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WO 2002/076901 A1 **DE 010042194 A1**
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(54) Abstract Title**: Multi layer solar control glass coating**

(57) The invention relates to a heat treatable coated glass pane with a low-e and/or solar control coating comprising in sequence at least the following transparent layers: a lower dielectric layer, a lower embedding layer comprising a suboxide of indium or of an indium-based alloy, a silver-based functional layer, an upper embedding layer, and an upper dielectric layer. The improvement consists in that the upper embedding layer comprises at least one metal or oxidizable metal compound excluding suboxides of indium or of an indium-based alloy, and the upper dielectric layer comprises an oxide of tin and zinc or an (oxi)nitride of silicon and/or aluminium. The invention furthermore relates to a process for the manufacture of such heat treatable coated glass panes.

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HEAT TREATABLE COATED GLASS PANE AND PROCESS FOR THE MANUFACTURE THEROF

The invention relates to heat treatable coated glass panes with a low-e and/or solar control coating and to a process for the manufacture thereof.

Heat treated glass panes which are toughened to impart safety properties and/or are bent are required for a large number of areas of application, for example for architectural or motor vehicle glazings. It is known that for thermally toughening and/or bending glass panes it is necessary to process the glass panes by a heat treatment at temperatures near or above the softening point of the glass used and then either to toughen them by rapid cooling or to bend them with the aid of bending means. The relevant temperature range is for standard float glass of the soda lime silica type is typically about 590 – 690 °C, the glass panes being kept in this temperature range for several minutes before initiating the actual toughening and/or bending process.

"Heat treatment", "heat treated" and "heat treatable" in the following description and in the claims refer to thermal bending and/or toughening processes such as mentioned before and to other thermal processes during which a coated glass pane reaches temperatures in the range of about 590 – 690 °C for a period of several minutes.

Difficulties can arise if these glass panes are to be provided with coatings, particularly with coatings comprising at least one silver-based functional layer, e.g. to impart solar control and/or low-e properties to reduce the energy transfer through the coated glass pane in certain spectral regions. Such coatings are not of themselves heat treatable. Silver-based functional layers are generally embedded between several auxiliary layers which, e.g., protect them, modify the reflection and transmission characteristics of the coating, etc.

Although it is fundamentally possible to apply such coatings to the glass pane after the heat treatment has taken place, it would be preferable if coatings able to withstand heat treatments without significant damages could be made available.

A number of proposals have been made in the past how to provide visibly transparent coatings with at least one silver-based functional layer which can be applied to flat glass panes and subsequently be subjected to a heat treatment without damaging the coating. The common feature of certain of these prior proposals is to use carefully chosen embedding layers directly above and/or below the silver-based functional layer which protect the silver-based functional layer(s) during the heat treatment, e.g. by capturing oxygen diffusing through the coating or by stabilizing the silver-based functional layer(s) or otherwise. Usually transparent dielectric layers, e.g. consisting of metal oxides, (oxi)nitrides or the like, are additionally provided below the lower embedding layer and above the upper embedding layer. Such dielectric layers mainly assist to anti-reflect the silver-based functional layer by optical interference. (Oxi)nitrides here and in the following encompasses oxinitrides and nitrides.

DE 36 28 057 A1 discloses heat treatable coated glass panes with a three-layer low-e coating wherein the silver functional layer is embedded between a lower and an upper embedding layer of ZnO to which Al_2O_3 has been added. The two doped metal oxide embedding layers are produced from doped metal oxide targets by means of DC cathode sputtering in a coating atmosphere containing 0 – 20 vol.% oxygen. The deposition process is carried out such that during the manufacture of the coating, even without a barrier layer usually provided on top of the silver layer, the silver layer comes into as little as possible contact with oxygen. For coatings wherein the functional layer comprises materials such as Au, Cu, Pd and Rh, DE 36 28 057 A1 proposes to use materials chosen from tin oxide, tin-containing indium oxide, antimony oxide and indium oxide for both embedding layers. The embedding layers of this prior publication serve at the same time as anti-reflection dielectric layers. No further dielectric layers are provided.

Heat treatable coated glass panes with a coating which comprises a series of layers including a silver functional layer and metallic lower and upper embedding layers are known from EP 0 229 921 A1. The transition metals Ta, W, Ni and/or Fe are specified as materials for both embedding layers.

Other heat treatable coated glass panes with a coating comprising a series of layers including a silver functional layer and an upper embedding layer, preferably complemented by a lower embedding layer, are known from EP 0 233 003 A1. The transition metals Al, Ti, Zn, Ta and/or Zr are specified as materials for the embedding layers. Although according to this publication the embedding layers shall be produced as far as possible without contact with oxygen, suboxides (= substoichiometric oxides) of the mentioned metals may also be used, if it is ensured that the embedding layers evidence an oxygen deficit sufficient to absorb oxygen diffusing through the coating during the heat treatment and thereby to protect the silver functional layer against potentially damaging influences.

EP 0 761 618 A1 likewise discloses a heat treatable coated glass pane with a coating comprising at least one series of layers each comprising a silver functional layer between two embedding layers. According to this publication the upper and lower embedding layers are selected and dimensioned so as to be capable of absorbing oxygen to a sufficient degree. Furthermore, the silver functional layer is sputtered in an oxygen-containing coating atmosphere. Metals, metal alloys, suboxides, nitrides or suboxidic oxinitrides whose affinity for oxygen is particularly high are specified as materials for the embedding layers. Mentioned specifically are Ti, Al, W, Ta, Zr, Hf, Ce, V, Ni, Cr, Zn, Nb, their alloys, suboxides, nitrides or suboxidic nitrides.

