Abstract: Disclosed herein is a substrate comprising a visible light reflector layer thereon. The composition of the visible light reflector layer varies between first refractive index material rich zone(s) and second refractive index material rich zone(s) with a compositional gradient between the zones.
PRIORITY DOCUMENT

[0001] The present application claims priority from Australian Provisional Patent Application No. 2013903653 titled “REFLECTOR COATINGS AND METHODS FOR PRODUCTION” and filed on 23 September 2013, the content of which is hereby incorporated by reference in its entirety.

TECHNICAL FIELD

[0002] The present invention relates to devices having highly reflective surfaces, such as solar reflectors, lighting elements (for example automotive headlights, aerospace lighting. Specialised optical applications including telescopes and cameras, and commercial/domestic lighting) and methods of manufacturing the highly reflective surfaces.

BACKGROUND

[0003] Highly reflective surfaces are commonly used in solar reflectors, automotive headlights, aerospace lighting, optical applications including telescopes and cameras, and commercial/domestic lighting. For ease of further discussion, reference will be made to reflective surfaces for use in solar reflector applications. However, it will be appreciated that the scope of the invention is not limited to this specific application.

[0004] Concentrated solar power (CSP) systems are receiving considerable attention as an effective renewable energy method of harnessing solar energy efficiently. CSP systems concentrate and/or collect sunlight using reflective or mirrored surfaces. There are several ways in which the harvested sunlight can be utilised. This includes: (1) concentrated solar thermal power, (2) concentrated solar photo-voltaic power or (3) concentrated solar power towers. In order to generate power, the CSP is converted into heat, and this is then typically used to drive some form of heat engine or turbine that is connected to an electrical generator.

[0005] The geometry of CSP collectors varies substantially, ranging from parabolic dishes, to parabolic troughs and flat mirror panels. CSP dishes and troughs offer inherently more efficient harvesting of solar energy, but this comes at a significant cost increase over optically flat mirror systems. It is therefore essential that such reflectors are made as optically efficient as possible, as every 1% increase in harvested and utilised solar power has a significant impact on the overall economic viability of the CSP plant.
Parabolic trough CSP systems consist of an array of parabolic reflectors (parabolic in one direction only) that concentrates light onto a receiver positioned along the focal line of the reflector. The receiver is typically a tube filled with a working fluid, which is heated by the focussed sunlight from which the heat is recovered for the generation of energy. In the case of a solar power tower system, the reflectors are typically (but not always) flat, and concentrate the sunlight on a central receiver atop a main tower. At the central focal point exists similar working-fluids as those used in the parabolic trough which are heated by the concentrated sunlight, followed by recovery (or storage) of the heat as energy. In the third case, the solar dish systems are similar in appearance to a satellite dish (parabolic reflector in two directions), but the working fluid is placed at the focal point (or just outside the focal point) of the dish from which heat is recovered as energy. Of the popular configurations described here, the parabolic trough has the advantage of simplicity.

One of the technical problems associated with these types of CSP systems is that the reflectors have to follow the sun to obtain a high solar energy ratio. Most current parabolic trough CSP systems use second-surface silvered glass Mirror panels with a peak total solar reflectivity (TSR) of less than 94%. These panels tend to be heavy in weight which increases the cost of the associated drive mechanism that is used to move the mirrors. Furthermore, the processes used to manufacture the large glass mirrors are complex and costly, particularly for non-planar mirrors such as parabolic reflectors used in many CSP systems.

Alternatives to second-surface silvered glass mirror panels have previously been proposed. For example, Kenney et al. suggest using plastic mirrors formed by coating polyethylene terephthalate (PET) with layers of copper and silver, and then capping with an alumina protective layer via ion-beam-assisted physical vapour deposition (Kenney et al., 1997). An adhesive backed silver on acrylic reflective film is also commercially available from 3M (3M™ Solar Mirror Film 1.100). However, there remains a need for alternatives to these systems. Furthermore, current CSP systems are expensive relative to some other forms of energy generation and considerable work needs to be done to reduce the costs of CSP systems in order for them to generate electricity cost effectively.

SUMMARY

In a first aspect, the present invention provides a substrate comprising a visible-light reflector layer thereon, wherein the composition of the visible light reflector layer varies between first refractive index material rich zone(s) and second refractive index material rich zone(s) with a compositional gradient between the zones.

In some embodiments of this first aspect, the substrate further comprises an infrared reflector layer between the surface of the substrate and the visible light reflector layer. The visible light
reflector layer of these embodiments is transparent in the infrared region. In these embodiments the interface between the infrared reflector layer and the visible light reflector layer is graded so that the composition between the infrared reflector layer and the visible light reflector layer varies between the material of the infrared reflector layer and the first material of the visible light reflector layer.

[001] In some embodiments of this first aspect, the outer surface of the visible light reflector layer further comprises a visibly transparent infrared reflector layer. In these embodiments, the visibly transparent infrared reflector layer is formed on the visible light reflector layer. Furthermore, in these embodiments the interface between the visible light reflector layer and the visibly transparent infrared reflector layer may be graded so that the composition between the visible light reflector layer and the visibly transparent infrared reflector layer varies between either the first or second material of the visible light reflector layer and the material of the visibly transparent infrared reflector layer.

[0012] In a second aspect, the present invention provides a process for forming a reflective surface on a substrate, the process comprising:

(i) exposing a surface of the substrate to a gas phase comprising species of a first refractive index material under conditions to deposit a substantially infrared transparent layer of the first refractive index material on the surface and then continuously decreasing the gas phase concentration of the species of the first refractive index material relative to the gas phase concentration of species of a second refractive index material under conditions to deposit a substantially Infrared transparent layer of the second material; then

(ii) contiguously increasing the gas phase concentration of the species of the first refractive index material relative to the gas phase concentration of the species of the second refractive index material under conditions to deposit a further substantially infrared transparent layer of the first refractive index material;

(iii) optionally, repeating step (i) and/or step (ii) to form a visible light reflector layer on the surface of the substrate;

wherein the composition of the visible light reflector layer varies between first refractive index material rich zone(s) and second refractive index material rich zone(s) with a compositional gradient between the zones,

[0013] In a third aspect, the present invention provides a process for forming a graded visible light reflector layer on surface on a substrate, the process comprising:
(i) exposing a surface of the substrate to a gas phase comprising species of a first refractive index material under conditions to deposit a substantially infrared transparent layer of the first refractive index material on the surface and then continuously decreasing the gas phase concentration of the species of the first refractive index material relative to the gas phase concentration of species of a second refractive index material under conditions to deposit a substantially infrared transparent layer of the second refractive index material; then

(ii) continuously increasing the gas phase concentration of the species of the first refractive index material relative to the gas phase concentration of the species of the second refractive index material under conditions to deposit a further substantially infrared transparent layer of the first refractive index material;

(iii) optionally, repeating step (i) and/or step (ii) to form a visible light reflector layer on the surface of the substrate;

wherein the composition of the visible light reflector layer varies between first refractive index material rich zone(s) and second refractive index material rich zone(s) with a compositional gradient between the zones.

[0014] In some embodiments of the second and third aspects, the surface of the substrate which is exposed to the gas phase comprises an infrared reflector layer on at least part of the surface. In these embodiments, the visible light reflector layer is formed on the infrared reflector layer. Furthermore, in these embodiments the interface between the infrared reflector layer and the visible light reflector layer may be graded so that the composition between the infrared reflector layer and the visible light reflector layer varies between the material of the infrared reflector layer and the first or second material of the visible light reflector layer.

