / solar-radiation-absorbing layer / aluminium or silicon nitride or a mixture thereof / intercalating transparent oxide / wetting layer based on zinc oxide / silver-based supplementary metal layer". It has been found that the use of a wetting layer based on ZnO with the insertion of an intercalating transparent oxide layer between the nitride layer protecting the solar-radiation-absorbing layer and the wetting layer allows the formation of unacceptable blemishes in the visual appearance of the coating substrate after the latter has undergone a high-temperature heat treatment, which blemishes have a tendency to form during the heat treatment in the absence of this specific succession of layers, to be greatly decreased or prevented. It has also been noted that without this intercalating transparent oxide layer, the electrical resistance per unit area, and therefore also the emissivity, have a tendency to increase undesirably following the heat treatment, whereas by virtue of the presence of this intercalating oxide layer the emissivity is at least preserved, or even advantageously decreased, following the heat treatment. The intercalating transparent oxide layer may be an oxide based on ZnO, SnO₂, TiO₂, ZrO₂ or a mixture thereof, while however being different from the wetting layer. Preferably, the intercalating transparent oxide layer is a mixed zinc-tin oxide containing at least 20% tin and at least 10% zinc.

According to a second preferred form of this second embodiment, the silver-based supplementary metal layer is located in the stack directly on and/or under the metal solar-radiation-absorbing layer.

The inventors have determined that, surprisingly, the presence of the solar-radiation-absorbing layer allows the risk of chemical deterioration of the silver-based layer to be decreased when said silver-based layer makes direct contact with the solar-radiation-absorbing layer.

Preferably, in this second form of the second embodiment, the glazing unit according to the invention is such that the one or more silver-based metal layers, if there are a plurality thereof, have a thickness of at least 9 nm, preferably of at least 13 nm and of at most 23 nm, and more preferably of at least 15 nm and of at most 22 nm.

According to this embodiment, the metal solar-radiation-absorbing layer preferably has a geometric thickness comprised between 0.5 and 8 nm, and advantageously between 0.5 and 5 nm.

According to this embodiment, this solar-radiation-absorbing layer may be placed either under the silver-based supplementary layer, or above the silver-based layer. Preferably, it is placed on either side of the silver-based supplementary metal layer, each layer preferably having a thickness comprised in the range indicated above, i.e. preferably between 0.5 and 5 nm. It has been found that this is the best

arrangement to distribute the absorption of the solar radiation on either side of the infrared-reflecting layer.

According to a first preferred implementation of the first embodiment, the glazing unit according to the invention is such that it includes, on at least one of the faces of a glazing substrate, a multilayer stack comprising at least successively:

- a layer made of a dielectric material based on at least one chemical compound selected from the group consisting of silicon oxide, aluminium oxide, silicon nitride, aluminium nitride, mixed aluminium-silicon nitrides, silicon oxynitride, and aluminium oxynitride, and preferably selected from silicon nitride, aluminium nitride and mixed aluminium-silicon nitrides, the layer made of dielectric material having an optical thickness of at least 10 nm and of at most 200 nm, and preferably of at least 20 nm and of at most 180 nm;
- a metal solar-radiation-absorbing layer comprising 20 to 75% and preferably 45 to 65% by weight zirconium and at least 25% and preferably at least 35% by weight chromium, and having a geometric thickness of at least 1 nm, preferably of at least 3 nm and of at most 30 nm, and preferably of at least 3 nm and of at most 25 nm;
- a layer made of a dielectric material based on at least one chemical compound selected from the group consisting of silicon oxide, aluminium oxide, silicon nitride, aluminium nitride, mixed aluminium-silicon nitrides, silicon oxynitride, and aluminium oxynitride, and preferably selected from silicon nitride, aluminium nitride, and mixed aluminium-silicon nitrides, the layer made of dielectric material having an optical thickness of at least 15 nm and of at most 200 nm.

According to a second preferred implementation of the first embodiment, the glazing unit according to the invention is such that it includes, on at least one of the faces of a glazing substrate, a multilayer stack comprising at least successively:

- a layer made of a dielectric material based on at least one chemical compound selected from the group consisting of silicon oxide, silicon nitride, and silicon oxynitride, the layer made of dielectric material having an optical thickness of at least 10 nm and of at most 200 nm, and preferably of at least 20 nm and of at most 180 nm;
- a metal solar-radiation-absorbing layer comprising 20 to 75% and preferably 45 to 65% by weight zirconium and at least 25% and preferably at least 35% by weight chromium, and having a geometric thickness of at least 1 nm, preferably of at least 3 nm and of at most 30 nm, and preferably of at least 3 nm and of at most 25 nm;
- a layer made of a dielectric material having an optical thickness of at least 15 nm and of at most 400 nm and preferably between 20 and 200 nm, based on at least one chemical compound selected from the group consisting of silicon nitride and silicon oxynitride.

According to one preferred implementation of the first form of the second embodiment, the system of layers comprises n silver-based supplementary metal layers, where $n \geq 1$, each silver-based

supplementary metal layer being surrounded by layers made of dielectric material, and comprises at least once the following succession of layers: "aluminium or silicon nitride or a mixture thereof / solar-radiation-absorbing layer / aluminium or silicon nitride or a mixture thereof / intercalating transparent oxide / wetting layer based on zinc oxide / silver-based supplementary metal layer", in which succession
5 the silver-based supplementary metal layer has a geometric thickness of at least 8 nm and the solar-radiation-absorbing layer has a geometric thickness comprised between 0.5 and 8 nm. It may be a question of a system of layers having two or three, or even four, silver-based metal layers, a solar-radiation-absorbing layer surrounded by its specific dielectric layers preferably being placed between the first and second silver-based layer as counted from the substrate. It has been discovered that this
10 particular succession of layers allows the formation of coloured blemishes that are observed after heat treatment when this sequence is not respected, and in particular when the intercalating transparent oxide layer is not present between the nitride layer that protects the solar-radiation-absorbing layer and the wetting layer based on ZnO, to be greatly decreased or prevented. It has also been observed that, by virtue of the presence of this intercalating oxide layer, the electrical resistance per unit area, and
15 therefore emissivity as well, is at least preserved, or even advantageously decreased, following the heat treatment, instead of increasing undesirably during the heat treatment.

