

STACK

TECHNICAL FIELD

[0001] The present invention relates to a stack in which an optical multilayer film is formed on a transparent substrate.

5

BACKGROUND

[0002] A metal-based optical multilayer film in which a metal layer with infrared ray reflection characteristics is sandwiched between dielectric layers, in particular, a silver-based optical multilayer film in which the metal layer is a silver layer containing silver as a main component has low reflecting property and high transmitting property in a visible spectrum and has high reflecting property in an infrared spectrum. A stack in which the silver-based optical multilayer film is formed on a transparent substrate such as a glass substrate or the like has low radiation performance and high heat ray reflection performance, and is thus used for Low-E glass, heat ray reflection glass with high visible light transmittance and so on. In recent years, there is a growing need for the silver-based optical multilayer film with growing consciousness in reducing greenhouse gasses such as CO₂ and so on and saving energy.

[0003] Further, the stack having the metal-based optical multilayer film generally has various color tones such as blue, green, brown, and gray and, when it is used for architectural structures such as a building and the like, becomes an important element deciding its design. The stack having the silver-based optical multilayer film has an appearance close to a neutral color, that is, an appearance close to a base plate glass. In recent years, the appearance equivalent to the base plate glass is preferred and therefore the demand for the stack having the silver-based optical multilayer film increases.

[0004] Here, when the stack having the silver-based optical multilayer film is used for a double glass, the silver-based optical multilayer film is arranged between a pair of glasses and is not exposed to the outside, and is therefore not necessarily required to have high chemical durability and mechanical durability.

[0005] Further, for the glass substrate of the stack, for example, the glass substrate for a window glass for building or the like, a tempered glass tempered by heat treatment is used from the viewpoint of wind pressure resistance and so on. Here, from the viewpoint of manufacturing cost, a method of performing film formation prior to cutting and
5 performing heat treatment for tempering or bending is more preferable than a method of performing film formation on a tempered or bent glass. Accordingly, it is preferable that the silver-based optical multilayer film is excellent also in thermal durability such as stability and so on of the silver layer during the heat treatment.

[0006] Conventionally, as the silver-based optical multilayer film, the one using an
10 oxide film, a nitride film or the like for the dielectric layer is known (refer to, for example, Patent Reference 1). Further, as the silver-based optical multilayer film having a high visible light transmittance and having durability equivalent to a thermal decomposition coating, for example, the one composed of a first silicon nitride layer, a first nickel-based layer, a silver layer, a second nickel-based layer, and a second silicon nitride layer formed
15 in order from the transparent substrate side, in which each of the first nickel-based layer and the second nickel-based layer is composed of nickel or a nickel-chromium alloy and which has a visible light transmittance more than 70% is known (refer to, for example, Patent Reference 2).

[0007] Further, as the silver-based optical multilayer film capable of being subjected
20 to heat treatment and having low emittance after the heat treatment, the one composed of, for example, a first silicon nitride layer, a first nickel-based layer, a silver layer, a second nickel-based layer, and a second silicon nitride layer formed in order from the transparent substrate side, in which the geometrical thickness of the first nickel-based layer is larger than the geometrical thickness of the second nickel-based layer and which has a visible
25 light transmittance more than 70% is known (refer to, for example, Patent Reference 3).

[Prior Art Document]

[Patent Reference]

[0008]

[Patent Reference1] JP-A 11-034216 (KOKAI)

[Patent Reference 2] JP-A 6-171984 (KOKAI)

[Patent Reference 3] JP-A 7-172872 (KOKAI)

[Summary of Invention]

5 [Problems to be Solved by the Invention]

[0009] The double glass has disadvantages in labor of assembly and manufacturing cost which are obstacles to widespread use in developing countries and so on. The glass with the silver-based optical multilayer film having excellent performance stacked, if usable in a state of a single plate, is expected to be widely spread in the developing
10 countries.

[0010] However, the conventional silver-based optical multilayer film is not always be sufficient in durability and therefore cannot be used in a state that the optical multilayer film surface is exposed on the glass surface like a single plate glass. According to the discussion of the present inventors, the silver-based optical multilayer films disclosed in
15 Patent References 2 and 3 are not sufficient in chemical durability such as perspiration resistance and so on and are difficult for use in the state like a single plate glass. Further, the conventional silver-based optical multilayer film provides a high visible light transmittance but is sometimes contrarily required to have a low visible light transmittance. For instance, the solar radiation is strong in the daytime in low-latitude area and
20 mid-latitude area such as Southeast Asia and so on, and therefore a window glass, in particular, for building is required to have a low visible light transmittance for the glare-proof purpose.

[0011] The present invention has been made to solve the above problems and its object is to provide a stack having a relatively low visible light transmittance suitable for use in
25 low-latitude area and mid-latitude area and suitable for used with an optical multilayer film surface exposed to the atmosphere like a single plate glass.

[Means for Solving the Problems]

[0012] A stack of an embodiment includes a transparent substrate and an optical

multilayer film formed on the substrate. The optical multilayer film includes at least a first silicon nitride layer, a first chromium-containing layer, a silver layer, a second chromium-containing layer, and a second silicon nitride layer formed in order from the transparent substrate side. The silver layer contains silver as a main component and at least one kind of metal selected from among palladium, gold, chromium, cobalt, and nickel in a proportion of 0.1 weight% to 10 weight% to a total weight of silver and the metal, and each of the first chromium-containing layer and the second chromium-containing layer is composed of chromium, a nickel-chromium alloy, a partial nitride of chromium, or a partial nitride of a nickel-chromium alloy, and formed to be in contact with the silver layer.

10 The stack has a visible light transmittance (T_v) of 40% to 65%.

[Effect of the Invention]

[0013] According to the present invention, it is possible to provide a stack having a relatively low visible light transmittance suitable for use in low-latitude area and mid-latitude area and suitable for used with an optical multilayer film surface exposed to the atmosphere like a single plate glass.

[Brief Description of the Drawings]

[0014] [Fig. 1] A cross-sectional view illustrating an embodiment of a stack.

[Fig. 2] A cross-sectional view illustrating another embodiment of the stack.