[0015] In some embodiments of the second and third aspects, the outer surface of the visible light reflector layer further comprises a visibly transparent infrared reflector layer. In these embodiments, the visibly transparent infrared reflector layer is formed on the visible light reflector layer. Furthermore, in these embodiments the interface between the visible light reflector layer and the visibly transparent infrared reflector layer may be graded so that the composition between the visible light reflector layer and the visibly transparent infrared reflector layer varies between either the first or second material of the visible light reflector layer and the material of the visibly transparent infrared reflector layer.
[0016] In a fourth aspect, the present invention provides a process for forming a reflective surface on a substrate, the process comprising:

(i) providing a substrate;

(ii) optionally, forming an infrared reflector layer on a surface of the substrate by exposing the surface to a gas phase comprising a species of copper or an alloy thereof under conditions to deposit a copper infrared reflector layer on the surface then decreasing the gas phase concentration of the copper or alloy thereof species over time relative to the gas phase concentration of a silicon species to form a gradient of copper and silicon; then

(iii) exposing the substrate surface to a gas phase comprising a silicon species and oxygen under conditions to deposit silicon dioxide on the surface of the substrate or on the infrared reflector layer (if present) and then continuously decreasing the ratio of oxygen to silicon species in the gas phase over time to deposit silicon; then

(iv) increasing the ratio of oxygen:to silicon species in the gas phase over time so as to deposit more silicon; dioxide; then

(v) decreasing the ratio of oxygen to silicon species in the gas phase over time so as to deposit more silicon; and

(vi) optionally, repeating step (iv) and/or step (v) to form a visible light reflector layer on the substrate or on the infrared reflector layer (if present); then

(vii) optionally, forming a visibly transparent infrared reflector layer on the visible light reflector layer by exposing the surface comprising the visible light reflector layer to a gas phase comprising a silicon species then decreasing the gas phase concentration of the silicon species over time whilst increasing the gas phase concentration of a copper or an alloy thereof species to form a visibly transparent infrared reflector layer with a gradient of copper and silicon between the visible light reflector layer and the visibly transparent infrared reflector layer;

wherein the composition of the visible light reflector layer varies between silicon dioxide rich zone(s) and silicon rich zone(s) with a Si and O gradient between the zones.

[0017] The present invention further provides a substrate comprising a reflective surface formed according to the process of the second, third or fourth aspects.
BRIEF DESCRIPTION OF THE FIGURES

[0018] Illustrative embodiments of the present invention will be discussed with reference to the accompanying figures wherein:

[0019] Figure 1 shows a schematic diagram of three embodiments of a reflector coating of the invention: an infrared reflector layer between the substrate and a visible light reflector layer (left image); a visibly transparent infrared reflector layer on a visible light reflector layer (middle image); and an infrared reflector layer between the substrate and a visible light reflector layer and a visibly transparent infrared reflector layer on the visible light reflector layer (right image).

[0020] Figure 2 shows a screen snapshot from the TFCaic™ software program showing the initial formula used for theoretical calculations for a visible light reflector layer over a copper infrared reflector layer.

[0021] Figure 3 shows a schematic diagram of an initial design for a visible light reflector layer over a copper infrared reflector layer.

[0022] Figure 4 shows a schematic diagram of the VW method for measuring reflection.

[0023] Figure 5 shows a plot of wavelength (nm) vs % reflection for a substrate comprising a visible light reflector layer over a copper infrared reflector layer as determined by TFCaic™ software program (solid line) and experimentally (dotted line).

[0024] Figure 6 shows the plot of Figure 5 with annotations showing characteristic features moving to higher wavelength.

[0025] Figure 7 shows a plot of wavelength (nm) vs % reflection for substrates having a 25% reduction of deposition times for each silica (solid line) or silicon layer (dotted line) compared to original experimental data (dashed line).

[0026] Figure 8 shows a plot of % thickness compared to standard vs TSR value (%) for substrates having a reduction of thickness far each silica (solid line) or silicon layer (dotted line) compared to original experimental data (dashed line).

[0027] Figure 9 shows plots of wavelength vs % reflection or solar intensity for an optimised coating (solid line) plotted with the solar spectrum (dotted line).
[0028] Figure 10 shows plots of wavelength (nm) vs % reflection or solar intensity (W·m⁻²·nm⁻¹) for substrates comprising graded (solid line) or ungraded (dashed line) coatings with the solar spectrum (dotted line).

[0029] Figure 11 shows photographs of substrates comprising graded (left) and ungraded (right) coatings.

[0030] Figure 12 shows plots of wavelength (ran) vs % reflection for substrates comprising different copper infrared reflector layers with TSR values shown in the legend.

[0031] Figure 13 shows plots of wavelength (ma) vs % reflection or solar intensity (W·m⁻²·nm⁻¹) for substrates comprising different copper infrared reflector layers with ungraded coatings with die solar spectrum (dotted line).

[0032] Figure 14 shows plots of wavelength vs % reflection or solar intensity (W·m⁻²·nm⁻¹) for substrates comprising different copper infrared reflector layers with an alternative coating design with the solar spectrum (dotted line).

[0033] Figure 15 shows a plot of thickness of silica layer (nm) vs TSR value (%).

[0034] Figure 16 shows plots of wavelength (nm) vs % reflection for substrates comprising varying thickness of a copper capping infrared reflector layer. For this figure the base layer Cu15 3:1 was used.

[0035] Figure 17 shows a plot of % transmission vs TSR value (%) for substrates comprising varying thickness of a copper capping infrared reflector layer.

[0036] Figure 18 shows plots of wavelength (nm) vs % reflection for substrates comprising a copper infrared reflector layer, visible light reflector layer and whole coating. TSR values are provided in the legend.

[0037] Figure 19 shows plots of wavelength (am) vs % reflection for substrates comprising a copper base infrared reflector layer on polycarbonate.

[0038] Figure 20 shows plots of wavelength (nm) vs % reflection for substrates comprising a sandwich reflector coating.

DETAILED DESCRIPTION
Referring to Figure 1, disclosed herein is a substrate 10 (not shown to scale) having a visible light reflector layer 12. The composition of the visible light reflector layer 12 varies between first refractive index material rich zone(s) 14 and second refractive index material rich zone(s) 16 with a compositional gradient 18 between the zones.

The substrate 10 also has an infrared reflector layer 20. The embodiment shown on the left of Figure 1 has an infrared reflector layer 20a between the substrate 10 and the visible light reflector layer 12. The embodiment shown in the centre of Figure 1 has a visibly transparent infrared reflector layer 20b on the visible light reflector layer 12. The embodiment shown on the right of Figure 1 has an infrared reflector layer 20a between the substrate 10 and the visible light reflector layer 12 and a visibly transparent infrared reflector layer 20b on the visible light reflector layer 12. The interface between the infrared reflector layer 12 and the visible light reflector layer 20a or 20b is graded so that there is a compositional gradient between the infrared reflector layer 20a or 20b and the visible light reflector layer 12 varies between the material of the infrared reflector layer 20a or 20b and the first or second material of the Visible light reflector layer 12. The combination of visible light reflector layer 12, infrared reflector layers 20a and 20b and any other layers (if present) forms a reflector coating.

The term "compositional gradient" as used herein in relation to the composition of the visible light reflector layer 12 and/or the infrared reflector layer 20a or 20b means that there is an increase or decrease in the atomic percentage of at least one element in the composition as the layers are deposited. In the coated end product this means that the atomic percentage of at least one element in the coating increases or decreases as one moves through the coating away from the substrate. The compositional gradient may be a continuous gradient which means that the atomic-percentage of at least one of the elements of the coating changes in an uninterrupted manner as the composition is deposited. The compositional gradient may also be a discontinuous gradient which means that the atomic percentage of at least one of the elements of the coating composition may increase or decrease overall as the coating is deposited, but there may be interruptions in the gradient. The compositional gradient of a coating may be determined using XPS.

The visible light reflector layer 12 is not a multilayer coating as that term is commonly understood in the field of optics. Multilayer coatings consist of alternate layers of materials having different refractive indices with a defined, sharp interface between the layers. An example of such a coating is provided in United States patent 4,189,205 which discloses a reflector layer comprising alternating low and high refractive index layers of magnesium fluoride and titanium dioxide with a defined interface between the layers. If the interface between alternate layers in coatings of this type is not sharp and defect free it can lead to optical distortions. Furthermore, there can be localised heating at the interface between the layers and this can affect the physical stability of the coating.
[0043] The lack of sharp defined interfaces between the different refractive index layers in the visible light reflector layer 12 and/or between the infrared reflector layer(s) 20a and 20b (if present) reduces problems that can occur with prior art multilayer coatings. For example, as shown in Figure 11, for coatings having the same composition the non-graded multilayer coatings are more likely to delaminate than the graded coating of the present invention. Furthermore, as described in more detail later, the process of the present invention is simple to carry out as it requires the continual adjustment of the vapour pressure of one or more of the reactants without the need to vary the nature of the reactants for each consecutive layer.