According to one preferred implementation of the second form of the second embodiment, the glazing unit according to the invention is such that it includes, on at least one of the faces of a glazing
20 substrate, a multilayer stack comprising at least successively:

- a layer made of a dielectric material based on at least one chemical compound selected from the group consisting of aluminium and/or silicon oxynitride or nitride, the layer made of dielectric material having an optical thickness of at least 10 nm and of at most 200 nm, and preferably of at least 20 nm and of at most 180 nm;
- 25 • a metal solar-radiation-absorbing layer comprising 20 to 75% and preferably 45 to 65% by weight zirconium and at least 25% and preferably at least 35% by weight chromium, and having a geometric thickness of at least 0.5 nm, preferably of at least 1 nm and of at most 8 nm, and preferably of at least 1 nm and of at most 5 nm;
- a silver-based supplementary metal layer having a geometric thickness of at least 9
30 nm, preferably of at least 13 nm, and of at most 22 nm;
- a second metal solar-radiation-absorbing layer comprising 20 to 75% and preferably 45 to 65% by weight zirconium, the remainder being formed from chromium, and having a geometric thickness of at least 0.5 nm, preferably of at least 1 nm and of at most 8 nm, and preferably of at least 1 nm and of at most 5 nm;
- 35 • a layer made of a dielectric material based on silicon nitride or oxynitride having an optical thickness of at least 15 nm and of at most 400 nm and preferably between 20 and 200 nm.

In the four preceding implementations, other additional layers may be added, either directly to the substrate, or by way of external protective layer, or in the interior of the multilayer stack stack, in

order to provide the basic multilayer stack with additional protection and/or additional properties, such as, for example, additional external protection from mechanical or chemical aggressions, a barrier to alkali metals originating from the substrate, different optical properties, an improvement in the electrical properties of the metal layers, an improvement in deposition rate, or any other additional function. The additional layers must however preferably be chosen so that they do not disrupt the ability of the multilayer stack to undergo a high-temperature heat treatment. In particular, care will advantageously be taken to ensure that these additional layers do not undergo substantial modifications, and in particular structural modifications, during the heat treatment in order to prevent them from being the cause of modifications of the optical properties of the multilayer stack during the heat treatment.

Heat treatments, in particular bending/tempering heat treatments, may also be the cause of relatively large modifications in optical properties and in particular hue. Preferably, these variations must be minimized such that whether heat-treated or not the glazing units have a practically unchanged appearance.

Conventionally, the measurement of colorimetric variations is performed in the coordinates of the CIELAB system. Colorimetric variation is expressed by the expression denoted ΔE^* , expression corresponding to the formula:

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

where ΔL^* is the difference between the L^* colour coordinates of the glazing unit before and after heat treatment;

Δa^* is the difference between the a^* colour coordinates of the glazing unit before and after heat treatment; and

Δb^* is the difference between the b^* colour coordinates of the glazing unit before and after heat treatment.

More particularly, and preferably, the glazing unit according to the invention exhibits a colorimetric variation in reflection glass-face side, ΔE^*_{Rg} :

$$\Delta E^*_{Rg} = (\Delta L^*_{Rg}{}^2 + \Delta a^*_{Rg}{}^2 + \Delta b^*_{Rg}{}^2)^{1/2}$$

smaller than 8, preferably smaller than 5, advantageously smaller than 3, and even preferably smaller than 2, when said glazing unit is subjected to a temperature of at least 630°C and of at most 670°C for 7 minutes.

The invention is particularly useful for obtaining a very good stability in the hue in reflection substrate side during a high-temperature tempering and/or bending heat treatment. The hue in reflection substrate side is, in many applications, the hue the most obvious to an observer, because it is this face that draws his attention under the conditions of use of the glazing unit. The slightest difference in hue is therefore more easily seen.

The inventors have observed that, surprisingly, the invention, with its metal absorbing layer based on chromium and zirconium, allows an exceptional hue stability in reflection glass side, that could not be so easily achieved with prior-art propositions, to be achieved, and in particular by using NiCr as the absorbing material such as proposed above.

In addition, the invention allows the substrate-side light reflectance to be increased a little, this often being desired in commercial applications.

Additionally, the glazing unit according to the invention also preferably exhibits a colorimetric variation in transmission, ΔE^*_{TL} :

$$\Delta E^*_{TL} = (\Delta L^*_{TL}{}^2 + \Delta a^*_{TR}{}^2 + \Delta b^*_{TL}{}^2)^{1/2}$$

5 smaller than 8, preferably smaller than 5, and more preferably smaller than 3, when said glazing unit is subjected to a temperature of at least 630°C and of at most 670°C for 7 minutes.

The glazing unit according to the invention additionally or not to the two preceding properties exhibits a colorimetric variation in reflection layer-face side, ΔE^*_{Rc} , such that:

$$\Delta E^*_{Rc} = (\Delta L^*_{Rc}{}^2 + \Delta a^*_{Rc}{}^2 + \Delta b^*_{Rc}{}^2)^{1/2}$$

10 smaller than 8, and preferably smaller than 5, when said glazing unit is subjected to a temperature of at least 630°C and of at most 670°C for 7 minutes.

According to one particular embodiment, the glazing unit according to the invention is such that the thickness of the metal solar-radiation-absorbing layer is chosen so that, for a substrate made of clear glass of 4 mm thickness, the light transmittance is at least equal to 2% and at most equal to 75%. In the case of use as a motor-vehicle roof, the light transmittance will preferably be between 2 and 10%, and advantageously between 6 and 8%. In the case of an architectural application, the light transmittance will preferably be between 10 and 70%, advantageously between 10% and 60%, favourably between 10 and 50%, and preferably between 20 and 40%. Specifically, the metal solar-radiation-absorbing layer sets the energy and light transmittance: the greater the thickness of said layer the greater its absorbance.