EP 0 963 960 A1 and EP 1 089 947 A1 teach in the same context the use of embedding layers comprising suboxides of alloys of two metals. The only specific example disclosed is Ni-Cr suboxide.

EP 1 140 721 A1 discloses low-e and/or solar control coatings, some of which being heat treatable, wherein above the silver functional layer a ceramic metal-doped metal oxide upper embedding layer is arranged. Fully oxidized Al-doped zinc oxide is the preferred material for the upper embedding layer. Optionally a ceramic metal-doped metal oxide lower embedding layer is provided.

EP 1 385 798 A1, from which the instant invention departs, discloses heat treatable coated glass panes with a low-e and/or solar control coating comprising in sequence from the glass surface at least the following transparent layers: a lower dielectric layer, a lower embedding layer, a silver-based functional layer, an upper embedding layer and an upper dielectric layer, wherein the upper embedding layer comprises a suboxide of indium or of an indium-based alloy in a sufficient thickness to make the coating heat treatable. Only in addition hereto it is preferred that the lower embedding layer also comprises a suboxide of indium or of an indium-based alloy.

While certain coated glass panes of the kind described above and specifically those disclosed in EP 1 385 798 A1 proved to be effectively heat treatable they were commercially less successful because of the comparably high production cost involved which was caused by the considerable target price increase for indium and indium oxide targets during the recent years.

The inventors of the instant invention furthermore found that several of the heat treatable coated glass panes described hereinbefore did not withstand one or the other test simulating ordinary environmental influences during storage, transport and use of the coated glass panes before and after a heat treatment and the mechanical and chemical conditions acting on the coated glass panes during usual handling and processing steps.

A further disadvantage noticed by the inventors is the difficulty to match coatings such as disclosed in EP 1 385 798 A1 to high light transmittance low-e coatings with an optimized layer arrangement below the functional layer(s) such as disclosed in WO 99/00528 A1.

The invention therefore primarily aims to provide heat treatable coated glass panes such as described hereinbefore which are less costly to produce. The inventive heat treatable low-e and/or solar control coatings should withstand ordinary environmental influences during storage, transport and use of the coated glass panes both before and after a heat treatment and survive the mechanical and chemical conditions acting on the coated glass panes during usual handling and processing steps without significant damages.

The invention furthermore aims to provide heat treatable coated glass panes with a high light transmittance and a low emissivity (corresponding to a low sheet resistance) and/or with good solar control properties, i.e. low solar energy transmittance combined with high light transmittance.

The inventions also aims to provide heat treatable coated glass panes which are easier to match in terms of colour characteristics to high light transmittance low-e coatings with an optimized layer arrangement below the functional layer(s) such as disclosed in WO 99/00528 A1.

Another aim is to keep the haze value of the heat treated coated glass pane low.

A further aim is to provide a coating with low changes of the optical properties of the coated glass pane due to a heat treatment.

The solution of one or more of the problems mentioned above is the subject of claim 1. Preferred embodiments are set out in product claims 2 - 25.

The invention also aims to provide an improved process for the manufacture of heat treatable coated glass panes such as specified in the product claims.

Solutions to achieve this aim are set out in claims 26 - 31.

Heat treated coated glass panes manufactured from coated glass panes according to the product claims cited above are set out in claim 32.

Surprisingly heat treatable coated glass panes with a silver-based functional layer embedded between upper and lower embedding layers complemented by lower and upper dielectric layers, the coated glass panes having a superior quality and being producible at reasonable cost, can be provided by using only a lower embedding layer which comprises a suboxide of indium or of an indium-based alloy, by using an upper embedding layer which comprises metals and/or oxidizable metal compounds excluding suboxides of indium or of an indium-based alloy, and by using an upper dielectric layer which comprises an oxide of tin and zinc (Zn-SnO$_x$) or an (oxi)nitride of silicon and/or aluminium.

Here as well as in other contexts of the invention "comprises" shall be understood as meaning "consists predominantly of". Such predominance is generally achieved if the atomic ratio of the specified material or of the specified partial layer to the total amount of material or of the whole layer is above 50 %, above 70 % or even above 90 %.

Apparently the heat treatability of the inventive coatings basically results from the combined effect of a carefully chosen outer dielectric layer which consists of Zn-SnO$_x$ or silicon and/or aluminium (oxi)nitride, which are known for their good diffusion barrier properties, of the lower embedding layer consisting of a suboxidic indium or indium-based alloy oxide which provides a well-suited growth base and surface for the silver-based functional layer which remains stable during the heat treatment even while oxidizing and of the presence of an oxidizable upper embedding layer specified hereinafter in more detail.

With such basic arrangement the upper embedding layer may be produced as a single layer or a multi-layer from a variety of metals or metal compounds known for barrier or oxygen scavenger purposes in this location to those skilled in the art, indium-based suboxides being excluded not only for cost reasons. It has been found that when the indium-based suboxide upper embedding layer of EP 1 385 798 A1 is replaced with other metals or oxidizable metal compounds well known in the art as having a barrier and/or oxygen scavenger function the light transmission of the heat treated coated glass pane for a given thickness of the silver-based functional layer may be increased.

The metals and/or oxidizable metal compounds of the upper embedding layer may be chosen from among those well known as oxygen scavenger materials usable to protect a silver-based functional layer against oxygen diffusion, e.g. those disclosed in EP 0 761 618 A1 mentioned above: Metals, metal alloys, suboxides, nitrides or suboxidic oxinitrides whose affinity for oxygen is particularly high, specifically Ti, Al, W, Ta, Zr, Hf, Ce, V, Ni, Cr, Zn, Nb, their alloys, suboxides, nitrides or suboxidic nitrides.