[0044] The substrate 10 may be any suitable material. The substrate 10 may be transparent or opaque. Examples of suitable substrates 10 include, but are not limited to, plastic substrates (such as acrylic polymers, such as polyacrylates; polyallyl methacrylates, such as polymethyl methacrylates, polyethyl methacrylates, polypropyl methacrylates, and the like; polyurethanes; polycarbonates; polyalkylterephthalates, such as polyethylene terephthalate (PET), polypropyleneterephthals, polybutyleneterephthalates, and the like; polysilo ne-containing polymers; or copolymers of any monomers for preparing these, or any mixtures thereof); metal substrates, such as but not limited to galvanized steel, stainless steel, and aluminum; ceramic substrates: tile substrates; glass substrates; fiberglass substrates; or mixtures or combinations of any of the above. Plastic substrates are particularly advantageous due to their relatively low cost, moldability and light weight. A range of plastic substrates are particularly useful, including (but not limited to) acrylic, stretched acrylic, polystyrene, polycarbonate, polyethylene terephthalate, polyvinylchloride, or polyamide (such as nylon). Glass substrates are also particularly useful.

[0045] The substrate 10 can be of any desired dimensions, e.g., length, width, shape, or thickness, and can be of any desired material having any desired characteristics, such as opaque, translucent, or transparent to visible light. The term "transparent" as used herein means having a transmittance of visible light through the substrate of greater than 0% up to 100%, whereas "opaque" means having a visible light transmittance of less than 0.001%. The methods for forming reflector coatings described herein may advantageously be used with large-area substrates. For example, the substrate may have a major dimension (e.g. a width or length) of about 1 metre or more. The thickness of the substrate may be from about 1 mm to about 10 mm. The substrate can be a flat substrate or can be shaped, bent, or curved. Advantageously, the substrate 10 can be a complex three-dimensional shape.

[0046] As used herein, spatial or directional terms, such as "inner", "outer", "above", "below", and the like, relate to the invention as it is shown in the figures. However, it is to be understood that the invention can assume various alternative orientations and, accordingly, such terms are not to be considered as limiting. Further, all numbers expressing dimensions, physical characteristics, and so forth, used in the specification and claims are to be understood as being modified in all instances by
the terms "about". Accordingly, unless indicated to the contrary, the numerical values recited in the specification and claims can vary depending upon the desired properties sought to be obtained. As used herein, the terms "deposited over", "applied over", or "formed over" mean deposited, applied, or formed on but not necessarily in contact with the surface. For example, a material "deposited over" a substrate does not preclude the presence of one or more other materials of the same or different composition located between the deposited material and the substrate. The terms "visible region" or "visible light" refer to electromagnetic radiation having a wavelength in the range of 400 nm to 700 nm. The terms "infrared", "infrared region" or "infrared radiation" refer to electromagnetic radiation having a wavelength in the range of greater than 700 nm to 100,000 nm. As used herein the term "layer" means a region of a coating having a desired or selected composition. A "coating" is comprised of one or more "layers".

[0047] The substrate having a visible light reflector layer is formed by exposing a surface of the substrate to a gas phase comprising species of a first refractive index material under conditions to deposit the first refractive index material on the surface. The gas phase concentration of the species of the first refractive index material in the plasma gas is then continuously decreased relative to the gas phase concentration of species of a second refractive index material under conditions to deposit the second refractive index material. The gas phase concentration of species of the first refractive index material is then increased relative to the gas phase concentration of species of the second refractive index material under conditions to deposit the first refractive index material. Optionally, the steps are repeated to form a visible light reflector layer on the substrate.

[0048] Whilst the process of the present invention can be used to manufacture reflective or mirror surfaces for a range of applications, it is particularly suitable for forming large mirror surfaces, such as those used in CSPs because plastic substrates are lighter in weight than glass, the reflector layer is economical to produce, the optical properties of the coating are good, and the optical properties of the coating can be adjusted by adjusting the composition, thickness, etc. of the first material rich zone(s) and/or the second material rich zone(s). Furthermore, the process allows substrates of different surface configurations, such as parabolic substrates, to be coated.

[0049] In practice, the visible light reflector layer is formed by physical vapour deposition. Suitable physical vapour deposition processes include:

- evaporative processes such as vacuum evaporation, electron-beam evaporation, molecular-beam epitaxy and reactive evaporation; or
- glow discharge processes such as sputtering, diode sputtering, reactive sputtering, bias sputtering, magnetron sputtering, ion beam deposition, ion beam sputter deposition, reactive ion plating, cluster beam deposition, and plasma processes.

[0050] Magnetron sputtering or electron-beam evaporation processes are particularly suitable.

[0051] Sputtering involves the physical vaporisation of atoms from a surface via bombardment of energetic atomic sized particles. This is commonly plasma-based sputtering, which is when a plasma is present and positive particles are accelerated to the target, with a negative potential with respect to the plasma. Magnetron sputtering uses a magnetic-field whereby with an effective arrangement of the magnets, ejections can be made to form a closed circular path on the target surface. This creates a high density plasma from which particles can be extracted to spotter the target material producing a magnetron sputtering configuration. During deposition it is also possible to "poison" the target via the introduction of a reactive gas, like oxygen. This allows the sputtering of metal complexes, such as metal oxides with the introduction of oxygen during the sputtering process. When this process occurs it is known as reactive sputtering.

[0052] Electron-beam evaporation (also known as E-beam evaporation) is a process in which a target material is bombarded with an electron beam given off by a tungsten filament under high vacuum. The electron beam causes atoms from the source material to evaporate into the gaseous phase. These atoms then precipitate into solid form, coating everything in the vacuum chamber (within line of sight) with a thin coating of the anode material. Electron-beam evaporation processes allow for high levels of control over deposition rates which can be as low as 1 μm per minute to as high as few micrometres per minute.

[0053] Thus, the physical vapour deposition processes involve exposing a surface of the substrate to a gas phase comprising species of the material to be deposited. As used herein, the term "species" in this context means an atom, molecular or ionic species present in the gas phase.

[0054] To deposit the coating by sputtering, the substrate is placed in a vacuum chamber with a target source material and an inert gas is introduced at low pressure. A gas plasma is struck using an RF power source, causing the gas to become ionised. The particles are then accelerated towards the surface of the target, causing species of the source material to break off from the target in vapour form and condense on the substrate.

[0055] In embodiments, the first material is silicon dioxide and the second material is silicon. Silicon dioxide is a low refractive index material whilst silicon is a high refractive index material. Thus, the substrate may be held in a vacuum chamber containing oxygen as a working gas and silicon as the
source material. The vapour pressure of oxygen in the chamber can be adjusted to form a low index silicon rich zone at low oxygen vapour pressure and the vapour pressure can then be continuously increased to a maximum to form a silicon dioxide rich zone and the vapour pressure can then be decreased continuously back to a minimum to form a subsequent silicon rich zone, etc. This process is advantageous in that a source of Si and a source of O are the only reactants required to form the visible light reflector layer and the compositional gradient can be formed by simply varying the concentration of silicon and oxygen species in the gas phase by varying the oxygen flow rate.

[0056] Silicon dioxide and silicon are particularly suitable for the first refractive index material and second refractive index material respectively because they are transparent in the infrared region and provide the desired spectral response in the visible region. However, it may be possible for other materials to be used for the first refractive index material and second refractive index material. The first refractive index material, which is the low refractive index material, preferably has a refractive index of less than about 1.7. The difference in refractive indices between the first refractive index material and the second refractive index material can be maximised by selection of appropriate materials to provide a visible light reflector layer with preferred optical properties.