[Modes for Implementing the Invention]

[0015] Hereinafter, embodiments of a stack will be described in detail referring to the drawings. Fig. 1 is a cross-sectional view illustrating an embodiment of the stack.

[0016] A stack 10 has a transparent substrate 11 and an optical multilayer film 12 provided on the transparent substrate 11. The optical multilayer film 12 is composed of at least a first silicon nitride layer 121, a first chromium-containing layer 122, a silver layer 123, a second chromium-containing layer 124, and a second silicon nitride layer 125 which are formed in order from the transparent substrate 11 side.

[0017] Generally, the stack 10 is used in such an orientation that the transparent substrate 11 side is located on the outdoor side and the optical multilayer film 12 side is

located on the indoor side. Further, use of the stack 10 with the optical multilayer film 12 exposed to the atmosphere is preferable in that the functions such as durability and so on of the optical multilayer film 12 are fully exhibited.

[0018] The silver layer 123 contains silver as a main component, and at least one kind
5 of metal selected from among palladium, gold, chromium, cobalt, and nickel in a proportion of 0.1 weight% to 10 weight% relative to the total weight of silver and the metal. Hereinafter, the at least one kind of metal selected from among palladium, gold, chromium, cobalt, and nickel is also referred to as a metal M. Further, that a certain component is contained as a main component in this specification means that the
10 proportion of the component contained as a main component to all constituent components exceeds 50 weight%.

[0019] The first chromium-containing layer 122 is made of chromium, a nickel-chromium alloy, a partial nitride of chromium, or a partial nitride of a nickel-chromium alloy. Further, the first chromium-containing layer 122 is formed to be
15 in contact with the silver layer 123. The second chromium-containing layer 124 is made of chromium, a nickel-chromium alloy, a partial nitride of chromium, or a partial nitride of a nickel-chromium alloy. Further, the second chromium-containing layer 124 is formed to be in contact with the silver layer 123. Note that the first chromium-containing layer 122 and the second chromium-containing layer 124 do not necessarily need to have the
20 same composition but may have different compositions from each other.

[0020] A visible light transmittance (T_v) of the stack 10 is 40% to 65%. The visible light transmittance (T_v) is defined in JIS R3106: 1998.

[0021] In the stack 10 of the embodiment, the silver layer 123 containing silver as a main component and a predetermined amount of the metal M is formed, the first
25 chromium-containing layer 122 and the second chromium-containing layer 124 are formed in a manner to be in direct contact with the silver layer 123, and the first silicon nitride layer 121 and the second silicon nitride layer 125 are formed to hold them sandwiched therebetween.

[0022] With the above structure, a relatively low visible light transmittance (T_v) of 40% to 65% can be achieved. In particular, the silver layer 123 contains the predetermined amount of the metal M, whereby the relatively low visible light transmittance (T_v) of 40% to 65% is achieved. The visible light transmittance (T_v) being 40% to 65% is preferable to a window glass for building in low-latitude area and mid-latitude area such as Southeast Asia and so on where solar radiation is strong in the daytime. The visible light transmittance (T_v) is more preferably 45% to 60%

[0023] Further, with the above structure, the chemical durability, the mechanical durability, and the thermal durability become excellent. More specifically, the chemical durability, the mechanical durability, and the thermal durability become excellent by forming layers containing chromium (the first chromium-containing layer 122 and the second chromium-containing layer 124) in a manner to directly hold the silver layer 123 sandwiched therebetween, and forming layers made of a silicon nitride (the first silicon nitride layer 121 and the second silicon nitride layer 125) in a manner to further hold the above layers sandwiched therebetween.

[0024] In particular, the silver layer 123 contains the predetermined amount of the metal M and thereby make the chemical durability excellent. Further, the silver layer 123 contains the predetermined amount of the metal M and thereby also make the mechanical durability excellent. The reason of improvement in mechanical durability is estimated that the hardness of the silver layer 123 improves by solid solution of the metal M to improve the strength of the whole film structure. The durability of the optical multilayer film becomes excellent in the stack with the above structure, thereby making the stack preferable for the usage in the state that the optical multilayer film is exposed to the atmosphere.

[0025] Note that the stack 10 is excellent in chemical durability, mechanical durability, and thermal durability and therefore can be independently used like a single plate glass but is not always limited to the independent use. For example, the stack 10 can be used also as a double glass, by arranging an opposed substrate composed of a transparent substrate,

at a predetermined gap, on one principal surface side thereof, generally, the side where the optical multilayer film 12 is provided.

[0026] Here, the stack 10 is roughly classified into a non-heat-treated product and a heat-treated product. The non-heat-treated product becomes a finished product being a final form made by only forming the optical multilayer film 12 and not performing heat treatment for tempering or bending after the film formation. The heat-treated product becomes a finished product being a final form made by forming the optical multilayer film 12 and then performing heat treatment for tempering or bending after the film formation. The stack 10 may be either the non-heat-treated product or the heat-treated product.

[0027] Note that the stack 10 only needs to be the one manufactured by forming the layers in the above-described order. After the whole film formation and after the heat treatment, the state at the time of formation of each layer, for example, the composition, thickness and so on do not necessarily need to be strictly maintained. However, as for the stack 10, the change of each layer at the time of film formation and at the time of heat treatment is basically suppressed. Therefore, each layer preferably maintains the state at the time of film formation even after the whole film formation and after the heat treatment. Further, the visible light transmittance (T_v) only needs to fall within a predetermined range in the state after the film formation, namely, the state without performing heat treatment, and preferably falls within the same range also after the heat treatment in the case of performing the heat treatment.

[0028] The transparent substrate 11 is not particularly limited, for which, for example, an inorganic and transparent glass plate can be used such as a window glass for architectural structures, a usually used float glass, or a soda-lime glass manufactured by the roll-out method or the like. For the glass plate, colorless glass such as clear glass, high-transmittance glass or the like, or colored glass colored in green or the like such as heat absorbing glass or the like can be used.