If a high light transmittance of the heat treated coated glass pane is aimed at, their thickness and their oxidation ability should be set such that they are highly transparent after the heat treatment, e.g. by their oxidation.

Good results are specifically achieved when the upper embedding layer comprises slightly suboxidic Al-doped ZnO (ZnO_x:Al), specifically if sputtered from a conductive, suboxidic Al-doped ZnO target. Surprisingly it has been found that a low oxygen deficit in the Al-doped ZnO layer is sufficient and well-suited which does not lead to a noticeable light absorption effect by the upper embedding layer already for the non-heat treated coated glass pane, e.g. reduces the light transmission via absorption by no more than about 1 %. Using such a low-absorbing upper embedding layer advantageously reduces the light transmission change during a heat treatment.

Alternatively or additionally the upper embedding layer may comprise titanium and/or a suboxide of titanium, preferably a suboxide of titanium sputtered from a conductive titanium (sub)oxide target. The adherence of the upper embedding layer to the silver-based functional layer may here as in the case of other metal suboxides be increased if the layer has a graded composition, the layer being more metallic near the functional layer than at its outer surface.

Both the Al-doped ZnO and the titanium oxide targets mentioned before are preferably at least slightly suboxidic to increase their electrical conductivity and to simplify the deposition process for the suboxidic Al-doped zinc oxide (ZnO_x:Al) or titanium suboxide upper embedding layer. In both cases the coating atmosphere should contain only a very low amount of oxygen, which can be achieved by pre-sputtering the targets to provide clean and well-defined target surfaces before starting the actual deposition process, by pumping for a sufficiently long period to evacuate the sputter chamber to a very low pressure of residual gases and specifically by depositing the layers in a sputtering atmosphere to which only inert gases such as argon have been added.

While the thickness of the upper embedding layer is apparently less critical than according to EP 1 385 798 A1 it is preferred that the upper embedding layer has a thickness of less than about 15 nm and preferably about 0.5 - 10 nm. As a rule the appropriate thickness of the upper embedding layer depends upon the oxidation state of its material. If the upper embedding layer is metallic or comprises a metal nitride, a thickness at the lower end of the range is preferred, whereas for suboxide or suboxidic oxinitride layers a thickness of about 10 nm is more appropriate.

The function of the inventive upper dielectric layer which may be a single layer or may be composed of several partial layers is primarily to anti-reflect the silver-based functional layer. In addition hereto the material of this layer is chosen according to the invention such that a barrier function against diffusion of oxygen and other atoms through the coating during a heat treatment is provided.

The invention specifically proposes to use zinc-tin oxide ($Zn\text{-}SnO_x$) for the upper dielectric layer or at least one partial layer thereof. While an atomic ratio Zn : Sn of about 90 : 10 to 10 : 90 is generally feasible, a ratio of about 50 : 50 is preferred. To achieve the desired anti-reflection property and to function properly as a diffusion barrier the upper dielectric layer should preferably have a thickness of 10 – 50 nm.

Alternatively or additionally the upper dielectric layer may comprise a layer of an (oxi)nitride of silicon and/or aluminium. The atomic ratio Si : Al is preferably in the range of about 90 : 10 to 10 : 90, a ratio of about 50: 50 and more being generally preferred. The relative proportions of nitrogen and oxygen may be set comparably freely, a ratio of about 1 : 1 to 10 : 1 and specifically of about 5 : 1 being preferred.

To minimize the light absorption in the coating and to reduce the light transmission increase during a heat treatment the upper (and lower) dielectric layer should be deposited with an essentially stoichiometric composition.

The lower dielectric layer also primarily serves anti-reflection purposes. Materials preferred to provide superior stability during heat treatments are oxides of zinc and/or tin, $Zn\text{-}SnO_x$ being preferred. Again an atomic ratio Zn : Sn of about 90 : 10 to 10 : 90 is generally feasible but a ratio of about 50 : 50 is preferred.

If an optimized optical performance, i.e. high light transmittance and low solar energy transmittance at neutral colours, is aimed at it is preferred to use a lower dielectric layer which has a refractive index at 550 nm of at least 2.3 or which comprises a partial layer with such a high refractive index. A preferred material is an oxide of titanium, specifically titanium dioxide. It is particularly preferred to use a medium-frequency-sputtered oxide of titanium, preferably titanium dioxide, for the lower dielectric layer or a sublayer thereof. Oxinitrides of titanium are less preferred in this context as the presence of a significant amount of nitrogen in the lower dielectric layer seems to reduce the heat treatability of the coating. It is therefore preferred to deposit the titanium oxide layer in an atmosphere to which no nitrogen is added.

To achieve a proper anti-reflection property it is preferred that the lower dielectric layer has a geometrical thickness of about 10 – 50 nm, the optimum thickness depending on the geometrical thickness of the lower embedding layer, the refractive index of the materials used for both layers and the intended colour characteristics of the coated glass pane.

Partially in accordance with the general teaching of EP 1 385 798 A1 it is preferred that

- the lower embedding layer comprises a suboxide of an indium-based alloy in which the atomic ratio of indium to the minority metallic additive is between about 70 : 30 and about 99 : 1, a ratio of about 90 : 10 and a suboxide of indium-tin being preferred;
- the lower embedding layer comprises a suboxide of an indium-based alloy containing tin, zinc, cerium and/or gallium;
- the oxygen deficit and the thickness of the lower embedding layer are set such that during a subsequent heat treatment the surface resistance of the coating remains constant or decreases, the light transmittance of the coated glass pane increases and the haze value of the coated glass pane does not exceed about 0.5 %, preferably does not exceed about 0.3 %;
- the oxygen deficit of the lower embedding layer is set such that the imaginary part of the complex refractive index of the lower embedding layer at a wavelength of 450 nm after the completion of the coating is higher than about 0.05 and after a heat treatment is lower than about 0.05; and/or
- the lower embedding layer has a thickness of about 2 – 20 nm, preferably about 5 – 15 nm.