According to one particular embodiment, the glazing unit according to the invention is such that the optical thickness of the dielectric layers is chosen so that the layer-side reflectance is at least 1% and at most 55%. The dielectric layers, and in particular the top layer, especially set the reflectance of the system. As is known, alternating layers of high refractive index and of low refractive index allows reflectance to be controlled. The thickness of the layers is also a determining factor. Within the limits of the thicknesses indicated above, increasing the thickness of the layer made of dielectric material located above the metal solar-radiation-absorbing layer decreases the brightness of the reflection layer side and increases the reflectance substrate side.

As a variant, when a low light reflectance is desired, in particular layer side, preferably two, or even more than two, functional layers formed from metal solar-radiation-absorbing layers are provided, with a dielectric layer between these two layers, the structure then for example being as follows: dielectric layer such as described in the main claim / solar-radiation-absorbing layer / dielectric layer such as described in the main claim / solar-radiation-absorbing layer / dielectric layer such as described in the main claim. The total thickness desired for the absorption of solar radiation is subdivided into two, or even into as many parts as there are absorbing layers used. By way of illustrative example, here is a preferred concrete structure: $Si_3N_4/CrZr/Si_3N_4/CrZr/Si_3N_4$. This structure makes it easier to obtain a very low light reflectance layer side, for example only 2% or even only 1%.

According to one preferred embodiment of the invention, the light reflectance measured substrate side is at least 27%, preferably at least 30%, and advantageously at least 35%. This feature allows an agreeable aesthetic effect that is greatly appreciated in the commercial markets of certain regions, in particular because of the glossy appearance of the face of the glazing unit, to be obtained.

40 The multilayer stack of the glazing unit according to the invention allows this aesthetic effect to

be more easily obtained, in particular by suitably adjusting the optical thickness of the dielectrics in order to correctly manage the optical interference effect. One suitable means consists in limiting the optical thickness of the first dielectric coating, i.e. the coating placed between the substrate and the solar-radiation-absorbing layer, to a low value. However, this solution is limited because the thickness of this first dielectric coating must be large enough to allow the layer system to be heat treated at high temperature without deterioration of its properties, in particular via the migration of elements from the substrate. Another preferred means consists in the second dielectric coating, i.e. the coating placed above the solar-radiation-absorbing layer, having a large optical thickness comprised in a specific range. Preferably, the second dielectric coating, i.e. the coating placed above the solar-radiation-absorbing layer, has an optical thickness (geometric thickness multiplied by the refractive index of the materials) comprised between 70 and 170 nm, preferably between 80 and 140 nm, and advantageously between 110 and 130 nm.

Preferably, the light reflectance measured substrate side is at least 2 times, advantageously at least 2.5 times, and preferably at least 3 times higher than the light reflectance measured on the side of the multilayer stack. Preferably, the light reflectance measured substrate side is at least 15% and advantageously at least 20% higher than the light reflectance measured on the side of the multilayer stack. Given that to obtain the best solar-control effect the layer is placed in position 2 (counting from the exterior), this feature makes it possible to obtain an exterior reflectance (measured substrate side) that allows the sought-after agreeable aesthetic effect to be achieved while preventing the mirror effect when the glazing unit is looked through from the interior of the spaced closed off by the glazing unit, thus improving light transmission and visibility through the glazing unit. This combination of a high exterior reflectance, to obtain a sought-after aesthetic effect, and a low interior reflectance is an essential feature of this embodiment of the invention. The mirror effect that would otherwise be seen from the interior, and that would otherwise prevent correct vision through the glazing unit from the enclosure closed off by the glazing unit, is thus prevented. A high optical thickness of the second dielectric coating is an essential condition.

According to one advantageous embodiment, to obtain this difference in light reflectance between the substrate side and the multilayer-stack side, the coating made of dielectric material placed above the solar-radiation-absorbing layer comprises a material having a high refractive index, i.e. a refractive index higher than 2. In the context of the present invention, this high-refractive-index dielectric is a material that withstands the heat treatment without significant structural modification. A specific example of such a material is doped titanium oxide, for example titanium oxide doped with zirconium or niobium, and in particular a mixture of titanium oxide and zirconium oxide in amounts of 40 to 60% each. Another example of such a material is zirconium oxide. Preferably, this high-index material is placed between the solar-radiation-absorbing layer and the most exterior dielectric layer of the stack.

Preferably, the system of layers terminates in a thin protective layer based on a mixed titanium-zirconium oxide.

The glazing units according to the invention may be used in various applications because their properties may be adapted by adjusting the layers and in particular their thicknesses.

Glazing units according to the invention may be used in double glazing units, and in this case the multilayer stack may be placed in the space between the two glass sheets, thereby limiting the risk of mechanical degradation in particular. Nevertheless, one of the significant features of the multilayer stacks proposed for the glazing units according to the invention is their resistance, both from a mechanical and chemical point of view. In the embodiments without any silver-based supplementary metal layer, or with silver-based supplementary metal layer but with no oxide in the multilayer stacks, this resistance is such that they may be used with the multilayer stack exposed, without any other protection. In the latter case, the glazing unit may equally well be composed of a single glass sheet, the multilayer stacks being applied to one face of this sheet. It may also be a question of a laminated glazing unit comprising two or more glass sheets, the sheets being joined by means of intercalating thermoplastic sheets according to techniques that are conventional in this field.

In these single glazing unit applications, the multilayer stack is not protected from the environment. Even in the case of a laminated glazing unit, the layers may be on an external face, so that they may play their role in the control of energy transmission while acting on the emissivity of the surface.

When the privileged functionality is the low-E character of the glazing unit, the multilayer stack is preferably placed on the face that is turned towards the interior of the vehicle or building. This position leads to the greatest reflection of infrared radiation of long wavelengths, so as to keep heat within the passenger compartment or building. For vehicles, this position corresponds to the layer being on the face that is turned towards the passenger compartment. In this position the resistance of the multilayer stack is all the better given that, in particular for fixed glazing units (roof, rear windscreen, etc.), the stresses are relatively limited.