[0029] To set the visible light transmittance (T_v) as the stack 10 within the above-described range, the visible light transmittance (T_v) of the transparent substrate 11 is

preferably 80% to 92%, and more preferably 83% to 90%. Considering the visible light transmittance, colorless glass such as clear glass, high-transmittance glass or the like is preferable.

[0030] As the transparent substrate 11, various kinds of tempered glass such as

5 air-cooled tempered glass, chemically tempered glass and the like can also be used.

Furthermore, various kinds of glass such as borosilicate glass, low expansion glass, zero-expansion glass, low expansion crystallized glass, zero-expansion crystallized glass and the like can be used. Moreover, as the transparent substrate 11, laminated glass made by laminating a plurality of glass plates via a resin intermediate film may be used. The

10 thickness of the transparent substrate 11 is not necessarily limited, but is preferably a thickness capable of achieving a visible light transmittance (T_v) of the transparent substrate 11 itself within the above-described range and securing a sufficient mechanical strength, and is preferably, for example, 0.5 mm to 20 mm.

[0031] The first silicon nitride layer 121 and the second silicon nitride layer 125 are

15 provided to adjust the reflectance and so on in the visible range so as to make the optical characteristics of the optical multilayer film 12 desired characteristics. Further, the first silicon nitride layer 121 and the second silicon nitride layer 125 are provided to improve the durability of the optical multilayer film 12.

[0032] The first silicon nitride layer 121 and the second silicon nitride layer 125 do not

20 necessarily need to be made of a stoichiometric silicon nitride (Si_3N_4), but may be made of, for example, a non-stoichiometric silicon nitride (SiN_x ($0.1 < x$)). Further, the first silicon nitride layer 121 and the second silicon nitride layer 125 do not necessarily need to be made of only a silicon nitride, but can contain an element to be added to a sputtering target for facilitating the sputtering, for example, an additive element imparting conductive

25 property, such as aluminum or the like. The content of the additive element is preferably 15 weight% or less in the total weight of the silicon nitride and the additive element.

Note that the silicon nitrides constituting the first silicon nitride layer 121 and the second silicon nitride layer 125 do not need to have the same composition but may have different

compositions from each other.

[0033] The thickness of the first silicon nitride layer 121 is preferably 25 nm to 70 nm. The thickness of the second silicon nitride layer 125 is preferably 35 nm to 70 nm. Here, as the thickness, the geometrical thickness is indicated (the same applies hereinafter). In the case where the thickness of the first silicon nitride layer 121 is 25 nm or more and the thickness of the second silicon nitride layer 125 is 35 nm or more, the visible light transmittance (T_v) of the stack 10 is likely to be within the predetermined range and the durability of the optical multilayer film 12 is also improved. Further, in the case where the thickness of each of the first silicon nitride layer 121 and the second silicon nitride layer 125 is 70 nm or less, the visible light transmittance (T_v) of the stack 10 is likely to be within the predetermined range and the productivity of the optical multilayer film 12 also becomes excellent.

[0034] The first chromium-containing layer 122 and the second chromium-containing layer 124 function as light absorption layers that improve heat insulating property by absorbing visible light and function as barrier layers that suppress oxidation of the silver layer 123 during heat treatment, and the like.

[0035] The first chromium-containing layer 122 is made of chromium (Cr) or a nickel-chromium alloy (NiCr alloy), or a partial nitride of chromium or a partial nitride of a nickel-chromium alloy made by nitriding part of chromium or a nickel-chromium alloy.

A preferable example of the partial nitride of chromium is CrN_x ($0.5 < x < 1.5$). A preferable example of the partial nitride of a nickel-chromium alloy is NiCrN_x ($0.5 < x < 1.5$). From the view point of the thermal durability of the stack 10, the first chromium-containing layer 122 is preferably made of chromium (Cr) or a nickel-chromium alloy (NiCr alloy) which are not nitrified.

[0036] In the case where the first chromium-containing layer 122 is made of a nickel-chromium alloy (NiCr alloy) or a partial nitride of a nickel-chromium alloy (NiCrN_x) made by nitriding part thereof, the proportion of the content of chromium relative to the total weight of chromium and nickel is preferably 10 weight% or more, and more

preferably 15 weight% or more.

[0037] The second chromium-containing layer 124 is also made of chromium (Cr) or a nickel-chromium alloy (NiCr alloy), or a partial nitride of chromium or a partial nitride of a nickel-chromium alloy made by nitriding part of chromium or a nickel-chromium alloy.

5 A preferable example of the partial nitride of chromium is CrN_x ($0.5 < x < 1.5$). A preferable example of the partial nitride of a nickel-chromium alloy is NiCrN_x ($0.5 < x < 1.5$). From the view point of the thermal durability of the stack 10, the second chromium-containing layer 124 is preferably made of chromium (Cr) or a nickel-chromium alloy (NiCr alloy) which are not nitrified.

10 [0038] In the case where the second chromium-containing layer 124 is made of a nickel-chromium alloy (NiCr alloy) or a partial nitride of a nickel-chromium alloy (NiCrN_x) made by nitriding part thereof, the proportion of the content of chromium relative to the total weight of chromium and nickel is preferably 10 weight% or more, and more preferably 15 weight% or more.

15 [0039] The first chromium-containing layer 122 and the second chromium-containing layer 124 do not necessarily need to have the same composition but may have different compositions from each other.

[0040] The thickness of the first chromium-containing layer 122 is preferably 0.5 nm to 10 nm. The thickness of the second chromium-containing layer 124 is preferably 0.5
20 nm to 10 nm. Note that the thickness of the first chromium-containing layer 122 and the thickness of the second chromium-containing layer 124 may be the same thickness or may be different thicknesses from each other. In the case where the thickness of each of the first chromium-containing layer 122 and the second chromium-containing layer 124 is 0.5 nm or more, the visible light transmittance (T_v) of the stack 10 is likely to be within the
25 predetermined range and the durability of the optical multilayer film 12 is also improved. Further, in the case where the thickness of each of the first chromium-containing layer 122 and the second chromium-containing layer 124 is 10 nm or less, the visible light transmittance (T_v) of the stack 10 is likely to be within the predetermined range and the

productivity of the optical multilayer film 12 also becomes excellent.