The increase in light transmittance during the heat treatment, which is in most cases in the range of some percent and is generally lower than following the teaching of EP 1 385 798 A1, is caused here mainly by the oxidation of the suboxidic lower embedding layer, whereas the remaining constant or the usually occurring decrease of the surface resistance of the coating indicates that the silver-based functional layer withstands the heat treatment without significant damage. Glass panes coated in accordance with the invention moreover evidence after heat treatment a very low haze. In the case of coatings produced according to the invention the haze is usually clearly less than 0.5 % and even less than about 0.3 %. Larger increases in the haze value if detected during the heat treatment are a good indicator that the coating is beginning to be damaged.

In some cases lower embedding layers of a suboxide of indium or of an indium-based alloy only about 2 nm thick will suffice to protect the silver layer during a heat treatment at the lower end of the applicable temperature and exposure time range. Coatings wherein the lower embedding layer has a thickness of about 10 nm or more withstand heat treatments of a longer duration and/or at higher temperatures without significant damage. For cost reasons the lower embedding layer will in practice usually be set to the lowest-possible value for the intended application of the heat treatable coated glass pane. In the case of relatively thin lower embedding layers experience shows that their oxygen deficiency should be set somewhat higher than that of thicker layers in order to impart heat treatability to the coating.

The silver-based functional layer will usually consist only of silver without other additives, as is normally the case in the area of low-e and/or solar control coatings. It is, however, within the scope of the invention to modify the properties of the silver-based functional layer by adding doping agents, alloy additives or the like or even thin metal or metal compound layers, as long as the properties of the silver-based layer necessary for its function as a highly light-transmitting and low light-absorbent IR-reflective layer are not substantially impaired thereby.

The thickness of the silver-based functional layer is dominated by its technical purpose. For typical low-e and/or solar control purposes its preferred thickness is about 8 – 15 nm and specifically about 10 – 12 nm.

The mechanical and chemical resistance of the inventive coating may in some cases be further improved if at least one thin adhesion promoting layer is provided which comprises Cr and/or, Ni, e.g. NiCr, stainless steel or suboxides and/or nitrides of one or more of these, the adhesion promoting layer being preferably disposed between the silver-based functional layer and the upper embedding layer and having a thickness of about 0.1 – 2 nm.

Adhesion promoting layers of this kind are known. Since they typically absorb visible light their thickness is preferably within the range of only a few nanometers or even less than one nanometre in order to reduce the light transmittance of the coated glass pane as little as possible. Within the scope of the invention the thickness of such thin adhesion promoting layers must for this reason in every case be clearly less than the thickness of the adjacent embedding layer and of the adjacent functional layer.

If the upper embedding layer comprises suboxidic Al-doped ZnO (ZnO_x:Al) an adhesion promoting layer may not be necessary. If however a thin adhesion promoting layer of NiCr is nevertheless used together with a ZnO_x:Al upper embedding layer it has been surprisingly found that such NiCr layer oxidizes much better than a NiCr layer provided between a silver-based functional layer and an indium or indium-based alloy suboxide upper embedding layer such as disclosed in EP 1 385 798 A1 so that a superior light transmittance can be achieved for a specific emissivity as compared to the known heat treatable low-e coatings.

A further improvement of the mechanical or chemical robustness of the coating may in some cases be achieved by the provision of a protective layer of a metal (alloy) oxide or (oxi)nitride above the upper dielectric layer, preferably comprising an oxide or (oxi)nitride of titanium, silicon and/or zirconium, titanium oxide or (oxi)nitride being preferred. The protective layer should have a thickness of no more than about 0.5 – 10 nm, preferably about 1 – 5 nm. Because of the low thickness of this protective layer and because of its ability to easily oxidize later when exposed to an oxygen-containing environment it may be preferable to deposit an oxidic protective layer in a suboxidic state and/or in a nitrogen-containing atmosphere to increase the deposition rate, without substantially impairing the optical properties or heat treatability of the coating thereby.

To optimize the optical properties of the coating the upper and/or lower dielectric layer may comprise at least one partial layer consisting of suitable materials generally known for dielectric layers of low-e and/or solar control coatings, in particular chosen from one or more of the oxides of Sn, Ti, Zn, Nb, Ce, Hf, Ta, Zr, Al and/or Si and/or of (oxi) nitrides of Si and/or Al. It will be appreciated that these layers may contain additives which modify their properties and/or facilitate their manufacture, e.g. doping agents or reaction products of reactive sputtering gases. In the case of oxide layers nitrogen may be added to the sputtering atmosphere leading to the formation of oxinitrides rather than oxides. It has, however, been found that within the scope of the invention oxidic lower dielectric layers are generally preferred to lower dielectric layers comprising (oxi)nitrides.

The optical thickness of any dielectric (partial) layer will normally be adjusted so that, together with the adjacent embedding layer, they anti-reflect the silver-based functional layer as much as possible. In particular cases, for example if a low solar energy transmission is aimed at, it may be desirable for the dielectric layers to comprise one or more light-absorbent partial layer(s). As a rule these will however be selected so as to reduce the light transmittance of the coated glass pane as little as possible.