[0057] In embodiments, the visible light reflector layer comprises at least two low refractive index material rich zones, with a high refractive-index material rich zone between the low refractive index material rich zones. In other embodiments, the visible light reflector layer comprises at least three low refractive index material rich zones, with high refractive index material rich zones between the low refractive index material rich zones, in still other embodiments, the visible light reflector layer comprises at least four low refractive index material rich zones, with high refractive index material rich zones between the low refractive index material rich zones. In other embodiments, the visible light reflector layer comprises at least five low refractive index material rich zones, with high refractive index material rich zones between the low refractive index material rich zones.

[0058] The thickness of the high refractive-index material rich zones and the low refractive index material rich zones can be controlled by reactive sputtering at a constant power from a suitable target with or without the reactive gas (depending on which zone is being deposited) for a time period sufficient to deposit the material to a required thickness. In the case of silica and silicon rich zones, silica can be reactively sputtered at constant power from a high purity silicon target with constant flow rates of inert gas and oxygen. This deposition is continued until the required thickness is achieved for the silica rich zone, based on the deposition rate, and then the oxygen flow is stopped. This causes the target to stop reactively sputtering, de-poison, and silicon sputtering begins. The reactive sputtering is stopped after a predetermined period, such as about 20 seconds, and silicon is not deposited until after this time. Silicon can then be sputtered with a constant flow rate of inert gas until the desired thickness is achieved for the silicon rich zone. After the desired thickness for the silicon rich zone is achieved
oxygen is reintroduced at a constant flow rate causing the target to poison and start reactively sputtering silica. Deposition of the intermediate phase does not begin until the silicon rich zone of desired thickness is deposited. This process is repeated until the desired number and/or configuration of layers is deposited.

[0059] Preferably, the substrate further comprises an infrared reflector layer. The infrared reflector layer is preferably a metal or metal alloy layer. The metal or metal alloy layer may be formed from any of the metals known for that purpose in the art, including copper, aluminium, silver, gold, and mixtures, alloys, or combinations including at least one of these metals. Copper is a particularly suitable metal for the infrared reflector layer. Other suitable materials may be alloys of copper, such as CuAl, CuRh, CuZr, CuCr, CuCo, etc. To ensure appropriate levels of transparency in the visible spectrum, the metal or metal alloy layer is preferably graded into a layer rich in silicon.

[0060] The infrared reflector layer may be located between the substrate surface and the visible light reflector layer. This layer may be referred to as a bottom infrared reflector layer. The bottom infrared reflector layer may be transparent or opaque.

(0061 ) Alternatively, or in addition, the infrared reflector layer may be located over the visible light reflector layer. This layer may be referred to as a top or capping infrared reflector layer. The top infrared reflector layer is preferably transparent to visible light so that most of the visible light incident on the layer passes through it and into the visible light reflector layer. Such a layer is referred to herein as a "visibly transparent" infrared reflector layer.

[0062] In specific embodiments, the infrared reflector layer is formed from copper. A bottom infrared reflector layer may have a thickness of about 50nm. However, as discussed in more detail later, the infrared reflector layer may be deposited by sputtering from a suitable copper source and a compositional gradient may be formed between the infrared reflector layer and the visible light reflector layer. In these cases, there is no sharp boundary or interface between the infrared reflector layer and the visible light reflector layer and therefore it is not possible to measure the thickness of the infrared reflector layer definitively. Nevertheless, the thickness of the infrared reflector layer may be equated with the thickness of the layer containing the substantially pure metal that is deposited prior to the start of the compositional gradient from the infrared reflector layer to the visible light reflector layer.

[0063] The process of the present invention may comprise a step of forming the infrared reflector layer on the substrate. For example, the infrared reflector layer may be deposited on the surface of the substrate using any of the methods known for this purpose in the art. Advantageously, the infrared reflector layer is deposited on the surface of the substrate by sputtering using a copper target material.
The infrared reflector layer may be formed directly on a surface of the substrate or there may be other materials, layers or coatings between the native substrate and the infrared reflector layer.

[0064] The visible light reflector layer is then formed on the infrared reflector layer. The visible light reflector layer may be formed directly on the infrared reflector layer or there may be other materials, layers or coatings between the infrared reflector layer and the visible light reflector layer.

[0065] Substrates comprising the reflective surface preferably have a total solar reflectance (TSR) value of greater than about 80%, such as about 80%, 81%, 82%, 83%, 84%, 85%, 86%, 87%, 88%, 89%, 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98%, 99% or 100%.

[0066] The reflector coating may also comprise one or more additional layers as required. For example, the reflector coating may be top coated with a transparent barrier layer and/or a transparent hard coat layer. For example, one or more layers that provide abrasion resistance and/or that protect the visibly transparent infrared reflector layer and/or the visible light reflector layer can be formed. Suitable coating materials for these purposes are known in the art and include polyfunctional acrylic coatings, urethane-based coatings, alkyl-based coatings, silicone based coatings or other organic or inorganic/organic coatings.

[0067] From the foregoing discussion it will be evident that the present invention further provides a process for forming a reflective surface on a substrate, the process comprising:

(i) providing a substrate;

(ii) optionally, forming an infrared reflector layer on a surface of the substrate by exposing the surface to a gas phase comprising a species of copper or an alloy thereof under conditions to deposit a copper infrared reflector layer on the surface then decreasing the gas phase concentration of the copper or alloy thereof species over time relative to the gas phase concentration of a silicon species to form a gradient of copper and silicon; then

(iii) exposing the substrate surface to a gas phase comprising a silicon species and oxygen under conditions to deposit silicon dioxide on the surface of the substrate or on the infrared reflector layer (if present) and then continuously decreasing the ratio of oxygen to silicon species in the gas phase over time to deposit silicon; then

(iv) increasing the ratio of oxygen to silicon species in the gas phase over time so as to deposit more silicon dioxide; then
(v) decreasing the ratio of oxygen to silicon species in the gas phase over time so as to deposit more silicon; and

(vi) optionally, repeating step (iv) and/or step (v) to form a visible light reflector layer on the substrate or on the infrared reflector layer (if present); then

(vi) optionally, forming a visibly transparent infrared reflector layer on the visible light reflector layer by exposing the surface comprising the visible light reflector layer to a gas phase comprising a silicon species then decreasing the gas phase concentration of the silicon species over time whilst increasing the gas phase concentration of a copper or an alloy thereof species to form a visibly transparent infrared reflector layer with a gradient of copper and silicon between the visible light reflector layer and the visibly transparent infrared reflector layer;

wherein the composition of the visible light reflector layer varies between silicon dioxide in rich zone(s) and silicon rich zone(s) with a Si and O gradient between the zones.

[0068] The present Invention also provides a substrate comprising an infrared reflector layer and a visible light reflector layer on the infrared reflector layer wherein the composition of the visible light reflector layer varies between first material rich zone(s) and second material rich zone(s) with a compositional gradient between the zones.

[0069] The present invention further provides a substrate comprising a reflective surface formed according to the process of the present invention.

DESCRIPTION OF EMBODIMENTS

[0071*] Example 1 - Modelling of a coating for a plastic mirror

[0071] Initially, a coating was designed theoretically on the thin film software TPCalc\textsuperscript{TM} (Software Spectra, Inc., Portland, OR, USA). TPCalc\textsuperscript{TM} enables analysis and design of multilayer thin film coatings with the ability to plot reflectance over a large spectral range at various incommens.

[0072] Figure 2 shows the coating formula initially designed based on the spectrum predicted from these coatings, and Figure 3 shows the cross section of the calculated coating.

[0073] Example 2 - formation of reflector layers on glass and plastic substrates
[0074] The coating designed in Example 1 was then formed on a glass slide. This initial work was conducted on glass since TFCalc™ models using glass as a substrate, and by using glass in experimental work it minimises any variables allowing a more accurate comparison.