[0041] In particular, in the case where the stack 10 is a heat-treated product and the heat treatment for obtaining the heat-treated product is the heat treatment of heating the surface temperature of a non-heat-treated product with the same configuration as that of the stack 10 to 600°C or more, the thickness of the first chromium-containing layer 122 is preferably within a range of 2.0 nm to 10 nm and the thickness of the second chromium-containing layer 124 is preferably within a range of 2.0 nm to 10 nm. Outside the above-described range, the optical multilayer film 12 of the stack 10 obtained as the heat-treated product may be insufficient in mechanical durability (abrasion resistance).

[0042] The silver layer 123 contains silver as a main component, and at least one kind of metal (metal M) selected from among palladium, gold, chromium, cobalt, and nickel in a proportion of 0.1 weight% to 10 weight% relative to the total weight of silver and the metal. In the stack 10 of the embodiment, provision of the silver layer 123 containing the metal M in the above-described proportion in place of the silver layer containing only silver as in the prior art makes the visible light transmittance (T_v) of the stack 10 fall within the predetermined range and makes the durability of the stack 10, in particular, the chemical durability such as perspiration resistance and so on excellent.

[0043] As the above-described metal M, one kind selected from among palladium, gold, chromium, cobalt, and nickel may be independently used, or two or more kinds of them may be used in combination. In the case where one kind of them is independently used as the metal M, palladium, gold or the like is preferable. As the combination of two or more kinds of them, nickel and gold, nickel and palladium or the like is preferable.

[0044] In the case where the content of the metal M relative to the total weight of silver and the metal M in the silver layer 123 is less than 0.1 weight%, the visible light transmittance (T_v) of the stack 10 may not become sufficiently low, and the durability of the stack 10, in particular, the chemical durability such as perspiration resistance and so on may not become excellent. In the case where the content of the metal M relative to the total weight of silver and the metal M in the silver layer 123 is more than 10 weight%, the

visible light transmittance (T_v) of the stack 10 may become excessively low, and the material cost of the silver layer 123 may increase. Hereinafter, the content of the metal M refers to, unless otherwise stated, the proportion of the metal M (weight%) relative to the total weight of silver and the metal M.

5 [0045] Here, the optimum content of the metal M in the silver layer 123 differs depending on the kind of the metal M. In the case where palladium is used as the metal M, the proportion of palladium relative to the total weight of silver and palladium is preferably 1 weight% to 5 weight%. Similarly, the proportion of gold is preferably 1 weight% to 10 weight%, the proportion of chromium is preferably 0.1 weight% to 5 weight%, the proportion of cobalt is preferably 0.1 weight% to 5 weight%, and the proportion of nickel is preferably 0.1 weight% to 7 weight%. Further, in the case of using nickel and gold in combination, it is preferable to contain 0.1 weight% to 7 weight% of nickel and 1 weight% to 10 weight% of gold (however, the total of nickel and gold is 10 weight% or less).

15 [0046] The silver layer 123 can contain an additive element other than silver and the metal M. Examples of the additive element include metal elements such as copper, titanium and so on. When additive elements are contained, the total content of the additive elements is preferably 5 weight% or less, more preferably 3 weight% or less, and further preferably 1 weight% or less in all components constituting the silver layer 123.

20 [0047] The thickness of the silver layer 123 is preferably 10 nm to 30 nm. In the case where the thickness of the silver layer 123 is 10 nm or more, the heat insulating property of the stack 10 becomes excellent, the visible light transmittance (T_v) falls within the predetermined range, and the durability, in particular, the chemical durability also improves. In the case where the thickness of the silver layer 123 is 30 nm or less, the visible light transmittance (T_v) of the stack 10 falls within the predetermined range, and the productivity of the optical multilayer film 12 also becomes excellent.

[0048] The optical multilayer film 12 is basically constituted by forming, in order from the transparent substrate 11 side, the first silicon nitride layer 121, the first

chromium-containing layer 122, the silver layer 123, the second chromium-containing layer 124, and the second silicon nitride layer 125, and other layers can be formed as necessary and within the scope of the present invention.

[0049] Fig. 2 is a cross-sectional view illustrating another embodiment of the stack 10 having the transparent substrate 11 and the optical multilayer film 12. It is preferable that, on the optical multilayer film 12, a protective layer 126 is formed on the top in order to improve the mechanical durability, in particular, the abrasion resistance of the surface. The protective layer 126 is not particularly limited as long as it improves the mechanical durability, and for example, a carbon layer containing carbon as a main component is preferable. Note that in the case where the protective layer 126 is a carbon film, it disappears at the time when heat treatment is performed but can improve the abrasion resistance from the film formation to the heat treatment. On the other hand, also in the non-heat-treated product, in the case where the protective layer 126 being a carbon film is formed, the abrasion resistance can be improved due to a decrease in friction coefficient of the uppermost surface.

[0050] The thickness of the protective layer 126 is preferably 1 nm or more. In the case where the thickness of the protective layer 126 is 1 nm or more, the mechanical durability effectively improves. The thickness of the protective layer 126 of 15 nm is enough to secure the mechanical durability, and a thickness equal to or less than that improves the productivity of the protective layer 126. The thickness of the protective layer 126 is preferably 10 nm or less, and more preferably 6 nm or less.

[0051] Though not illustrated, on the optical multilayer film 12, other layers, in addition to the above-described layers, may be formed as necessary and within the scope of the present invention. For example, between the first silicon nitride layer 121 and the first chromium-containing layer 122 or between the second chromium-containing layer 124 and the second silicon nitride layer 125, a light absorption layer, or a metal layer, an oxide layer, a nitride layer, a carbide layer or a complex compound layer of them functioning as a barrier layer or the like may be provided. Concrete examples of the other layers include a

metal layer, an oxide layer, a nitride layer, a carbide layer or a complex compound layer containing an element such as titanium, zirconium, niobium, tantalum, chromium, zinc, aluminum, gallium, indium, silicon or tin.

[0052] The stack 10 of the embodiment preferably has the following optical

5 characteristics. Note that the optical characteristics of the present invention are obtained by measurement using "D 65 light source, 10-degree visual field" as a light source.