While the invention is primarily directed to low-e and/or solar control coatings with only one functional layer it is within the scope of the invention to use two or more series of layers comprising a lower dielectric layer, a lower embedding layer, a silver-based functional layer, an upper embedding layer and an upper dielectric layer, the upper dielectric layer of one series of layers and the lower dielectric layer of a subsequent series possibly being combined to function as a Fabry-Perot separation layer between subsequent silver-based functional layers. By providing more than one series of layers the optical properties of the solar control and/or low-e coating may be further optimized for the respective application as is well known in the art. In these cases preferably each lower embedding layer comprises a suboxide of indium and/or of an indium-based alloy according to the invention and at least the outermost dielectric layer comprises an oxide of tin and zinc (Zn-SnO$_x$) or an (oxi)nitride of silicon and/or aluminium.

The invention is not limited to a certain production process for the coating. However, it is particularly preferred if at least one of the layers and most preferred all layers are applied by magnetron cathode sputtering, either in the DC mode or in the medium frequency mode, wherein metallic or semiconducting targets are sputtered reactively or non-reactively in a suitable sputtering atmosphere. Depending on the materials to be sputtered planar or rotating targets may be used.

In each case the coating process needs to be carried out by setting up suitable coating conditions such that the oxygen deficit of the lower embedding layer needed in accordance with the invention is achieved. Care should be taken by setting up suitable coating conditions that in each case the lower embedding layer is still sufficiently suboxidic even after the completion of the coating and does not already fully oxidise during the application of further layers of the coating. The same applies to the upper embedding layer.

It has been found that the coating process is more stable if suboxidic sputter targets are used and that the desired oxygen deficit of the suboxidic lower embedding layer is substantially easier to set than if metal or metal alloy, e.g. indium or indium-based alloy targets are used. Surprisingly it is not essential that the oxygen deficit of the suboxidic target is very precisely specified. What is apparently decisive for the improved controllability of the sputtering process is merely that there is actually an appreciable oxygen deficit in the suboxidic target.

The process for the manufacture of heat treatable coated glass panes according to the invention is carried out such that the deposition parameters determining the oxygen deficit and thickness of the lower embedding layer are set such that during a subsequent heat treatment the surface resistance of the coating remains constant or decreases, the light transmittance of the coated glass pane increases and the haze value of the coated glass pane does not exceed 0.5 %, preferably remains below 0.3 %.

The lower embedding layer is preferably deposited under such process conditions that the imaginary part of its complex refractive index at a wavelength of 450 nm after the completion of the coating is higher than 0.05 and after a heat treatment is lower than 0.05. The imaginary part of the complex refractive index has been found to be typically decreasing from about 0.1 before to about 0.01 after a heat treatment indicating an oxygen deficit and a resulting light absorbance in the layer before and a practically absorption-free, essentially fully oxidized state of the layer thereafter.

One option for depositing the lower embedding layer consists in sputtering an indium suboxide or indium-based alloy suboxide target, preferably a target of a suboxide of an indium-based alloy containing tin, zinc, cerium and/or gallium, tin being most preferred, in a coating atmosphere containing little or - preferably - no added oxygen. It is particularly preferred if the oxygen partial pressure in the sputtering chamber resulting from residual gases is reduced to values in the range of 10^{-6} to 10^{-5} mbar or even less.

Another option consists in sputtering an indium or an indium-based alloy target, preferably an indium-based alloy target containing tin, zinc, cerium and/or gallium, tin again being preferred, in a coating atmosphere the oxygen content of which is set lower than would be necessary for the deposition of a completely oxidised layer.

Particularly preferred is a manufacturing process wherein the upper embedding layer is sputtered from a conductive oxide or suboxide target, preferably comprising suboxidic Al-doped zinc oxide (ZnO_x:Al) or a suboxide of titanium.

Particularly high quality coatings can be achieved if the lower dielectric layer is medium-frequency sputtered from metal or metal oxide targets. Medium-frequency sputtering is well known in the art of sputter deposition and encompasses AC sputtering of two or more targets at a frequency in the range of about 5 – 100 kHz.

The invention is further explained in the following with the aid of examples.

For all examples the coatings were deposited on 4 mm thick standard float glass samples with a light transmittance of about 89 – 90 % using a conventional AC and/or DC magnetron sputtering device, medium-frequency sputtering being applied where appropriate, e.g. for sputtering lower dielectric layers of TiO_2.

The lower dielectric layers of either titanium dioxide (TiO_2) or zinc-tin oxide (Zn-SnO_x, atomic ratio Zn : Sn $\approx$ 50 : 50) were reactively sputtered from titanium or zinc-tin targets in an Ar/O_2 sputter atmosphere.

The lower embedding layers of either indium-tin suboxide (In-SnO_x) or suboxidic Al-doped zinc oxide (ZnO_x:Al) were in all but the third examples sputtered from conductive indium-tin suboxide or suboxidic Al-doped zinc oxide targets in a pure Ar sputter atmosphere without added oxygen. The targets had been pre-sputtered to clean and condition them and the sputtering chamber had been pumped for a sufficient period to reduce the oxygen partial pressure to below 10^{-5} mbar. In example 3 an indium-tin alloy target (atomic ratio In : Sn = about 90 : 10) was reactively sputtered in an Ar/O_2 sputter atmosphere, the oxygen content of which being set sufficiently low to produce a suboxidic indium-tin oxide layer with an imaginary part of its refractive index of around 0.1 before heat treating the coated glass pane.

The functional layer which in all examples consisted of pure silver (Ag) was sputtered from silver targets in an Ar sputter atmosphere without any added oxygen and a partial pressure of residual oxygen below 10^{-5} mbar.

In the examples no adhesion promoting layer was used. If such a very thin layer, e.g. a NiCr layer, were to be deposited between the silver-based functional layer and the upper embedding layer a pure sputter atmosphere without added oxygen should be used to deposit a layer which is as metallic as possible.