The glazing unit according to the invention may therefore be used as a glazed motor-vehicle element: roof, windscreen, side window, rear windscreen (the multilayer stack preferably being on the face exposed to the passenger compartment); and as an architectural glazing element.

More particularly, the glazing unit according to the invention may be used as an openable motor-vehicle roof.

Specifically, motor-vehicle manufacturers are looking for a solution that avoids having to place a curtain (screen) under the roof to provide protection from the sun. The absence of such a curtain would lead to a weight saving (~6 kg) and therefore to a lower fuel consumption, and hence to lower CO₂ emissions. Passenger thermal comfort must nonetheless be guaranteed even when no curtain is present, i.e. the passenger compartment must not get too hot in summer nor too cold in winter. In an electric vehicle, there is no heat engine producing heat that may be used to heat the passenger compartment of the vehicle, and it is absolutely essential to maintain body heat in the interior (no loss through the roof).

The glazing unit according to the invention may also be used as a glazed element of a household electrical appliance such as an oven door, where it may also provide a sought-after aesthetic effect. It resists well the various chemical and/or mechanical aggressions encountered in this particular type of application.

As already indicated above a number of times, the glazing unit according to the invention may of course also be used as a glazed element in a building. In this type of application, the glazing unit may

form a double or triple glazing unit with the multilayer stack placed facing the space enclosed in the interior of the multiple glazing unit. The glazing unit may also form a laminated glazing unit, the multilayer stack of which may make contact with the thermoplastic adhesive material joining the substrates - in general, PVB. The glazing unit according to the invention is however particularly useful when the multilayer stack is placed facing the external environment, whether this be in a single glazing unit or a laminated glazing unit, or indeed also, optionally, a multiple glazing unit.

Of course, the glazing substrate may be a bulk-tinted glass, such as a glass tinted grey, blue or green, in order to in addition absorb solar radiation, or so as to form a private space from which little light is transmitted, in order to conceal the passenger compartment of a vehicle, or an office in a building, from external observers.

As a variant of the various embodiments including a silver-based supplementary metal layer, the invention also includes the introduction not only of a single silver-based metal layer but also of two, or even three, or even four, silver-based metal layers. In this case, the one or more metal solar-radiation-absorbing layers may be placed in immediate proximity (on either side or on one side or the other) of a plurality of silver-based layers, or of each thereof. According to a first implementation of this variant, the metal solar-radiation-absorbing layers will preferably be placed on either side of the first silver-based metal layer counting from the substrate. According to a second implementation of this variant, the metal solar-radiation-absorbing layers will preferably be placed between two dielectric layers of a given dielectric coating. Dielectric layers based on aluminium and/or silicon oxynitride or nitride are preferably placed between each silver-based metal layer, in a repetition of the examples comprising a single functional layer.

5. Description of preferred embodiments of the invention

Examples of glazing units according to the invention, but also comparative examples ("R"), are given in Table I below. The optical properties are defined, for glazing units the substrate, a single pane of glass, of which was made of ordinary clear "float" glass of 4 mm thickness. The layers are in order, from left to right, starting from the glass. The approximate geometric thicknesses are expressed in nm.

Tables I and Ia: Examples of glazing units according to the invention and comparative examples allowing the performance of glazing units according to the invention to be compared with glazing units of the prior art, the coatings being placed on clear glass having a thickness of 4 mm. The light transmittances (TL) and light reflectances layer side (Rc) and glass side (Rg) are also indicated (in %) for certain examples. In the comparative examples below, NiCr is an alloy containing 80% Ni and 20% by weight Cr. In the examples according to the invention below, CrZr is an alloy containing 40% Cr and 60% by weight Zr.

Table I:

Ex.	Coating	TL	Rc	Rg	ΔE^*_{T1}	ΔE^*_{Rg}
1R	SiN (20nm)/NiCr (8.5nm)/SiN (35nm)	39	11	17	1.70	3.84
2R	SiN (20nm)/NiCr (13.7nm)/SiN (35nm)	27	15	25	2.61	2.32
3R	SiN (20nm)/NiCr (22nm)/SiN (35nm)	14	22	36	3.56	1.74

Ex.	Coating	TL	Rc	Rg	ΔE^*_{Tl}	ΔE^*_{Rg}
4R	SiN (87nm)/NiCr (13.7nm)/SiN (30nm)	28	22	17	1.95	4.60
1	SiN (20nm)/CrZr (12.5nm)/SiN (35nm)	34	17	25	0.96	0.30
2	SiN (20nm)/CrZr (20.5nm)/SiN (35nm)	23	20	32	3.25	1.03
3	SiN (20nm)/CrZr (33nm)/SiN (35nm)	12	22	39	3.72	0.96
4	SiN (87nm)/CrZr (20.5nm)/SiN (30nm)	23	24	23	2.76	1.74

Table Ia:

Ex.	Coating (thickness in nm)					TL	Rc	Rg	ΔE^*_{Tl}	ΔE^*_{Rc}	ΔE^*_{Rg}
	SiN	CrZr	SiN	CrZr	SiN						
18	28.5	7.8	27.4	0.0	0.0	33.3	24.1	17.4	0.8	1.1	1.2
19	22.9	7.9	23.9	0.0	0.0	31.1	25.4	17.6	0.7	0.9	1.1
20	10.0	4.3	34.0	2.0	26.5	38.4	9.0	25.0	0.7	1.7	1.3
21	26.0	11.0	46.0	0.0	0.0	32.6	7.4	31.0	0.5	7.3	0.6
22	54.1	4.4	64.5	7.0	44.8	22.5	5.2	6.6	1.1	2.5	2.6
23	22.9	7.9	23.9	0.0	0.0	31.1	25.4	17.6	0.7	0.9	1.1
24	72.1	4.0	50.9	6.5	20.0	20.9	16.2	8.3	1.1	0.6	0.6
25	54.5	2.9	89.4	9.6	34.2	21.2	19.8	12.0	1.2	2.0	2.3
26	95.0	5.7	70.7	4.5	19.0	20.9	21.9	13.5	0.7	2.3	2.2
27	100.0	1.8	28.7	5.1	51.0	38.6	3.4	26.5	0.7	0.9	3.9
28	100.0	1.8	28.7	5.1	47.0	38.5	3.6	25.5	0.7	1.0	3.7
29	129.1	5.2	52.0	0.0	0.0	45.8	4.9	30.0	0.9	1.2	3.8
30	140.0	6.8	39.0	0.0	0.0	37.4	10.3	26.3	1.0	2.6	3.6
31	138.0	6.8	39.0	0.0	0.0	37.4	10.1	26.0	1.0	2.2	3.6
32	39.0	1.0	79.3	6.0	118.7	29.0	28.0	13.9	1.4	2.6	1.8
33	17.7	4.4	60.0	4.9	25.0	24.6	14.1	9.8	0.6	0.1	0.6
34	78.3	3.0	69.4	5.8	62.6	30.9	4.7	10.8	1.8	7.8	4.6
35	15.0	6.1	55.0	5.5	33.7	19.2	8.8	13.2	0.6	0.4	0.3
36	15.0	6.1	57.5	5.5	33.7	19.0	9.0	12.6	0.7	0.5	0.3
37	14.6	4.7	62.1	3.1	95.0	27.6	16.7	12.1	0.4	1.2	2.5
38	14.6	4.7	62.1	3.1	92.5	28.2	15.9	11.8	0.4	1.3	2.4
39	9.5	5.7	61.3	3.3	100.0	23.9	15.4	15.7	0.4	2.2	2.3
40	90.0	12.0	12.0	0.0	0.0	19.0	42.3	17.4	1.3	0.8	3.8
41	24.2	19.9	25.0	0.0	0.0	47.0	39.8	37.3	3.6	4.2	3.4

The metal solar-radiation-absorbing layers and the dielectric layers were applied using a cathode sputtering technique under conditions conventionally used in this type of technique. As a variant, the dielectric layers could have been applied using the well-known plasma-enhanced chemical vapour deposition (PECVD) technique.

5

The silicon-nitride dielectric layers were produced from metal targets in an atmosphere consisting of a mixture of argon (30-70%) and nitrogen (70-30%) at a total pressure of 4 mtorr (0.53 Pa).

The chromium-zirconium layers (40% by weight Cr and 60% zirconium in the CrZr alloy) were deposited from metal cathodes in an atmosphere of argon alone. As a variant, the deposition atmosphere of this CrZr metal alloy could have contained a little nitrogen or oxygen originating from neighbouring zones of deposition. As a result thereof, the CrZr layer formed, while preserving its essentially metal character, would have contained a little nitrogen or oxygen. The obtained properties are similar. The silicon-oxide dielectric layers were initially produced from a silicon-based target in an atmosphere containing argon and oxygen.

On samples, the light transmittance TL and light reflectance substrate side were measured under illuminant D65, 2°. The CIE L*,a*,b* colour coordinates were also measured before and after heat treatment under illuminant D65, 10°. The angle at which the measurements were taken was 8°.

The samples were subjected to a heat treatment comprising maintenance at 670°C for 7 min and 30 sec. The ΔE^* variations in transmission and reflection are also given in the tables. In the examples, the notation SiN designates silicon nitride without representing a chemical formula, it being understood that the products obtained are not necessarily rigorously stoichiometric, but are those obtained under the indicated deposition conditions and that are neighbours of stoichiometric products. The layers made of SiN may contain up to about at most 10% by weight aluminium originating from the target. The dielectric layer according to the invention may furthermore consist of a plurality of individual layers comprising or consisting essentially of the same materials as above.

The mechanical and chemical resistances of the glazing units according to the invention without any silver-based layer were characterized by successful passing of the tests defined in standard EN 1096-2 for what are referred to as class B coatings. Furthermore, the glazing units according to the invention also met the requirements of the following tests:

- the neutral salt spray (NSS) test according to standard ISO 9227-2006, preferably for at least 10 days;
- the climatic chamber test according to standard EN 1036-2008, preferably for at least 10 days;
- the Cleveland test according to standard ISO 6270-1:1998, preferably for at least 10 days;
- the (SO₂) acid resistance test according to standard EN 1096-2;
- the automatic web rub test (AWRT) described below: a piston covered with a cloth made of cotton was brought into contact with the layer to be evaluated and oscillated over its surface. The piston bore a weight so as to apply a force of 33 N to a finger having a diameter of 17 mm. The rubbing of the cotton over the coated surface will damage (remove) the layer after a certain number of cycles. The test is used to define the limit before the layer discolours (partial removal of the layer) and scratches appear in the layer. The test was carried out for 10, 50, 100, 250, 500 and 1000 cycles in various separate locations on the sample. The sample was observed under an artificial sky in order to determine whether a discolouration or scratches could be seen on the sample. The AWRT result indicates the number of cycles resulting in no or very little degradation (invisible to the naked eye under a uniform artificial sky at 80 cm distance from the sample); and
- the dry brush test (DBT) according to standard ASTM D2486-00 (test method "A"), preferably

for at least 1000 cycles,
both before and after heat treatment if indeed one were carried out.

Table II: the following examples were produced with other proportions of Cr and Zr in the solar-radiation-absorbing metal alloy. Just as for the preceding examples, example reference numbers including the letter ("R") are comparative examples, reference numbers without this letter being examples according to the invention. The results (OK for good; KO for unacceptable; and S for satisfactory) of two chemical resistance tests are also indicated: climatic chamber (CC) and Cleveland test (Clev).

The same structure, as follows, was used: 30 nm SiN/15 nm functional layer/30 nm SiN (SiN means Si₃N₄, possibly doped with aluminium so as to make the initial silicon target conductive). The various layers were deposited in the same way as in the preceding examples. The make-up of the functional layer is given in Table II below. The Cr and Zr percentages with respect to the total alloy are given by weight.