Further, the stack 10 of the embodiment only needs to have the following optical characteristics in the state after film formation, namely, in the state that it is not subjected to heat treatment, and preferably has the following optical characteristics even after the
10 heat treatment. In the stack 10 of the embodiment, the optical multilayer film 12 has the above-described specific layer configuration and thereby basically suppresses change of the layers due to the heat treatment, so that the optical characteristics do not change depending on the presence or absence of the heat treatment.

[0053] The color tone of the reflected light on the transparent substrate 11 side of the
15 stack 10 preferably has $a^* \leq 10$, $b^* \leq 5$ in a CIE 1976 $L^*a^*b^*$ chromaticity coordinates. The case where $a^* \leq 10$, $b^* \leq 5$ is preferable because the redness of the reflected light on the transparent substrate 11 side is suppressed. As for a^* , it is more preferable that $-5 \leq a^* \leq 7$, and further preferable that $-5 \leq a^* \leq 3$. As for b^* , it is more preferable that $-25 \leq b^* \leq 5$, and further preferable that $-23 \leq b^* \leq 5$.

20 [0054] The color tone of the reflected light on the optical multilayer film 12 side of the stack 10 preferably has $a^* \leq 15$, $b^* \leq 0$ in the aforementioned coordinates. The case where $a^* \leq 15$, $b^* \leq 0$ is preferable because the redness of the reflected light on the optical multilayer film 12 side is suppressed. As for a^* , it is more preferable that $0 \leq a^* \leq 15$, further preferable that $0 \leq a^* \leq 12$, and particularly preferable that $0 \leq a^* \leq 8$. As for b^* ,
25 it is more preferable that $-35 \leq b^* \leq 0$, and further preferable that $-35 \leq b^* \leq -10$.

[0055] Further, a visible light reflectance (R_{v1}) on the transparent substrate 11 side of the stack 10 is preferably 25% or less, and a visible light reflectance (R_{v2}) on the optical multilayer film 12 side is preferably 20% or less. Note that the visible light reflectance

(R_v) is defined in JIS R3106: 1998.

[0056] Further, the solar heat gain coefficient (SHGC) indicating the ratio of solar heat radiated to the optical multilayer film 12 side when the solar heat incident from the transparent substrate 11 side of the stack 10 is 1, is preferably 0.43 or less. Here, the solar heat gain coefficient (SHGC) is the index used in National Fenestration Rating Council (United States), and the heat insulating property, namely, how the heat (solar heat) generated by solar light can be blocked can be known from the value of the solar heat gain coefficient (SHGC).

[0057] The solar heat gain coefficient is the ratio of the total of the directly transmitted heat (hereinafter, referred also to as "transmitted heat") and the heat absorbed and then radiated to the optical multilayer film side (hereinafter, referred also to as "radiation heat") to the solar heat incident from the transparent substrate side. The solar heat gain coefficient is expressed by a numeral from 0 to 1. Note that the solar heat gain coefficient can be concretely calculated by measuring the spectral characteristics of the stack and introducing them into a predetermined calculation expression. As the solar heat gain coefficient is smaller, the ratio of the total of the transmitted heat and the radiation heat to the solar heat incident from the transparent substrate side becomes smaller in the stack. The stack 10 of the embodiment having the optical multilayer film 12 with the above configuration can provide an appearance close to the base plate glass and can decrease the solar heat gain coefficient.

[0058] The selectivity of the stack 10, calculated as the value " $T_v / (\text{SHGC} \times 100)$ " obtained by dividing the visible light transmittance (T_v) by the value obtained by multiplying the solar heat gain coefficient (SHGC) by 100, is preferably 1.0 to 1.6. The selectivity is the index indicating the balance between the visible light transmittance and the solar heat gain coefficient, and the selectivity falling within the aforementioned range can realize suitable visible light transmitting property and high shielding property.

[0059] The stack 10 preferably causes no corrosion and no film peeling in a test for resistance to perspiration according to ISO 12870 (where, the test period is 1 day). The

test for resistance to perspiration can be concretely carried out by injecting an artificial sweat solution containing 50 g/L of lactic acid and 100 g/L of sodium chloride into an airtight container, arranging the stack in the airtight container and distant from the artificial sweat solution and keeping it in an airtight state at $55\pm5^{\circ}\text{C}$ for 1 day, and then visually
5 checking the appearance of the stack. The stack 10 particularly preferably causes no corrosion and no film peeling when the test period is 3 days in the same test for resistance to perspiration as described above.

[0060] Next, the manufacturing method of the stack 10 will be described. The stack 10 is obtained by performing cleaning treatment on the surface of the transparent substrate
10 11 and then forming the layers on the surface. The film formation method is not particularly limited, and the CVD method, the deposition method, the sputtering method and so on can be employed. In the case where the area of the transparent substrate 11 is large, the direct-current or alternate-current dual sputtering method is preferable because it easily controls the uniformity of the thickness and excellent in productivity.

15 [0061] The first silicon nitride layer 121 and the second silicon nitride layer 125 are formed, for example, by performing sputtering in an atmosphere containing only nitrogen or an atmosphere containing nitrogen and argon, using a target containing silicon as a main component as the sputtering target.

[0062] The first chromium-containing layer 122 and the second chromium-containing
20 layer 124 are formed, for example, by performing sputtering in an atmosphere containing only argon or an atmosphere containing nitrogen and argon, using a target containing chromium or a nickel-chromium alloy as a main component as the sputtering target.

[0063] The silver layer 123 is formed, for example, by performing sputtering in an atmosphere containing only argon, using a target containing silver as a main component
25 and containing at least one kind of metal (metal M) selected from among palladium, gold, chromium, cobalt, and nickel in a proportion of 0.1 weight% to 10 weight% relative to the total weight of silver and the metal M as the sputtering target.

[0064] In the case where the optical multilayer film 12 has, for example, the carbon

layer containing carbon as a main component as the protective layer 126 on the top, the carbon layer only need to be formed by performing sputtering in an atmosphere containing only argon, using a carbon target.