The upper embedding layers of either suboxidic Al-doped zinc oxide (ZnO_x:Al) or titanium suboxide (TiO_x) were sputtered from conductive ZnO_x:Al or titanium suboxide targets in a pure Ar sputter atmosphere without added oxygen. In the case of the TiO_x upper embedding layer the deposition process was controlled such that the oxygen content of the layer increased from the silver layer outwards.

The outer dielectric layers of either zinc-tin oxide (Zn-SnO_x) or tin oxide (SnO_2) were reactively sputtered from zinc-tin or tin targets in an Ar/O_2 sputter atmosphere. The atmosphere might also have contained nitrogen to increase the deposition rate.

The outer protective layers of titanium oxide (TiO_x) were reactively sputtered from titanium targets in an Ar/O_2 sputter atmosphere. The oxygen content in the sputter atmosphere was set at a relatively low level to increase the deposition rate so that the protective layers were presumably not fully oxidized after their deposition.

The coatings of examples 1 to 6 (examples 5 and 6 being comparative examples not featuring the invention) had the layer sequences as shown in Table 1 (thicknesses in nm):

Table 1

	lower dielectric layer	**lower embedding layer**	**functional layer**	**upper embedding layer**	**upper dielectric layer**	**protective layer**
Ex. 1	TiO_2 15	In-SnO_x 10	Ag 10	ZnO:Al 7	Zn-SnO_x 30	TiO_x 2.5
Ex. 2	Zn-SnO_x 20	In-SnO_x 12	Ag 10	ZnO:Al 10	Zn-SnO_x 30	TiO_x 2.5
Ex. 3	TiO_2 15	In-SnO_x 10	Ag 10	ZnO:Al 8	Zn-SnO_x 30	TiO_x 2.5
Ex. 4	TiO_2 15	In-SnO_x 10	Ag 10	TiO_x 3.5	Zn-SnO_x 30	TiO_x 2.5
Ex. 5	TiO_2 15	In-SnO_x 12	Ag 10	ZnO:Al 10	SnO_2 30	TiO_x 2.5
Ex. 6	TiO_2 15	ZnO:Al 10	Ag 10	In-SnO_x 10	Zn-SnO_x 30	TiO_x 2.5

The optical thicknesses of the lower and upper dielectric layers were not optimized to provide neutral colour characteristics but were essentially kept constant to provide a good basis for comparison of the behaviour of the exemplified coatings during a subsequent heat treatment. It will be appreciated that for production purposes the layer thicknesses would need to be adapted to the optical properties aimed at according to well known rules, e.g. to provide coated glass panes with a relatively neutral appearance, which in some embodiment preferably match well with non-heat treatable low-e coatings of the kind disclosed in WO 99/00528 A1 mentioned above.

After the deposition of the coatings of examples 1 to 6 the optical and some other properties of the coated glass panes were measured (values "before HT"). The samples were then heat treated at about 650 °C for about 5 minutes. Thereafter the properties referred to above were measured again (values "after HT"). The results are listed in Tables 2 and 3:

Table 2

	Haze before HT [%]	**Haze after HT [%]**	**Sheet resistance before HT [Ω/sq.]**	**Sheet resistance after HT [Ω/sq.]**	**T_L before HT [%]**	**T_L after HT [%]**
Ex. 1	0.07	0.09	6.0	3.2	82.5	86.6
Ex. 2	0.07	0.08	6.4	3.6	75.6	78.7
Ex. 3	0.08	0.14	6.5	3.5	79.0	84
Ex. 4	0.07	0.09	6.8	4.0	74.2	76.7
Ex. 5	0.08	0.47	6.2	4.5	85.5	87.9
Ex. 6	0.07	2.16	5.0	36.1	78.0	78.0

The values stated for the light transmittance T_L of the coated glass panes in the examples were derived from measurements according to EN 140. The sheet resistance was measured using a NAGY SRM-12 non-contact sheet resistance meter.

The haze values designate the percentage of transmitted light which in passing through the coated glass pane deviates from the incident beam direction by forward scattering (measured in accordance with ASTM D 1003-61). A haze value which remains low during a heat treatment is a good indicator for heat treatability.

The results listed in Table 2 demonstrate that the coatings of examples 1, 2 and 4 delivered a reasonably low increase in light transmission during a heat treatment and a nearly negligible increase in haze, its absolute value remaining extremely low and being not higher than haze values of typical non-heat treatable low-e coatings.

The haze after heat treatment of example 6 was unacceptably high whereas the haze of example 5 was just at the upper acceptable limit.

In the examples 1 - 4 the sheet resistance of the coatings which is correlated to the emissivity of the coatings decreased significantly by more than one third thereby improving the IR reflectance and emissivity of the coated glass panes by about one third and more.

Table 3

	Transm. colour before HT (a* / b*)	**Transm. colour after HT (a* / b*)**	**ΔE* Tran**	**Refl. colour film side before HT (a* / b*)**	**Refl. colour film side after HT (a* / b*)**	**ΔE* Refl. film side**	**Refl. colour glass side before HT (a* / b*)**	**Refl. colour glass side after HT (a* / b*)**	**ΔE* Refl. glass side**
Ex. 1	-3.4/1.7	-3.0/2.4	2.0	8.4/- 8.1	6.9/-9.4	2.2	4.4/-10.1	5.6/-11.0	2.5
Ex. 2	-1.2/6.3	-0.4/5.3	1.9	-3.7/- 15.6	-4.2/- 13.5	2.2	-5.3/-8.1	-5.1/-10.3	2.3
Ex. 3	not avail.	-1.5/4.3	-	not avail.	-4.9/-9.8	-	not avail.	-4.8/-7.8	-
Ex. 4	-2.2/1.7	0.3/4.4	4.7	-1.7/-16.2	-4.4/-11.4	7.3	-3.8/-8.2	-6.2/-11.2	4.4
Ex. 5	-3.0/2.9	-2.3/1.7	1.7	5.5/-10.5	2.9/-5.1	6.4	2.9/-10.5	2.1/-6.2	4.4
Ex. 6	-3.2/4.9	-1.6/3.8	2.0	5.4/-16.6	-1.1/-6.3	16.9	2.8/-15.5	-2.4/-6.1	12.2