Ex.	Functional layer	ΔE^*_{Ti}	ΔE^*_{Rc}	ΔE^*_{Rg}	TL	Rc	Rg	CC	Clev
5	80% Cr/20% Zr	1.44	1.44	1.55	21	30	28	OK	OK
6	60% Cr/40% Zr	0.94	1.65	1.80	24	27	25	OK	OK
7	40% Cr/60% Zr	0.63	1.43	1.46	26	25	22	OK	OK
8	25% Cr/75% Zr	2.44	3.56	2.42	26	26	21	OK	OK

Table III: the comparative example and the example according to the invention of multilayer stacks, each deposited on a glazing substrate, collated in Table III below contain a silver-based supplementary metal layer inserted between two metal solar-radiation-absorbing layers. The terminological conventions are the same as for the preceding tables.

Ex.	Coating	TL	Rc	Rg	ΔE^*_{Ti}	ΔE^*_{Rg}	CC	Clev
5R	SiN (40nm)/NiCr (1nm)/Ag (18nm)/NiCr (1nm)/SiN (56nm)	54	13	24	2.26	1.88	OK	OK
9	SiN (40nm)/CrZr (1nm)/Ag (18nm)/CrZr (1nm)/SiN (56nm)	59	15	23	1.61	1.03	OK	OK

The variation in the thicknesses of the dielectric layers, within reasonable limits, did not significantly affect the modification in hue during the heat treatment, nor durability, but of course it modified initial aesthetic appearance (and in particular initial hue).

As for the preceding examples, the metal solar-radiation-absorbing layers, the silver-based supplementary metal layers and the dielectric layers were applied using a cathode sputtering technique under conditions conventionally used in this type of technique. As a variant, the dielectric layers could have been applied using the well-known plasma-enhanced chemical vapour deposition (PECVD) technique.

Table IV: examples 10-17 of the multilayer stack, each of which was deposited on a glazing substrate, and the results of which are collated in Table IV below, more particularly related to the embodiment of the invention in which the light reflectance substrate side was high, and in particular higher than the light reflectance multilayer-stack side. The solar-radiation-absorbing layer was an alloy comprising 40% chromium and 60% zirconium. The terminological conventions are the same as for

Table I. The numbers between parentheses are the physical thicknesses in nm of the various layers. The properties (in % for the light transmittance and light reflectance) are given for a monolithic glazing unit after heat treatment. The term "TZO" represents a mixed oxide comprising 50% TiO₂ and 50% ZrO₂.

Ex.	Coating	TL	Rc	Rg
10	SiN (13)/CrZr (6.7)/SiN (50.6)	33.8	7.4	34.6
11	SiN (13)/CrZr (10.3)/SiN (46.7)	23.5	13.8	39.9
12	SiN (17)/CrZr (17)/SiN (40)	12.6	29.2	45.5
13	SiN (79.2)/CrZr (14)/SiN (50.1)	22.2	15	30.9
14	SiN (16.4)/CrZr (7.6)/TZO (24.1)/SiN (25)	31.3	8.6	39
15	SiN (13)/CrZr (11.6)/TZO (21.4)/SiN (25)	21.6	12.7	44.7
16	SiN (13.4)/CrZr (21.3)/TZO (18.2)/SiN (31.3)	10.8	15.7	51.2
17	SiN (78)/CrZr (14.7)/TZO (22.5)/SiN (25.1)	22	13.4	33

5 Table Va below gives examples with two silver-based supplementary metal layers, the solar-radiation-absorbing layer being in the first dielectric coating placed between the substrate and the first silver-based layer. The various layers were deposited under the same conditions as for the examples of Table I. The properties were measured in the same way and are given in Table Vb. The examples of Table Va also underwent a heat treatment identical to that described for the examples of Table I, and the variations in the properties thereof are, in the same way, given in terms of ΔE^* , either in transmission ΔE^*_{T1} (or ΔE^*_{T2}) or in reflection layer side (ΔE^*_{Rc}) or in reflection glazing-substrate side (ΔE^*_{Rg}). In addition, the following are also indicated: the coordinates L^*, a^*, b^* , and Y (Y representing either the total light transmittance, or the total light reflectance) in transmission (TL), in reflection glazing-substrate side (Rg) and in reflection on the side of the systems of layers (Rc); the variation in total light transmittance (Δ_{T1}); and the variation in total reflection glazing-substrate side (Δ_{Rg}) and on the side of the system of layers (Δ_{Rc}). The term "ZSO5" represents a mixed zinc-tin oxide formed from a cathode of a zinc-tin alloy containing 52% by weight zinc and 48% by weight tin, in such a way as to form the spinel structure of zinc stannate Zn₂SnO₄. The expression "AZO" relates to an aluminium-doped zinc oxide, obtained by cathode sputtering, of a ceramic cathode formed by the oxide to be deposited, in a neutral or slightly oxidizing atmosphere. As a variant, AZO could have been replaced by other barriers well known in the field and appropriate for the properties desired for the layer system formed, such as, for example, an optionally niobium- or zirconium-doped Ti oxide preferably obtained from a ceramic target formed from the oxide to be deposited; or pure ZnO. B represents a layer that forms a barrier to the oxidation of the silver, such barriers being well known in the field. D represents one or more dielectric layers, in particular based on zinc stannate, optionally doped ZnO, or another material known in the field and adapted to this type of layer stack, for example a nitride such as AlN. M represents the optionally aluminium-doped ZnO-based wetting layer. IR represents the infrared-reflecting functional layers. ABS represents the solar-radiation-absorbing layer.

25 The examples given in Table VIa are, in the same way, examples with two silver-based supplementary metal layers, just as for Table Va, but this time the solar-radiation-absorbing layer was in

the second dielectric coating placed between the first silver-based layer and the second silver-based layer. The properties obtained are given in Table VIb in the same way as for Table Vb. The term TZO_{65} means a mixed titanium-zirconium oxide with 35% zirconium and 65% titanium, i.e. an oxide that is not TZO (50/50).