[0065] Thus, the non-heat-treated product of the stack is obtained. To make the stack
5 into a heat-treated product, the stack obtained in the above is heated for a predetermined time in a heating furnace at a heating temperature according to the purpose, for example, a heating temperature for tempering or a heating temperature for bending work. For example, in the case where air-cooling tempering is performed on the float glass of the stack using it as the transparent substrate, the heat treatment is preferably performed for 1
10 minute to 30 minutes at 500°C to 700°C as the surface temperature of the stack.

[0066] While embodiments of the present invention have been described, these embodiments have been presented by way of example only, and are not intended to limit the scope of the inventions. The novel embodiments described herein may be embodied in a variety of other forms, and various omissions, substitutions, and changes in the form of
15 the embodiments described herein may be made without departing from the spirit of the inventions. For example, the stack is suitable for architectural structures, but is not used necessarily only for architectural structures and can also be used for vehicles such as automobile and so on within an applicable range.

20 [Examples]

[0067] Hereinafter, the present invention will be more concretely described using Examples and Comparative Examples.

[0068] (Example 1)

A stack having an optical multilayer film on a transparent substrate was manufactured by
25 forming films so as to have the film configuration and thicknesses illustrated in Table 1 by the sputtering method on a soda-lime glass plate with a thickness of 3 mm as the transparent substrate.

[0069] For the film formation, an inline-type sputtering apparatus was used, and a

silicon target containing 10 weight% of aluminum, a nickel-chromium target containing 80 weight% of nickel, a silver-palladium target containing 1 weight% of palladium, and a carbon target were set in a sputtering chamber.

[0070] Into the inline-type sputtering apparatus, a cleaned soda-lime glass plate was introduced, and a load lock chamber was evacuated until the degree of vacuum reached 2×10^{-6} Torr. Subsequently, the soda-lime glass plate was introduced into the sputtering chamber, and a silicon nitride film (Si_3N_4 film) containing aluminum as the first silicon nitride layer, a nickel-chromium alloy film (NiCr film) as the first chromium-containing layer, a silver-palladium alloy film (AgPd film) as the silver layer, a nickel-chromium alloy film (NiCr film) as the second chromium-containing layer, and a silicon nitride film (Si_3N_4 film) containing aluminum as the second silicon nitride layer were formed in order into the optical multilayer film. The film formation conditions of the respective films are as described below. Note that the film formation pressure was set to 3 mTorr to 5 mTorr for each of them.

[0071] The silicon nitride film (Si_3N_4 film) was formed using a silicon target containing 10 weight% of aluminum by using nitrogen/argon = 3/7 in flow ratio as an introduced gas and setting the power density to 3.6 W/cm^2 .

[0072] The nickel-chromium alloy film (NiCr film) was formed using a nickel-chromium target containing 80 weight% of nickel by using 100% of argon as an introduced gas and setting the power density to 0.4 W/cm^2 .

[0073] The silver-palladium alloy film (AgPd film) was formed using a silver-palladium target containing 1 weight% of palladium by using 100% of argon as an introduced gas and setting the power density to 0.7 W/cm^2 .

[0074] (Example 2)

A stack was manufactured by forming an optical multilayer film similarly to Example 1 except that a carbon film (C film) as the protective layer was formed on the top. Note that the carbon film was formed using a carbon target by using 100% of argon as an introduced gas and setting the power density to 2.1 W/cm^2 .

[0075] (Example 3)

A stack was manufactured by forming an optical multilayer film similarly to Example 1 except that a partial nitride film (NiCrN_x ($x = 1.0$)) of a nickel-chromium alloy made by nitriding part of a nickel-chromium alloy as the first chromium-containing layer and the second first chromium-containing layer and that the film thicknesses were changed. Note that the partial nitride film of a nickel-chromium alloy was formed using a nickel-chromium target containing 80 weight% of nickel by using nitrogen/argon = 3/7 in flow ratio as an introduced gas and setting the power density to 0.7 W/cm^2 .

[0076] (Example 4)

10 A stack was manufactured by forming an optical multilayer film similarly to Example 3 except that a carbon film (C film) as the protective layer was formed on the top. Note that the carbon film was formed using a carbon target by using 100% of argon as an introduced gas and setting the power density to 2.1 W/cm^2 .

[0077] (Comparative Example 1)

15 A stack was manufactured by forming an optical multilayer film similarly to Example 1 except that a pure silver film (Ag film) containing no palladium was formed in place of the silver-palladium alloy film and that the film thicknesses were changed. Note that the pure silver film was formed using a pure silver target containing no palladium by using 100% of argon as an introduced gas and setting the power density to 0.7 W/cm^2 .

20 [0078] Next, the following evaluation was performed about Examples and Comparative Example. The results are illustrated in Table 2 and Table 3.

[0079] (Chemical Durability)

[Test for resistance to perspiration]

The test for resistance to perspiration was carried out according to ISO 12870. More specifically, an artificial sweat solution was injected into an airtight container, the stack was arranged in the airtight container and distant from the artificial sweat solution and then kept in an airtight state at $55 \pm 5^\circ\text{C}$ for 1 day or 3 days. Note that the artificial sweat solution contains 50 g/L of lactic acid and 100 g/L of sodium chloride. Thereafter, the

stack was taken out of the airtight container, and visual check of the appearance of the stack was carried out. In Table 1, “A” indicates that there is no deterioration such as corrosion, film peeling and so on in visual observation, “B” indicates that there is some deterioration such as corrosion, film peeling and so on in visual observation, and “C” indicates that there is deterioration such as corrosion, film peeling and so on over the whole surface in visual observation.

[0080]

[Chemical Resistance]

The stack was immersed in each of 1N-NaOH and 1N-HCL at a temperature of 23°C for 6 hours, then washed with pure water, and subjected to the appearance visual check. In Table, “A” indicates that there is no deterioration such as corrosion, film peeling and so on in visual observation, and “C” indicates that there is deterioration such as corrosion, film peeling and so on in visual observation.