The colour characteristics were measured and reported using the well established CIE LAB L*, a*, b* coordinates (see e.g. [0030] and [0031] in WO 2004-063 111 A1). $\Delta E^* = ((\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2)^{1/2}$, wherein ΔL*, Δa* and Δb* are the differences of the colour values L*, a*, b* of the coated glass pane each before and after a heat treatment. ΔE* values of less than 3 indicate a low colour change caused by the heat treatment.

It can be seen that the coatings of examples 1 and 2 provided reasonably well colour-stable products with all ΔE* values being clearly below 3. The coating of example 4 with its TiO_x upper embedding layer which had a comparably high oxygen deficit before the heat treatment was expectedly less colour-stable. For example 3 the colour parameters before the heat treatment were not measured but the coated glass pane had a very similar appearance before and after the heat treatment such as in examples 1 and 2.

All invention examples 1 - 4 were well matchable in colour characteristics to a non-heat treatable Pilkington **Optitherm™** SN coating produced by the applicant according to WO 99/00528 A1.

In addition to the quantitative properties given in the tables above the visual appearance of the coated samples before and after the heat treatment was evaluated using an internal evaluation system on a perfectness scale of 0 (perfect, no faults) to 3 (high number of clearly visible faults). The internal evaluation system considers both the microscopic light scattering effect of the coating (haze, see Table 2) and the more macroscopic effect of visible faults in the coating which cause local colour variations where the coating is damaged or imperfect. All examples showed a reasonably low number of faults (perfectness value 0 – 1) before the heat treatment. The coatings of examples 1 to 4 did not show a substantially increased amount of faults after the heat treatment whereas the coatings of the comparative examples 5 and 6 were visibly damaged (perfectness value 3) after the heat treatment making these coatings unacceptable for commercial purposes.

The coated glass panes of examples 1 to 4 not only proved to be heat treatable but also survived a number of tests simulating ordinary environmental influences during storage, transport and use of the coated glass panes both before and after a heat treatment. The tests comprised specifically a Taber test, a humidity test and an HCl test.

A Taber test provides a measure of the relative scratch resistance of coated glass panes. The test consists in placing the coated glass samples on a Taber abrader and to subject them to 10 revolutions with a standard 500 g weight. Then by microscopy, image and data analysis the average area of the non-abraded coating is determined. The harder the coating is the more of the coating remains on the glass.

A humidity test is an accelerated test that is carried out in a cabinet simulating the environmental influences the coating is expected to experience during its lifetime. The purpose of this test is to determine the relative durability of the coating when subjected to high temperature and high humidity conditions. The test involves visual analysis (monitor the development of characteristic corrosion spots) of the coated glass panes before and after a period of 30 hours in the test cabinet held at 70 °C and 75 % relative humidity.

The purpose of an HCl test is to assess the chemical durability of the coatings. The coated glass panes are submerged in a 0.01M solution of hydrochloric acid at 40 °C for five minutes. The sheet resistance of the coating before and after submerging the sample is determined. The HCl test is regarded as passed if the change in sheet resistance is below 5%.

Needless to say that the invention is not restricted to the exact layer sequences of the examples 1 - 4.

It is particularly within the scope of the invention to use other indium-based suboxides than suboxidic indium-tin oxide for the lower embedding layer, especially suboxides of indium and of indium-cerium, indium-zinc and/or indium-gallium, as long as indium is the predominant metal in the alloys used.

It is furthermore within the scope of the invention to use other materials than TiO_2 or Zn-SnO_x for the lower dielectric layer. Other materials than the exemplified suboxidic Al-doped zinc oxide and TiO_x may be used for the upper embedding layer.

The Zn-SnO_x outer dielectric layer may be replaced or supplemented by a layer of silicon and/or aluminium (oxi)nitride.

It is furthermore within the scope of the invention to refrain from applying a protective layer of TiO_x or the like on top of the coating if scratch resistance is not an issue.

Finally multiple layer systems using more than one silver-based functional layer may be derived from the principal teaching disclosed above.

Claims

1. Heat treatable coated glass pane with a low-e and/or solar control coating comprising in sequence at least the following transparent layers:
   - a lower dielectric layer,
   - a lower embedding layer comprising a suboxide of indium or of an indium-based alloy,
   - a silver-based functional layer,
   - an upper embedding layer, and
   - an upper dielectric layer,

   characterized in that
   - the upper embedding layer comprises at least one metal or oxidizable metal compound excluding suboxides of indium or of an indium-based alloy, and
   - the upper dielectric layer comprises an oxide of tin and zinc or an (oxi)nitride of silicon and/or aluminium.

2. Coated glass pane according to claim 1, characterised in that the upper embedding layer comprises suboxidic Al-doped ZnO.

3. Coated glass pane according to claim 2, characterised in that the upper embedding layer comprises suboxidic Al-doped ZnO sputtered from a suboxidic Al-doped ZnO target.

4. Coated glass pane according to claim 1, characterised in that the upper embedding layer comprises titanium and/or a suboxide of titanium.

5. Coated glass pane according to claim 4, characterised in that the upper embedding layer comprises a suboxide of titanium sputtered from a titanium suboxide target.

6. Coated glass pane according to any of the foregoing claims, characterised in that the upper embedding layer has a thickness of 0.5 – 10 nm.