5 Table VIIa below gives examples with three silver-based supplementary metal layers, the solar-radiation-absorbing layer being in the first dielectric coating placed between the substrate and the first silver-based layer. The corresponding properties are given in Table VIIb, for a substrate made of a single non-heat-treated pane of clear glass of 6 mm thickness. The value of the solar factor (g) is also indicated.

10 Table VIIa below also gives examples with three silver-based supplementary metal layers, but this time the solar-radiation-absorbing layer was in the second dielectric coating placed between the first silver-based layer and the second silver-based layer. The corresponding properties are given in Table VIIb, for a substrate made of a single non-heat-treated pane of clear glass of 6 mm thickness. The value of the solar factor (g) is also indicated.

Of course, the invention is not limited to the mentioned exemplary embodiments.

Table Vfb:

Ex.	Δ_{TL}	Δ_{gc}	Δ_{Rg}	ΔE^*_{TL}	ΔE^*_{Rg}	ΔE^*_{Rc}	TL			Rg			Rc					
							Y	L*	a*	b*	Y	L*	a*	b*	Y	L*	a*	b*
45	2.0	1.4	0.8	0.9	2.7	3.9	60.3	81.9	-4.1	4.8	11.9	41.2	-2.6	-8.0	6.9	32.0	-2.2	-16.2
46	1.2	1.8	0.3	1.5	2.5	4.4	55.9	79.6	-4.5	3.6	12.3	41.8	-2.2	-4.8	5.9	29.6	0.6	-16.4
47	1.0	2.1	-0.4	2.1	1.4	5.4	39.3	69.0	-5.8	1.8	20.7	52.6	-1.3	1.1	7.6	33.7	5.4	-18.9
48	-0.7	2.0	-0.1	2.0	2.2	5.2	55.9	79.6	-4.4	3.7	12.3	41.8	-1.9	-4.9	5.9	29.6	0.5	-15.4
49	2.8	1.6	-0.8	1.6	2.0	4.7	55.9	79.6	-4.6	3.5	12.3	41.8	-2.3	-4.7	5.9	29.6	0.4	-17.4

Table Vlla

Ex.	D1a	ABS	CrZr	D1b		M	IR1	B	D2		M	IR2	B	D3		M	IR3	B	D4			
				SiN	ZSO5				SiN	ZSO5				SiN	ZSO5				SiN	ZSO5	SiN	ZSO5
50	16.2	1.8	13.4	1.1	5	5	11.5	4	20	20	21.1	5	15.2	4	15	17	29.1	5	16.2	4	14	18
51	16.2	1.8	13.4	1.1	5	5	11.5	4	61.1	0	0	5	15.2	4	32	0	29.1	5	16.2	4	14	18

Table Vllb:

Ex.	g	ΔE^*_{TL}	ΔE^*_{Rg}	ΔE^*_{Rc}	ΔE^*_{Rg}	TL			Rg			Rc					
						Y	L*	a*	b*	Y	L*	a*	b*	Y	L*	a*	b*
50	37	3	4	8	8	36.5	80	-6	-0.8	6.7	31.1	-3.9	-0.9	2.9	19.6	12.8	-9
51	37	3	4	8	8	36.5	80	-6	-0.8	6.7	31.1	-3.9	-0.9	2.9	19.6	12.8	-9

Table VIIIa:

Ex.	D1		M		IR1		B		D2a		ABS		D2b		M		IR2		B		D3		M		IR3		B		D4						
	ZSO5	17.7	ZnO	5	Ag	9.2	AZO	4	ZSO5	19	SiN	20	CrZr	0.8	SiN	15	ZnO	5	Ag	15.1	AZO	4	ZSO5	20	ZnO	5	Ag	15.5	AZO	4	ZSO5	14	SiN	18.9	
52																																			

Table VIIIb:

Ex.	g	ΔE^*_{TL}	ΔE^*_{Rc}	ΔE^*_{Bg}	TL			Rg			Rc					
					Y	L*	a*	Y	L*	a*	Y	L*	a*			
52	37.5	1.5	7.1	3.5	57	80.3	-5.9	-1.5	5.1	27.1	1.6	-5.8	4.1	24.8	5.4	-13.5

NAPFÉNYVÉDŐ RÉTEGGEL ELLÁTOTT ÜVEG



Szabadalmi igénypontok

1. Napfényvédő üveg, amely egy üveg hordozónak legalább az egyik oldalán többrétegű struktúrát tartalmaz, melyben legalább egy napsugárzás-elnyelő réteg és a napsugárzás-elnyelő réteget közrefogó dielektrikumbevonatok vannak, **azzal jellemezve**, hogy a napsugárzás-elnyelő réteg cirkóniumot és krómot tartalmazó fémötvözetreteg, amely legalább 25 tömeg% krómot és legalább 20 tömeg% cirkóniumot tartalmaz, a többrétegű struktúra a hordozó és a napsugárzás-elnyelő réteg között és a napsugárzás-elnyelő réteg felett a szilícium-oxid, alumínium-oxid, szilícium-nitrid, alumínium-nitrid, alumínium-szilícium-nitrid keverék, szilícium-oxinitrid és alumínium-oxinitrid alkotta csoportból választott vegyületet tartalmazó legalább egy dielektrikumanyag-bevonatot tartalmaz.

2. Az 1. igénypont szerinti üveg, **azzal jellemezve**, hogy a napsugárzás-elnyelő réteg 25-75 tömeg% cirkóniumot tartalmaz.

3. A 2. igénypont szerinti üveg, **azzal jellemezve**, hogy a napsugárzás-elnyelő réteg 45-65 tömeg% cirkóniumot tartalmaz.

4. Az előző igénypontok bármelyike szerinti üveg, **azzal jellemezve**, hogy a napsugárzás-elnyelő rétegnek 0,5 és 30 nm közötti, előnyösen 2 és 25 nm közötti geometriai vastagsága van.