[0075] Magnetron sputter deposition was used to form the samples. To do this, samples were firstly placed under a vacuum, on a variable speed rotating substrate holder, and an initial infrared reflector layer of copper was deposited. Specifically, copper was sputtered at 40 W from a high purity 3” diameter circular target with an argon flow rate of 15 standard cubic centimetres per minute (seem). Towards the end of sputtering copper, silicon was co-sputtered -from a high purity 5” x 12” target at 1 kW. During this co-sputtering stage the argon flow rate remained the same. Once the copper target was turned off oxygen was introduced at a flow rate of 6 seem, causing the silicon to be reactively sputtered into silica. Co-sputtering with silicon and then addition of oxygen while continually sputtering results in the formation of a layer in which the composition varies between an initial copper rich zone, a silicon rich zone and then a silica rich zone with a compositional gradient between the zones and no sharp interface between the initial reflector layer of copper and the visible light reflector layer or the silicon rich zone and the silica rich zone.

[0076] The process of depositing the visible light reflector layer was similar to that of the initial reflector layer. Again samples were placed under vacuum on a variable speed rotating substrate holder and silica was reactively sputtered at a constant power, from a high purity 5” x 12” target with an argon flow rate of 15 seem and oxygen flow rate of 6 seem. This was continued until the required thickness was achieved for the silica rich zone, based on the deposition rate 0.123 nm/s, and then the oxygen flow was stopped. This caused the target to stop reactively sputtering, de-poison, and start sputtering-silicon. The reactive sputtering was stopped when the voltage reading had increased to around 570 V, this change over typically took 20 seconds, and silicon was not deposited until this level was reached. Silicon was then sputtered with a constant argon flow rate of 15 seem until the desired thickness was achieved, using the deposition rate 0.25 nm/s. After this thickness was achieved oxygen was reintroduced at a flow rate of 6 seem causing the target to poison and start reactively sputtering silica. A value of about 270 V was expected for silica deposition and, until this level was reached, deposition of an intermediate phase which is different to the silica phase occurred. This process was repeated until the desired amount of layers were deposited.

[0077] Any substrate can be placed in the sputtering chamber to be coated, allowing coating of glass or plastic substrates and coating of substrates having complex three-dimensional shapes. Also during pump-down to vacuum a heater can be connected to the sputtering chamber, allowing for heating of the substrates prior to sputtering.
Spectra were collected using a Cary 5000 absorption spectrometer. The spectra were measured over the range of 280 - 3000 nm with increments of 0.5 ran between 280 - 400 nm, of 1 between 40.1 -1702 nm and increments of 5 nm from 1705 - 3000 nm. The reflection was measured via the VW method described by Strong (Strong, 1938). This method was used to calculate absolute specular reflectance by using a pair of mirrors, standardised to each other. These mirrors are referred to as "A" and "B". A baseline is first established with both mirrors in a "V" position, and then an absolute zero is established by mirror A changing to the "W" position. Once the baseline and absolute zero values are established the sample is incorporated into mirror A system. The positions are referred to as V and W because of the path light undertakes through the mirrors. Figure 4 shows a simple diagram to demonstrate the set up.

Due to the W position involving reflection from the sample twice, the values collected at each wavelength is actually percentage reflection squared. To correct for this, a calculation was conducted for each value collected. The calculation is shown in the following equation:

\[ \%R = \left( \frac{\%R^2}{100} \right) \times 100 \]

This allows for a plot of percentage reflection vs wavelength and then conversion into TSR values.

**Results & Discussion**

Initial work using TFCalc™ software showed the reflector coating shown in Figure 3 had the desired spectrum, and hence was the first coating formed on a glass substrate. Figure 5 shows the theoretical result along with the first experimental result from the same coating designs.

The results obtained using the TFCalc™ software show a spectrum quite different from that gained experimentally. The difference between the calculated spectrum and the experimental spectrum was attributed the presence of a graded coating in the latter case. Unlike the coating design created using the TFCalc™ software, there are no sharp gradients between any of the materials in the coating formed as each of the layers gradually grade into one another. The formation of a graded coating is a method of limiting stresses within the thin films due to the lack of clearly defined interfaces. As is known, there are associated stresses with a solid-solid interface. In addition, a general solid-solid interface has two associated interface stresses (Brooks, 1963). This is a key issue in multilayer structures since the more stress within a coating the lower the mechanical stability, causing the coating to delaminate (Frohlica et al., 2013). By removing the interfaces between layers in the coating, thicker coatings can be made without increasing the stress built up in the coatings and, hence, without reducing the mechanical stability. This provides flexibility to tune the optical properties of the reflector coating by varying the thickness of layers in the coating.
[0083] The periods of blending the materials together during deposition, creating the graded interfaces, were not taken into account in the calculations and therefore have an effect on the positions of peaks in the reflection spectra, appearing in this case to shift positions to a higher wavelength. This is seen in the characteristic features from the TFCalc ™ software data appearing at higher wavelengths that with the experimental data (Figure 6).

[0084] In order to make this experimental data a viable option as a solar reflector for CSP the spectral features needed to be shifted to lower wavelengths, allowing an overlap with the peak in the solar intensity. Subsequent coating designs that were tested experimentally worked on establishing trends between altering the overall thickness of the layers in the coatings and the spectrum produced. Figure 7 shows a slight reduction of each silica and silicon rich zone individually to see how this affects the reflectivity. Both results show characteristic points moving to positions of a lower wavelength. Further experiments were conducted, varying the silica and silicon thicknesses individually and together, as well as reducing the thickness of the whole coating design whilst maintaining the ratios of the materials. This was done to determine if there were any trends.

[0085] To better compare the results, in the context of making a mirror for CSP, the spectra were converted into TSR values. The values were then plotted on a graph (Figure 8) to show any trends established. From Figure 8, it can be seen that using 75% of the initial amount of silica and 25% of the initial amount of silicon is likely to give a high value for TSR. This sample thus had a thickness of 41 nm for the Si₃N₄ rich zone and 16 nm for the Si rich zone. This sample was given the code TQSQSOL and was tested. The spectrum obtained was then compared to that of the solar intensity and a TSR value was calculated to determine the effectiveness of the coating. The data are shown in Figure 9.

[0086] From the TQSQSOL coating a TSR value of 83.95% was achieved, showing the validity of the established trends. Also, as seen in Figure 9, the reflectivity of the TQSQSOL coating radically increases at the same point that the solar intensity spectrum does. This is a desired trait in the final coating.

[0087] To determine the effect of the graded coating relative to a non-graded coating with interlaces between the layers, the TQSQSOL coating was formed without any gradients (S-TQSQSOL). This was achieved by removing the substrate from under the target during the poisoning and depoisoaing process. This was firstly to ensure mechanical stability was enhanced by the introduction of the gradient and also to check how the intermediate graded layers effect the reflection. Figure 10 shows a graph comparing the graded and ungraded versions of this coating.

[0088] The TSR value obtained for the ungraded S-TQSQSOL coating was 76.7% (Figure 10). This is dramatically reduced from the TQSQSOL graded version, almost 10% less. As already established,
reducing the overall thickness of the layers moves the spectrum to lower wavelengths. This is seen in Figure 10, as certain features were shifted to lower wavelengths. Normally this would be a positive, allowing for more reflection at significant areas of the solar spectrum. However due to reduced reflecting layers within the gradient the overall reflectivity in the visible region dropped. This leads to the resulting lower TSR values.

[0089] It was also noted front the physical appearance of the samples that the mechanical stability of the ungraded S-TQSOS1 coating was compromised. This is apparent from the cracks forming on the coating, showing deamination (Figure 11). The S-TQSOS1 coating was also easily rubbed off when touched which was not the case with the graded TQSOS1 coating. Only a few scratches can be seen on the graded version and these were attributed to handling and use in the spectrometer. However, as well as similar scratching seen on the ungraded S-TQSOS1 version, an orange peel effect can be seen around the edges of the slide. This is due to the build-up of stress between layers of the coating causing deJamination. Over time this feature will spread across the coating and cause complete-deJamination.

[0090] We also investigated the effect of the underlying copper infrared reflector layer on the reflectance of the sample. Four variations of this underlying infrared reflector layer were investigated. The original underlying infrared reflector layer was formed by 15 minutes of copper deposition with one minute of silica deposition starting 10 seconds before the end of the copper deposition. As well as this underlying layer the effect of a longer gradient into the silicon was investigated, starting the deposition 30 seconds before the end while oxygen was still introduced 10 seconds before the end of copper deposition. Furthermore, these two variables were repeated without the introduction of oxygen. These underlying infrared reflector layers are referred to as Cu15 1:1, Cu15 3:1, Cu5 1:0 and Cu15 3:0 respectively. The TSR values of these underlying copper infrared reflector layers were calculated and reflectivity spectrum was obtained. See Figure 13 for reflection plots and TSR values.