7. Coated glass pane according to any of the foregoing claims, characterised in that the upper dielectric layer comprises zinc-tin oxide with an atomic ratio Zn : Sn of 90 : 10 to 10 : 90, preferably of about 50 : 50.

8. Coated glass pane according to any of the foregoing claims, characterised in that the upper dielectric layer has a geometric thickness of 10 – 50 nm.

9. Coated glass pane according to any of the foregoing claims, characterised in that the lower dielectric layer comprises an oxide of zinc and/or tin, preferably zinc-tin oxide with an atomic ratio Zn : Sn of 90 : 10 to 10 : 90, preferably of about 50 : 50.

10. Coated glass pane according to any of claims 1 to 8, characterised in that the lower dielectric layer has a refractive index at 550 nm of at least 2.3.

11. Coated glass pane according to claim 10, characterised in that the lower dielectric layer comprises an oxide of titanium, preferably titanium dioxide.

12. Coated glass pane according to claim 11, characterised in that the lower dielectric layer comprises a medium-frequency-sputtered oxide of titanium, preferably titanium dioxide.

13. Coated glass pane according to any of the foregoing claims, characterised in that the lower dielectric layer has a geometric thickness of 10 – 50 nm.

14. Coated glass pane according to any of the foregoing claims, characterised in that the lower embedding layer comprises a suboxide of an indium-based alloy in which the atomic ratio of indium to the minority metallic additive is between 70 : 30 and 99 : 1.

15. Coated glass pane according to any of the foregoing claims, characterised in that the lower embedding layer comprises a suboxide of an indium-based alloy containing tin, zinc, cerium and/or gallium.

16. Coated glass pane according to any of the foregoing claims, characterised in that the oxygen deficit and the thickness of the lower embedding layer are set such that during a subsequent heat treatment the surface resistance of the coating remains constant or decreases, the light transmittance of the coated glass pane increases and the haze value of the coated glass pane does not exceed 0.5 %, more preferably does not exceed 0.3 %.

17. Coated glass pane according to any of the foregoing claims, characterised in that the oxygen deficit of the lower embedding layer is set such that the imaginary part of the complex refractive index of the lower embedding layer at a wavelength of 450 nm after the completion of the coating is higher than 0.05 and after a heat treatment is lower than 0.05.

18. Coated glass pane according to any of the foregoing claims, characterised in that the lower embedding layer has a thickness of 2 – 20 nm, preferably 5 – 15 nm.

19. Coated glass pane according to any of the foregoing claims, characterised in that the silver-based functional layer has a thickness of 8 – 15 nm, preferably 10 – 12 nm.

20. Coated glass pane according to any of the foregoing claims, characterised in that at least one thin adhesion promoting layer is provided which comprises Cr and/or Ni, stainless steel or suboxides and/or (oxi)nitrides of these.

21. Coated glass pane according to claim 20, characterised in that the adhesion promoting layer is disposed between the silver-based functional layer and the upper embedding layer.

22. Coated glass pane according to claim 20 or 21, characterised in that the adhesion promoting layer has a thickness of 0.1 – 2 nm.

23. Coated glass pane according to any of the foregoing claims, characterised in that a protective layer of a metal (alloy) oxide or (oxi)nitride is additionally provided over the upper dielectric layer.

24. Coated glass pane according to claim 23, characterised in that the protective layer comprises an oxide or (oxi)nitride of titanium.

25. Coated glass pane according to claim 23 or 24, characterised in that the protective layer has a thickness of 0.5 – 10 nm, preferably 1 – 5 nm.

26. Process for the manufacture of a heat treatable coated glass pane with a low-e and/or solar control coating according to any of the foregoing claims, **characterised in that** the deposition parameters determining the oxygen deficit and thickness of the lower embedding layer are set such that during a subsequent heat treatment the surface resistance of the coating remains constant or decreases, the light transmittance of the coated glass pane increases and the haze value of the coated glass pane does not exceed 0.5 %, preferably does not exceed 0.3 %.

27. Process according to claim 26, characterised in that the lower embedding layer is deposited under such process conditions that the imaginary part of its complex refractive index at a wavelength of 450 nm after the completion of the coating is higher than 0.05 and after a heat treatment is lower than 0.05.

28. Process according to claim 26 or 27, characterised in that the lower embedding layer is deposited by sputtering an indium suboxide or indium-based alloy suboxide target,

preferably a target of a suboxide of an indium-based alloy containing tin, zinc, cerium and/or gallium, in a coating atmosphere containing little or no added oxygen.

29. Process according to claim 26 or 27, characterised in that the lower embedding layer is deposited by sputtering an indium or an indium-based alloy target, preferably an indium-based alloy target containing tin, zinc, cerium and/or gallium, in a coating atmosphere the oxygen content of which is set lower than would be necessary for the deposition of a completely oxidised layer.

30. Process according to any of claims 26 to 29, characterised in that the upper embedding layer is sputtered from a conductive oxide or suboxide target, preferably comprising suboxidic Al-doped ZnO or a suboxide of titanium.

31. Process according to any of claims 26 to 30, characterised in that the lower dielectric layer is medium-frequency sputtered from metal or metal oxide targets.

32. Heat treated coated glass pane with a solar control and/or low-e coating according to any of claims 1 to 25 which has a haze value of less than 0.5 %, preferably at most 0.3 %.

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Application No: GB0514119.7 **Examiner:** Nicola Keeley

Claims searched: 1-32 **Date of search:** 4 October 2006

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1 at least	DE 10042194 A1 (ARCON) See especially WPI abstract Accession No. 2003-031095-03
Y	1 at least	KR 0003979 B1 (PPG) See especially EPODOC abstract
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