5. A 4. igénypont szerinti üveg, **azzal jellemezve**, hogy a napsugárzás-elnyelő rétegnek 10 és 25 nm közötti, előnyösen 12 és 22 nm közötti geometriai vastagsága van.

6. A 4. igénypont szerinti üveg, **azzal jellemezve**, hogy a napsugárzás-elnyelő rétegnek 0,5 és 10 nm közötti, előnyösen 2 és 5 nm közötti geometriai vastagsága van.

7. Az előző igénypontok bármelyike szerinti üveg, **azzal jellemezve**, hogy a hordozó és a napsugárzás-elnyelő réteg között lévő dielektrikumanyag-réteg optikai vastagsága legalább 10 nm és legfeljebb 200 nm, előnyösen legalább 20 nm és legfeljebb 180 nm.

8. Az előző igénypontok bármelyike szerinti üveg, **azzal jellemezve**, hogy a napsugárzás-elnyelő réteg felett lévő dielektrikumanyag-réteg optikai vastagsága legalább 15 nm és legfeljebb 200 nm.

9. Az előző igénypontok bármelyike szerinti üveg, **azzal jellemezve**, hogy a többrétegű struktúra legalább két napsugárzás-elnyelő réteget tartalmaz.

10. Az előző igénypontok bármelyike szerinti üveg, **azzal jellemezve**, hogy a többrétegű struktúra legalább egy további ezüstöt tartalmazó fémréteget tartalmaz, amely ezüstöt tartalmazó fémréteg(ek) mindegyike dielektrikum bevonattal van körülveve.

11. A 10. igénypont szerinti üveg, **azzal jellemezve**, hogy a dielektrikum bevonatok legalább egyike legalább két dielektrikumréteget tartalmaz és a napsugárzás-elnyelő réteg a dielektrikum bevonat ezen két dielektrikumrétege között van elhelyezve.

12. A 11. igénypont szerinti üveg, **azzal jellemezve**, hogy a napsugárzás-elnyelő fémréteget körülvevő két dielektrikumréteg szilícium-nitridet vagy alumínium-nitridet tartalmaz.

13. A 10. igénypont szerinti üveg, **azzal jellemezve**, hogy a további ezüstöt tartalmazó fémréteg a struktúrában közvetlenül a napsugárzás-elnyelő fémrétegen és/vagy az alatt van.

14. A 10-13. igénypont szerinti üveg, **azzal jellemezve**, hogy az egy vagy több további ezüstöt tartalmazó fémrétegnek legalább 9 nm, előnyösen legalább 13 nm és legfeljebb 23 nm, előnyösen legalább 15 nm és legfeljebb 22 nm vastagsága van.

5 15. A 10-14. igénypont szerinti üveg, **azzal jellemezve**, hogy a napsugárzás-elnyelő rétegnek 0,5 és 8 nm, előnyösen 0,5 és 5 nm közötti geometriai vastagsága van.

16. Az előző igénypontok bármelyike szerinti üveg, **azzal jellemezve**, hogy az üveg legalább 630°C és legfeljebb 670°C hőmérsékletnek 7 percig tartó alávetésekor a transzmisszió kolorimetriai változása ΔE^*TLr 8-nál kisebb, előnyösen 5-nél kisebb, még előnyösebben 3-nál kisebb.

10 17. Az előző igénypontok bármelyike szerinti üveg, **azzal jellemezve**, hogy az üveg legalább 630°C és legfeljebb 670°C hőmérsékletnek 7 percig tartó alávetésekor az üvegoldali reflexió kolorimetriai változása ΔE^*Rg 8-nál kisebb, előnyösen 5-nél kisebb, még előnyösebben 3-nál kisebb.

18. Az előző igénypontok bármelyike szerinti üveg, **azzal jellemezve**, hogy a napsugárzás-elnyelő fémréteg vastagsága úgy van választva, hogy 4 mm vastagságú átlátszó üveg hordozó esetén a fény transzmissziója legalább 2% és legfeljebb 75%.

15 19. Az előző igénypontok bármelyike szerinti üveg, **azzal jellemezve**, hogy a dielektrikum bevonatok optikai vastagsága úgy van választva, hogy a rétegoldali reflexió legalább 1% és legfeljebb 55%.

20. Az előző igénypontok bármelyike szerinti üveg, **azzal jellemezve**, hogy a fény hordozóoldalon mért reflexiója legalább 27%, előnyösen legalább 30% és különösen legalább 35%.

20 21. Az előző igénypontok bármelyike szerinti üveg, **azzal jellemezve**, hogy a hordozó oldalán mért fényreflexió legalább 2-szer, előnyösen legalább 2,5-szer, különösen legalább 3-szor nagyobb, mint a rétegrendszer oldalán mért fényreflexió.

25 22. A 12. igénypont szerinti üveg, **azzal jellemezve**, hogy a többrétegű struktúra az alábbi sorozatot tartalmazza: szilícium-nitrid vagy alumínium-nitrid réteg / napsugárzás-elnyelő réteg / szilícium-nitrid vagy alumínium-nitrid réteg / Zn, Sn, Ti vagy Zr oxidot vagy ezek keverékét tartalmazó közbeiktatott átlátszó oxidréteg, amely réteg a nedvesítőrétegtől különböző / cink-oxid nedvesítőréteg / további ezüstöt tartalmazó fémréteg.

23. A 22. igénypont szerinti üveg, **azzal jellemezve**, hogy a napsugárzás-elnyelő fémrétegnek 0,5 és 8 nm közötti geometriai vastagsága van.

30 24. A 22. vagy a 23. igénypont szerinti üveg, **azzal jellemezve**, hogy a közbeiktatott átlátszó oxidréteget cink-ón-oxid keverék vagy titánium-cirkónium-oxid keverék és előnyösen legalább 20% ónt és 10% cinket tartalmazó cink-ón oxid keverék képezi.

25. Az előző igénypontok bármelyike szerinti napfényvédő üveg alkalmazása gépjármű üveges elemeként, épületek üveges elemeként vagy háztartási elektromos készülékek, például sütőajtó üveges elemeként.