[0081]

15 [Moisture Resistance]

The stack was let stand for 2 weeks in a constant temperature and constant humidity test device (TOKYO RIKAKIKAI CO., LTD., KCH-1000) set at a temperature of 60°C and a humidity of 95%RH. Thereafter, visual check of the appearance of the stack was carried out. “A” indicates that there are defects (white spots) with a diameter of 0.1 mm or more at 5 defects/10 cm² or less in visual observation, and “C” indicates that there are defects (white spots) at 6 defects/10 cm² or more in visual observation.

[0082]

[Thermal Cycle]

A thermal cycle of -30°C × 5 hours to 80°C × 5 hours (humidity of 95 %RH) was repeated 30 times. Thereafter, visual check of the appearance of the stack was carried out. In Table, “A” indicates that there is no deterioration such as corrosion, film peeling and so on in visual observation, and “C” indicates that there is deterioration such as corrosion, film peeling and so on in visual observation.

[0083] (Mechanical Durability)

The stack and an abrasive (Sumitomo 3M Limited, brand name: Scotch Brite #7448B, size: 90 mm × 40 mm) were immersed in water using Erichsen tester (manufactured by Erichsen GMBH & CO. KG, Model 494), and reciprocated 1000 times with a load of 324 g applied to the abrasive in contact with the optical multilayer film side of the stack.

Thereafter, an arbitrary portion with a width of 5 mm of a polished portion of the stack was observed under an optical microscope. In Table, "A" indicates that the number of abrasions at the observed portion was 5 or less, "B" indicates that the number of abrasions was 6 to 10, and "C" indicates that the number of abrasions was 11 or more. Note that the number of abrasions with a width of 0.1 mm or more was measured as the abrasions.

[0084] (Thermal Durability)

The haze before and after the heat treatment performed on the stack at 730°C and for 4 minutes was measured according to JIS K6714. In Table, "A" indicates that the haze value is 0% or more and less than 0.4%, "B" indicates that the haze value is 0.4% or more and less than 0.8%, and "C" indicates that the haze value is 0.8% or more.

[0085] (Optical Characteristics)

Spectrometry was carried out on the stack using Hitachi Spectrophotometer (U-4100 model) to obtain the visible light transmittance (T_v), the visible light reflectance (R_{v1}) on the transparent substrate 11 side and the visible light reflectance (R_{v2}) on the optical multilayer film 12 side. Note that the visible light transmittance (T_v) and the visible light reflectances (R_{v1} , R_{v2}) were obtained according to the rule of JIS R3106: 1998. Further, the color tones of the transmitted light and the reflected light of the stack were measured according to JIS Z 8722 and obtained according to JIS Z 8729. Further, the solar heat gain coefficient (SHGC) of the stack was obtained, and the selectivity " $T_v / (SHGC \times 100)$ " was calculated.

[0086] [Table 1]

	Configuration of the optical multilayer film
Example 1	G/Si ₃ N ₄ film (40nm)/NiCr film (1.5nm)/AgPd film (15nm)/NiCr film (1.5nm)/Si ₃ N ₄ film (53.5nm)
Example 2	G/Si ₃ N ₄ film (40nm)/NiCr film (1.5nm)/AgPd film (15nm)/NiCr film (1.5nm)/Si ₃ N ₄ film (53.5nm)/C film (3nm)
Example 3	G/Si ₃ N ₄ film (60nm)/NiCrN _x film (2nm)/AgPd film (25nm)/NiCrN _x film (1.5nm)/Si ₃ N ₄ film (55nm)
Example 4	G/Si ₃ N ₄ film (60nm)/NiCrN _x film (2nm)/AgPd film (25nm)/NiCrN _x film (1.5nm)/Si ₃ N ₄ film (55nm)/C film (3nm)
Comparative Example 1	G/Si ₃ N ₄ film (40nm)/NiCr film (2.5nm)/Ag film (8nm)/NiCr film (2.5nm)/Si ₃ N ₄ film (58nm)

[0087] [Table 2]

	Silver layer Ag:Pd (weight ratio)	Chemical durability					Mechanical durability	Thermal durability
		Test for resistance to perspiration		Chemical resistance	Moisture resistance	Thermal Cycle	by Erichsen tester	Haze
		1 day	3 days					
Example 1	99.0:1.0	A	B	A	A	A	A	A
Example 2	99.0:1.0	A	B	A	A	A	A	A
Example 3	99.0:1.0	A	B	A	A	A	A	A
Example 4	99.0:1.0	A	B	A	A	A	A	A
CE1	100:0	C	C	A	C	C	B	B

CE1= Comparative Example 1

5

[0088] [Table 3]

	Tv [%]	Substrate side			Film side			SHGC [-]	Tv / (SHGC ×100)
		R _{v1} [%]	Reflected color tone		R _{v2} [%]	Reflected color tone			
			a*	b*		a*	b*		
Example 1	63.0	14.0	1.5	-20.5	8.0	8.0	-33.0	0.420	1.50
Example 2	56.0	20.0	-2.0	-5.5	8.8	2.0	-28.0	0.400	1.40
Example 3	55.0	20.0	0	-15.0	15.0	5.0	-27.0	0.360	1.53
Example 4	50.0	22.0	-3.0	-2.5	12.0	0	-24.0	0.330	1.52
CE1	52.0	16.6	-0.1	-5.0	4.0	18.1	-4.2	0.410	1.27

CE1= Comparative Example 1

[0089] As is clear from the tables, the stacks in Examples 1 to 4 have visible light

10 transmittances (T_v) within 40% to 65%, and are excellent in chemical durability,

mechanical durability and thermal durability. Among them, the stacks in Examples 2 and 4 in which the carbon film is formed as the protective layer are excellent particularly in mechanical durability. Further, the stacks in Examples 1 to 4 obtain an appearance close to the base plate glass and are excellent in optical characteristics. On the other hand, the stack in Comparative Example 1 has a reflected color on the film surface side strong in red, and is low in chemical durability and mechanical durability.

[0090] (Example 5 and Example 6)

An optical multilayer film was formed similarly to Example 1 except that thicknesses of the layers were changed. Thereafter, heat treatment was performed for 5 minutes at a furnace temperature of 700°C (stack surface temperature = 660°C). The mechanical durability of the stack before and after the heat treatment was evaluated by the same method as described above.