[0091] The data shows that all the samples maintain high reflectivity in the infra-red region, with the main differences occurring below 800 nm. In this region it was established that silicon deposited without the introduction of oxygen causes lower TSR values.

[0092] Using this data, the effect of the underlying copper infrared reflector layer was investigated. To determine the effect of the copper infrared reflector layer on the final reflectivity of the entire coating the graded TQSOS1 coating was deposited on top of the copper infrared reflector layer. Reflection spectra were collected for each (Figure 13). The results showed that, regardless of the TSR values of the underlying copper infrared reflector layer, the spectrum maintained similar levels of reflection across the visible range of the spectrum with the same characteristic shape. This suggests that the underlying copper infrared reflector layer has little effect on the overall coating TSR values.
To ensure this result was not an anomaly another sharp interface coating was deposited this time with coating thicknesses calculated from the TFCalc™ software. This involved the coating formula: (BAB)\(^4\). For this formula B equates to 55 nm. of silica and A is 49 nm of silicon.

[0093] The new coating design was established as it allowed a greater overlap of the significant parts of the solar spectrum creating a better solar reflector than the original design. Applying this coating onto the various copper infrared reflector layers indicated if there is any merit in using different copper infrared reflector layers in this way. Again, spectra for these were obtained and compared to each other and the solar spectrum (Figure 14).

[0094] Results were again similar regardless of the composition of the copper infrared reflector layer. However, it was noted that the rear sides of the reflective substrates appeared different. These were also measured. All but one of the coatings had a lower TSR value than the front side. The rear side of the Cu15 3:0 gave a TSR value of 87.97%. This showed that the reflective substrate was improved when inverted.

[0095] The effect of the upside-down reflective substrate was investigated further. Firstly the upside-down coating was recreated so it could be measured without needing to measure through the glass slide. Then in stages silica was deposited to the top, recreating the effect of measuring through the glass slide, a 'bulk' silica coating, to determine if there was a trend with the TSR values. Through the use of modelling software it was decided to deposit 70 nm of silica at a time because the modelling software showed peaks in reflectivity at desired wavelengths when just this silica layer is deposited and it was proposed that the associated increase in reflectivity would be superimposed on the overall spectrum. The spectra were recorded and TSR values were calculated. A plot of the TSR values related to the silica capping layer thickness was then made (Figure 15).

[0096] The data shows that when increasing the amount of silica the initial TSR value drops significantly before eventually reaching a plateau. From previous evidence, it was thought to increase up to a value near 88.0% as when measured through the rear side of the microscope slide. This increase was expected to be gradual until the bulk amount of silica had been reached, or at least the thickness of the glass slide of roughly 2mm. However, due to the large amount that would be required to reach this bulk concentration it would not be a feasible option on a large scale.

[0097] Subsequently, the best sample from original graded work conducted, TQSQSO1, was tested to determine whether or not depositing the copper infrared reflector layer as the top instead of the bottom infrared reflector layer had the same effect on graded samples. We found higher TSR values when the copper infrared reflector layer was on top of the visible light reflector layer than underneath it, showing the gradient had little effect. However, it was also noted that the coating had some
transparency, which was roughly 9% average throughout the spectrum. This indicated that high TSR values could never have been reached fully.

[0098] To further investigate this effect, samples of the TQSQSOI coating were prepared with four different copper base infrared reflector layers. Corresponding TSR values were measured before and after coating the top with a reverse copper infrared reflector layer, creating a 'sandwich' reflector system. The thickness of the top copper infrared reflector layer was gradually increased to determine the effects of the top infrared reflector layer. The values obtained for increasing the copper infrared reflector layer are provided in the following table. Figure 16 is a graph showing the spectra for various samples.

<table>
<thead>
<tr>
<th></th>
<th>Blank</th>
<th>Cu15 1:1</th>
<th>Cu15 3:1</th>
<th>Cu15 1:0</th>
<th>Cu15 3:0</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TSR Values without</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>top layer</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>62.9%</td>
<td>83.6%</td>
<td>82.9%</td>
<td>82.9%</td>
<td>82.5%</td>
</tr>
<tr>
<td><strong>TSR Values with top</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>layer Cu5 3:0</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>reversed</strong></td>
<td>74.2%</td>
<td>77.8%</td>
<td>78.4%</td>
<td>75.7%</td>
<td>76.1%</td>
</tr>
<tr>
<td><strong>TSR Values with top</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>layer Cu10 3:0</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>reversed</strong></td>
<td>82.8%</td>
<td>84.2%</td>
<td>84.5%</td>
<td>83.4%</td>
<td>83.1%</td>
</tr>
<tr>
<td><strong>TSR Values with top</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>layer Cu15 3:0</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>reversed</strong></td>
<td>82.5%</td>
<td>83.3%</td>
<td>83.3%</td>
<td>83.2%</td>
<td>82.9%</td>
</tr>
</tbody>
</table>

[0099] The samples featured in Figure 16 were then coated with this same method but with varying thicknesses. The most obvious difference with increasing the thickness of the top layer is the difference in the interference patterns. When a copper capping layer is deposited for five minutes the amount of interference increases causing extreme minima and maxima. From this it was established that the interference resulting from the top layer is detrimental at first due to the significant minima which occur throughout the spectra. However, a copper capping layer that is deposited for ten minutes was found to have the best reflectivity. In contrast to the five minute capping layer, the minima are not as extreme with the ten minute capping layer and, therefore, the negative effects of the interference are
not as significant. Moreover, the peaks which are also caused by these interference effects remain at the same height, if not better, allowing higher TSR values to be reached. These positive effects were not observed in a sample having a copper capping layer deposited for fifteen minutes because the transparency of the layer was reduced and this did not result in significant interference patterns. For further investigation a relationship between the TSR values relating to the transmission of the capping layer was established for every base layer (Figure 17).

[00100] Figure 17 shows that, regardless of the base infrared reflector layer, or even with the absence of a base infrared reflector layer, the highest TSE values were observed with a transmission at around 3%. With this irradiation, it was decided to use the capping infrared reflector layer Cu15 3:0 reversed and for only ten minutes of copper deposition in total.

[00101] It is important for the top infrared reflector layer to have m associated transparency to allow the underlying visible light reflector layer to have an impact. When looking at reflection spectra of each of the components and then the whole coating combined (Figure 18) the benefits of having the top infrared reflector layer transparent become obvious. The two spectra are almost superimposed together creating a better TSR value than they would otherwise reach.

[00102] The effect of the base infrared reflector layer on the interference pattern caused by the top infrared reflector layer was then investigated. To do this, one coating was formed without a base infrared reflector layer and one with aluminium as the base infrared reflector layer. Aluminium was investigated due to its increased reflectivity in the visible range of the spectra.

[00103] The following table shows the TSR values before and after this capping layer for each of the different bases.

<table>
<thead>
<tr>
<th></th>
<th>Blank</th>
<th>Al 50nm</th>
<th>Cu15 1:1</th>
<th>Cu15 3:1</th>
<th>Cu15 1:0</th>
<th>Cu15 3:0</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSR Values</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>before capping</td>
<td>58.0%</td>
<td>80.2%</td>
<td>82.1%</td>
<td>81.0%</td>
<td>81.4%</td>
<td>80.6%</td>
</tr>
<tr>
<td>TSR Values</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>after capping</td>
<td>87.4%</td>
<td>87.5%</td>
<td>88.8%</td>
<td>87.6%</td>
<td>88.0%</td>
<td>87.4%</td>
</tr>
</tbody>
</table>

[00104] Without exception every bottom layer improved when a top capping infrared reflector layer was added. This shows that all of the base layers, including aluminium, can be used as they all interact with the intermediate and capping layers differently giving different TSR values. However, it was noted that aluminium is lower in the infrared region, and this could possibly be the cause of its
lower TSR value. Alloys of aluminium could be used as the base infrared reflector layer and/or the top infrared reflector layer. For example, by alloying aluminium with copper or another infrared reflecting metal, the spectrum would be expected to increase at greater wavelengths and in turn increase the TSR obtained. These alloys could also cause variances in the rest of the spectrum due to different interference patterns.