[0091] [Table 4]

	Configuration of the optical multilayer film
Example 5	G/Si ₃ N ₄ film (56nm)/NiCr film (2nm)/AgPd film (17nm)/NiCr film (2nm)/Si ₃ N ₄ film (55nm)
Example 6	G/Si ₃ N ₄ film (56nm)/NiCr film (3nm)/AgPd film (17nm)/NiCr film (3nm)/Si ₃ N ₄ film (56nm)/C film (3nm)

[0092] [Table 5]

	Mechanical durability (by Erichsen tester)	
	Before heat treatment	After heat treatment
Example 5	A	B
Example 6	A	A

[0093] As is clear from the tables, the stacks in Examples 5 and 6 are excellent in mechanical durability even after the heat treatment.

[0094] (Examples 7 to 18)

Stacks in Examples 7 to 18 having the same film configuration as that in Example 1 except that the AgPd film (Ag: Pd (weight ratio) = 99:1) being the silver layer in the optical multilayer film configuration of the stack in Example 1: G/Si₃N₄ film (40 nm)/NiCr film (1.5 nm)/AgPd film (15 nm)/NiCr film (1.5 nm)/Si₃N₄ film (53.5 nm) was replaced with a

film with compositions illustrated in Table 6 were obtained.

[0095] Note that the silver layer in each of the examples was formed under the same conditions as those in Example 1 except that a target composed of silver and metal M in the composition illustrated in Table 6 was used as the target. On the obtained stacks, the measurement of the visible light transmittance (T_v) as evaluation of the optical characteristics, the test for resistance to perspiration (1 day, 3 days) as evaluation of the chemical durability, the test with the Erichsen tester as the evaluation of the mechanical durability were carried out similarly to the above. The results are illustrated in Table 6.

10 [0096] [Table 6]

	Silver layer		Chemical durability		Mechanical durability by Erichsen tester	Optical characteristics Tv (%)
	Kind	Ag:metal M (weight ratio)	Test for resistance to perspiration			
			1 day	3 days		
Example 7	AgAu Film	99.0:1.0	B	B	A	63.5
Example 8	AgAu Film	98.0:2.0	A	A	A	62.0
Example 9	AgAu Film	97.3:2.7	A	A	A	61.8
Example 10	AgAu Film	91.2:8.8	A	A	A	60.0
Example 11	AgPd Film	97.0:3.0	A	B	A	56.0
Example 12	AgPd Film	95.0:5.0	A	B	A	54.0
Example 14	AgNi Film	99.8:0.2	A	B	A	63.0
Example 15	AgNi Film	99.6:0.4	A	B	A	62.0
Example 16	AgNi Film	99.4:0.6	A	B	A	61.2
Example 17	AgCo Film	99.4:0.6	A	B	A	60.5
Example 18	AgCr Film	99.5:0.5	A	B	A	59.5

WHAT IS CLAIMED IS:

1. A stack comprising a transparent substrate and an optical multilayer film formed on the substrate,

5 wherein the optical multilayer film comprises at least a first silicon nitride layer, a first chromium-containing layer, a silver layer, a second chromium-containing layer, and a second silicon nitride layer formed in order from the transparent substrate side,

the silver layer contains silver as a main component and at least one kind of metal selected from among palladium, gold, chromium, cobalt, and nickel in a proportion of 0.1

10 weight% to 10 weight% to a total weight of silver and the metal, and

each of the first chromium-containing layer and the second chromium-containing layer is composed of chromium, a nickel-chromium alloy, a partial nitride of chromium, or a partial nitride of a nickel-chromium alloy, and formed to be in contact with the silver layer; and

15 wherein the stack has a visible light transmittance (T_v) of 40% to 65%.

2. The stack according to claim 1,

wherein a geometrical thickness of the first silicon nitride layer is 25 nm to 70 nm, a geometrical thickness of the first chromium-containing layer is 0.5 nm to 10 nm, a
20 geometrical thickness of the silver layer is 10 nm to 30 nm, a geometrical thickness of the second chromium-containing layer is 0.5 nm to 10 nm, and a geometrical thickness of the second silicon nitride layer is 35 nm to 70 nm.

3. The stack according to claim 1 or 2,

wherein no corrosion and no film peeling are caused in a test for resistance to
25 perspiration according to ISO 12870 (where, a test period is 1 day).

4. The stack according to any one of claims 1 to 3,

wherein a solar heat gain coefficient (SHGC) of the stack, indicating a ratio of solar heat radiated to the optical multilayer film side when solar heat incident from the

transparent substrate side is 1, is 0.43 or less.

5. The stack according to any one of claims 1 to 4,

wherein a selectivity of the stack, calculated as a value " $T_v / (\text{SHGC} \times 100)$ " obtained by dividing the visible light transmittance by a value obtained by multiplying the solar heat gain coefficient by 100, is 1.0 to 1.6.

6. The stack according to any one of claims 1 to 5,

wherein a color tone of a reflected light on the transparent substrate side of the stack has $a^* \leq 10$, $b^* \leq 5$ in a CIE 1976 $L^*a^*b^*$ chromaticity coordinates, and a color tone of a reflected light on the optical multilayer film side has $a^* \leq 15$, $b^* \leq 0$ in the coordinates.

7. The stack according to any one of claims 1 to 6,

wherein a visible light reflectance on the transparent substrate side of the stack is 25% or less, and a visible light reflectance on the optical multilayer film side is 20% or less.

8. The stack according to any one of claims 1 to 7,

wherein the optical multilayer film further comprises a protective layer with a thickness of 1 nm to 6 nm containing carbon as a main component formed on a top farthest from the transparent substrate.

9. The stack according to any one of claims 1 to 8,

wherein a geometrical thickness of the first chromium-containing layer is 2.0 nm to 10 nm, and a geometrical thickness of the second chromium-containing layer is 2.0 nm to 10 nm.

10. The stack according to any one of claims 1 to 9,

wherein the stack is used in a state where the optical multilayer film is exposed to the atmosphere.