[00105] Manipulation of the gradient coatings by increasing and decreasing the gradient between the layers may also be used to vary the reflectivity of the coating. These variations can be achieved by changing the power used during deposition and therefore the deposition rate.

[00106] The application of these coatings onto plastic substrates was then investigated. When depositing onto polycarbonate it can be common to heat the substrate while obtaining the required vacuum. It has been established (Pelleg et al., 1991) that when heating the substrate before sputtering the average grain size of the structure is larger. This would alter the macroscopic properties recorded, including reflection. Therefore the application of a coating onto polycarbonate was performed with one sample heated before application of each layer of the coating and another sample that was not heated. A glass slide was also coated alongside the polycarbonate samples as a control. In this experiment the base infrared reflector layer was Cu15 3:1, the same middle layer was TQSOSOL and the whole reflector was capped with Ca10 3:0.

[00107] initially, it seemed that heating the sample had an adverse effect. When the polycarbonate was heated prior to coating with the base copper infrared reflector layer the TSR value was 69%. This is roughly 7% lower than the unheated counterpart. The reason for this is apparent from an analysis of the reflection spectra (Figure 19). The reflectivity of the heated polycarbonate sample decreased throughout the whole spectrum but more significantly in the infrared region. For the glass sample this decrease was not as dramatic but was still apparent. This decrease may be associated with the larger grain size associated with substrate heating prior to deposition. As is known, when a substrate is heated larger grains are formed and the surface roughness increases (Yi et al, 2007). When light comes into contact with a surface of a material it can ‘bounce’ off in multiple directions due to irregularities in the material thereby undergoing diffuse reflection. Therefore, if the surface is rough there will be larger amounts of these irregularities within the material causing more diffuse reflection, decreasing the overall reflection measured.

[00108] The TQSOSOL coating was then coated on polycarbonate to investigate whether the same effect could be noted on the visible light reflector layer when the sample is heated before sputtering. Results again showed lower reflectivity when just this coating was coated onto a polycarbonate sample that was heated. This is likely to be due again to the increased grain size causing the amount of diffuse reflection to be higher. Due to this the copper capping infrared reflector layer
was not applied with heat since it had been established that the copper is less reflective when heated prior to sputtering.

Following is a table of the TSR values obtained for various components of the coating design.

<table>
<thead>
<tr>
<th></th>
<th>Glass</th>
<th>Polycarbonate</th>
<th>Glass Heated</th>
<th>Polycarbonate Heated</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cu Base</strong></td>
<td>76.78%</td>
<td>75.92%</td>
<td>73.42%</td>
<td>68.97%</td>
</tr>
<tr>
<td><strong>Visible Light</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Reflector Layer</strong></td>
<td></td>
<td>59.40%</td>
<td>56.86%</td>
<td></td>
</tr>
<tr>
<td><strong>Bottom Infrared</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Reflector Layer</strong></td>
<td>80.83%</td>
<td>80.84%</td>
<td>80.77%</td>
<td>79.78%</td>
</tr>
<tr>
<td><strong>Top Infrared</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Reflector Layer</strong></td>
<td></td>
<td>85.81%</td>
<td>85.77%</td>
<td></td>
</tr>
<tr>
<td><strong>Sandwich Reflector</strong></td>
<td>86.70%</td>
<td>86.61%</td>
<td>86.54%</td>
<td>84.72%</td>
</tr>
</tbody>
</table>

It was also concluded that the coating having the top infrared reflector layer always out-performed the coating having the bottom infrared reflector layer. This is counter to what has been established in the past. The requirement for the bottom reflector is to not have any transparency, causing all remaining light to be reflected. This is not the case when this reflector is used as a top reflector, as shown in Figure 19, since it becomes less effective with increased thickness and decreased transparency. The top infrared reflector layer works on being transparent in the visible region of the spectrum allowing the lower visible light reflector layer to boost reflectivity, along the same lines as previous multicomponent reflectors, but the visible light reflector layer is transparent in the infrared allowing the underlying infrared reflector layer to boost the rest of the spectrum.

However, for all but the heated polycarbonate the highest TSR values were obtained from the sandwich type reflector.

Figure 20 shows the spectra obtained for the heated and unhealed samples with the sandwich type-reflector. All of the spectra have a similar shape. Minima in the spectra were noted and attributed to the interference between the top and bottom infrared reflector layers. It is likely that with changes to each reflector layer these minima will change and could be removed.
In summary, the data has shown that either a sandwich type reflector or top reflector system may be used to form a highly reflective mirror surface. We have also shown that heating of the substrate has adverse effects which can most likely be attributed to an increase in surface roughness which in-turn increases the amount of diffuse reflection. For the visible light reflector layer the importance of graded interfaces was shown due to increased mechanical stability over time compared to their sharp interface counterparts.

Manipulation of the shape of the gradients in the visible light reflector layer is expected to not only affect the reflectivity of this layer and result in higher reflectivity, but also change the interference patterns between components of the coatings which will affect the overall reflectivity. Furthermore, variations in the material used in the reflector layers may be used to alter the reflectivity in the visible part of the spectrum.

Reflective surfaces formed according to the methods described herein may be used in concentrated solar power systems, as well as other applications requiring highly reflective materials, such as LED automotive headlights and commercial/domestic LED luminaries.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

Throughout this specification the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

All publications mentioned in this specification are herein incorporated by reference. Any discussion of documents, acts, materials, devices, articles or the like which has been included in the present specification is solely for the purpose of providing a context for the present invention. It is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed in Australia or elsewhere before the priority date of each claim of this application.
REFERENCES


CLAIMS

1. A substrate comprising a visible light reflector layer thereon, wherein the composition of the visible light reflector layer varies between first refractive index material rich zone(s) and second refractive index material rich zone(s) with a compositional gradient between the zones.

2. The substrate according to claim 1, further comprising at least one infrared reflector layer.

3. The substrate according to claim 2, wherein the infrared reflector layer is between the surface of the substrate and the visible light reflector layer.

4. The substrate according to claim 3, wherein the interface between the infrared reflector layer and the visible light reflector layer is graded so that the composition between the infrared reflector layer and the visible light reflector layer varies between the material of the infrared reflector layer and the first refractive index material of the visible light reflector layer.

5. The substrate according to any one of claims 2 to 4, wherein an outer surface of the visible light reflector layer further comprises a visibly transparent infrared reflector layer.

6. The substrate according to claim 5, wherein the interface between the visible light reflector layer and the visibly transparent infrared reflector layer is graded so that the composition between the visible light reflector layer and the visibly transparent infrared reflector layer varies between either the first refractive index material or second refractive index material of the visible light reflector layer and the material of the visibly transparent infrared reflector layer;

7. The substrate according to any one of claims 2 to 6, wherein the infrared reflector layer is copper, aluminium or compositions, alloys or mixtures containing at least one of these.

8. The substrate according to any one of claims 1 to 7, wherein the first refractive index material has a low refractive index.

9. The substrate according to any one of claims 1 to 8, wherein the second refractive index material has a high refractive index.

10. The substrate according to claim 8, wherein the first refractive index material is silicon dioxide.

11. The substrate according to claim 9, wherein the second refractive index material is silicon.

12. A process for forming a reflective surface on a substrate, the process comprising:
(i) exposing a surface of the substrate to a gas phase comprising species of a first refractive index material under conditions to deposit a substantially infrared transparent layer of the first refractive index material on the surface and then continuously decreasing the gas phase concentration of the species of the first refractive index material relative to the gas phase concentration of species of a second refractive index material under conditions to deposit a substantially infrared transparent layer of the second material; then

(ii) continuously increasing the gas phase concentration of the species of the first refractive index material relative to the gas phase concentration of the species of the second refractive index material under conditions to deposit a further substantially infrared transparent layer of the first refractive index material;

(iii) optionally, repeating step (i) and/or step (ii) to form a visible light reflector layer on the surface of the substrate:

wherein the composition of the visible light reflector layer varies between first refractive index material rich zone(s) and second refractive index material rich zone(s) with a compositional gradient between the zones.

13. The process according to claim 12, further comprising a step of forming an infrared reflector layer on the substrate prior to step (i).

14. The process according to claim 13, wherein the step of forming an infrared-reflector layer on the substrate comprises exposing the surface of the substrate to a gas phase comprising species of an infrared reflective material under conditions to deposit the infrared reflector layer on the surface.

15. The process according to claim 14, wherein the interface between the infrared reflector layer and the visible light reflector layer is graded so that the composition between the infrared reflector layer and the visible light reflector layer varies between the infrared reflector layer material and the first or second refractive index material of the visible light reflector layer.

16. The process according to any one of claims 12 to 15, further comprising-forming a visibly transparent infrared reflector layer on the visible light reflector layer.

17. The process according to claim 16, wherein the step of forming a visibly transparent infrared reflector layer on the substrate comprises exposing the substrate comprising the visible light reflector layer to a gas phase comprising the species of the infrared reflective material under conditions to deposit the visibly transparent infrared reflector layer on the visible light reflector layer.
18. The process according to claim 17, wherein the interface between the visible light reflector layer and the visibly transparent infrared reflector layer is graded so that the composition between the visible light reflector layer and the visibly transparent infrared reflector layer varies between either the first or second material of the visible light reflector layer and the visibly transparent infrared reflector layer material.

19. The process according to any one of claims 12 to 18, wherein the infrared reflector layer and/or the visibly transparent infrared reflector layer is formed from copper, aluminium or compositions, alloys or mixtures containing at least one of these.

20. The process according to any one of claims 12 to 19, wherein the first refractive index material has a low refractive index and the second refractive index material has a high refractive index.

21. The process according to claim 20, wherein the first refractive index material is silicon dioxide and the second refractive index material is silicon.

22. A process for forming a graded reflector layer on surface on a substrate, the process comprising:

(iv) exposing a surface of the substrate to a gas phase comprising species of a first refractive index material under conditions to deposit a substantially infrared transparent layer of the first refractive index material on the surface and then continuously decreasing the gas phase concentration of the species of the first refractive index material relative to the gas phase concentration of species of a second refractive index material under conditions to deposit a substantially infrared transparent layer of the second refractive index material; then

(v) continuously increasing the gas phase concentration of the species of the first refractive index material relative to the gas phase concentration of the species of the second refractive index material under conditions to deposit a further substantially infrared transparent layer of the first refractive index material;

(vi) optionally, repeating step (i) and/or step (ii) to form a visible light reflector layer on the surface of the substrate;

wherein the composition of the visible light reflector layer varies between first refractive index material rich zone(s) and second refractive index material rich zone(s) with a compositional gradient between the zones.
23. The process according to claim 22, further comprising a step of forming an infrared reflector layer on the substrate prior to step (i).

24. The process according to claim 23, wherein the step of forming an infrared reflector layer on the substrate comprises exposing the surface of the substrate to a gas phase comprising species of an infrared reflective material under conditions to deposit the infrared reflector layer on the surface.

25. The process according to claim 24, wherein the interface between the infrared reflector layer and the visible light reflector layer is graded so that the composition between the infrared reflector layer and the visible light reflector layer varies between the infrared reflector layer material and the first refractive index material of the visible light reflector layer.

26. The process according to any one of claims 22 to 25, further comprising forming a visibly transparent infrared reflector layer on the visible light reflector layer.

27. The process according to claim 26, wherein the step of forming a visibly transparent infrared reflector layer on the substrate comprises exposing the substrate comprising the visible light reflector layer to a gas phase comprising species of the infrared reflective material under conditions to deposit the visibly transparent infrared reflector layer on the visible light reflector layer.

28. The process according to claim 27, wherein the interface between the visible light reflector layer and the visibly transparent infrared reflector layer is graded so that the composition between the visible light reflector layer and the visibly transparent infrared reflector layer varies between the first or second material of the visible light reflector layer and the visibly transparent infrared reflector layer material.

29. The process according to anyone of claims 22 to 28, wherein the infrared reflector layer and/or the visibly transparent infrared reflector layer is formed from copper, aluminium or compositions, alloys or mixtures containing at least one of these.

30. The process according to claim 29, wherein the first refractive index material has a low refractive index and the second refractive index material has a high refractive index.

31. The process according to any one of claims 22 to 30, wherein the first refractive index material is silicon dioxide and the second refractive index material is silicon.

32. A process for forming a reflective surface on a substrate, the process comprising:

   (i) providing a substrate;
(ii) optionally, forming an infrared reflector layer on a surface of the substrate by exposing the surface to a gas phase comprising a species of copper or an alloy thereof under conditions to deposit a copper infrared reflector layer on the surface then decreasing the gas phase concentration of the copper or alloy thereof species over time relative to the gas phase concentration of a silicon species to form a gradient of copper and silicon; then

(iii) exposing the substrate surface to a gas phase comprising a silicon species and oxygen under conditions to deposit silicon dioxide on the surface of the substrate or on the infrared reflector layer (if present) and then continuously decreasing the ratio of oxygen to silicon species in the gas phase over time to deposit silicon; then

(iv) increasing the ratio of oxygen to silicon species in the gas phase over time so as to deposit more silicon dioxide; then

(v) decreasing the ratio of oxygen to silicon species in the gas phase over time so as to deposit more silicon; and

(vi) optionally, repeating step (iv) and/or step (v) to form a visible light reflector layer on the substrate or on the infrared reflector layer (if present); then

(vii) optionally, forming a visibly transparent infrared reflector layer on the visible light reflector layer by exposing the surface comprising the visible light reflector layer to a gas phase comprising a silicon species then decreasing the gas phase concentration of the silicon species over time whilst increasing the gas phase concentration of a copper or an alloy thereof species to form a visibly transparent infrared reflector layer with a gradient of copper and silicon between the visible light reflector layer and the visibly transparent infrared reflector layer:

wherein the composition of the visible light reflector layer varies between silicon dioxide rich zone(s) and silicon rich zone(s) with a Si and O gradient between the zones.

33. A substrate comprising a reflective surface formed according to the process of any one of claims 12 to 32.
Figure 3
Figure 4

[Diagram showing a schematic with mirrors and a sample]

Figure 5

[Graph showing wavelength vs. %Reflection with curves labeled %R from Tcalc and %R Experimental]
Figure 6

Figure 7
Figure 20
INTERNATIONAL SEARCH REPORT

International application No. PCT/AU2014/000931

A. CLASSIFICATION OF SUBJECT MATTER

G02B 5/08 (2006.01)  G02B 1/00 (2006.01)  G02B 1/02 (2006.01)  G02B 1/10 (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

Electronic database consulted during the international search (name of database and, where practicable, search terms used)

Databases: WPI and EPODOC. Keywords: reflector, mirror, G02B 5/08 (and sub marks in CPC and IPC); layer, film, coating; refractive index, index of refraction; first, second primary, initial; gradient, transition, graded, gradual; G02B 5/0883 (CPC); substrate, plate, base, support; composition; silicon, Si; silicon dioxide, SiO2, quartz; copper, Cu, aluminium, Al; decrease, increase, lower, raising, high, rich, change, vary, alter, adjust, mix, blend; zone, area, region; deposit; gas, vapour; sputter, physical vapour deposition, PVD; AND LTKE TERMS.

Database: Espacenet. Keywords: reflecting layer, reflector layer; refractive index, first refractive index, second refractive index; gradient; University South Australia as the applicant; Evans, Hall, Bishop, Mmpthy as the inventors.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Date of the actual completion of the international search 8 December 2014
Date of mailing of the international search report 08 December 2014

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<td>WO 1985/001 115 A1 (HUGHES AIRCRAFT COMPANY) 14 March 1985 Abstract, page 3 lines 1 to 10, page 6 lines 14 to 16, page 7 line 21 to page 9 line 33, page 22 lines 30 to 34</td>
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