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(19) **United States**(12) **Patent Application Publication**  
**Welser et al.**(10) **Pub. No.: US 2011/0168261 A1**(43) **Pub. Date: Jul. 14, 2011**(54) **HIGH TRANSMITTANCE OPTICAL  
WINDOWS AND METHOD OF  
CONSTRUCTING THE SAME****Publication Classification**(51) **Int. Cl.****H01L 31/0232** (2006.01)**G02B 1/10** (2006.01)**H01L 31/18** (2006.01)(52) **U.S. Cl. .... 136/259; 359/586; 438/69; 257/E31.127**

(57)

**ABSTRACT**

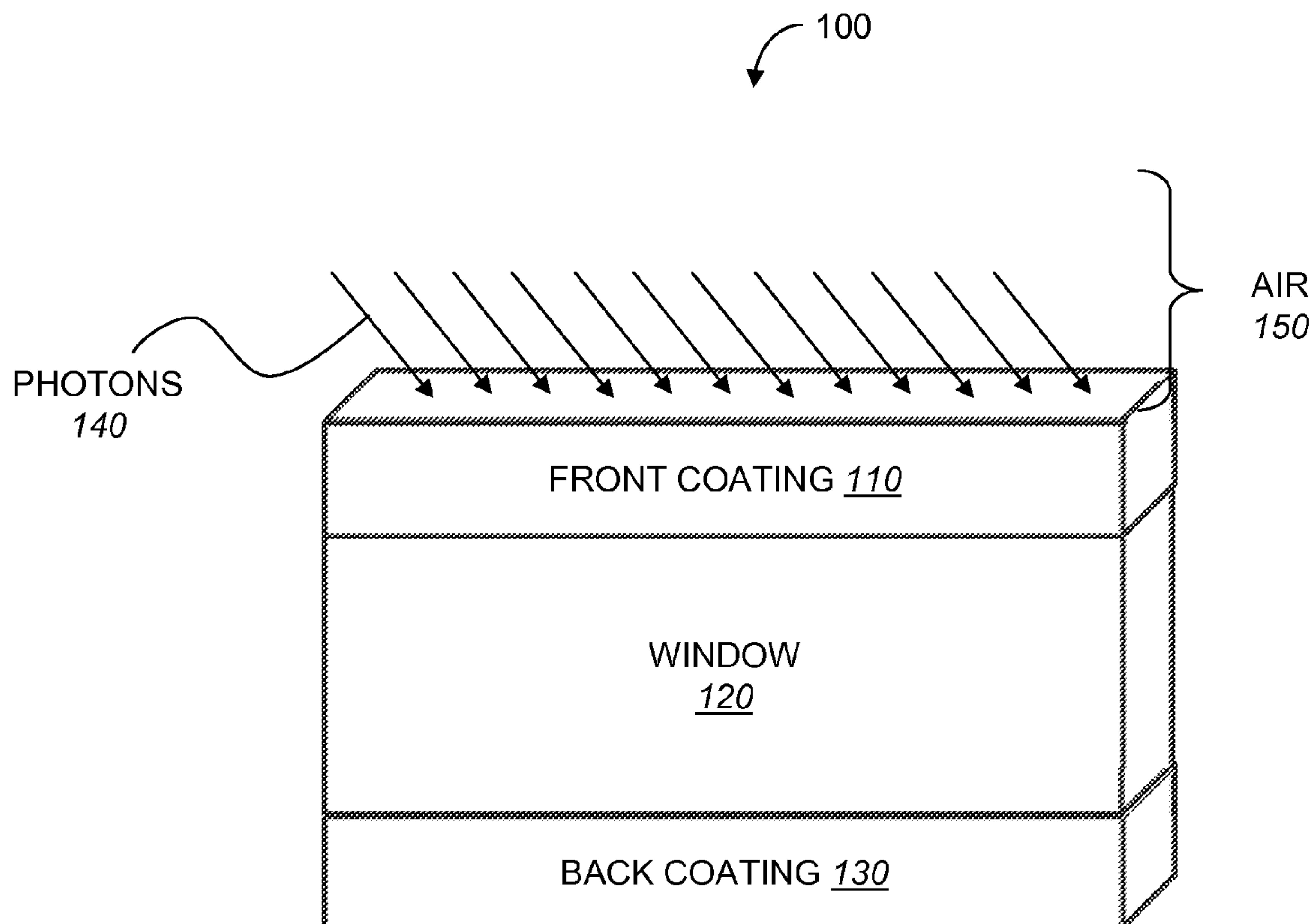
Designs for ultra-high, broadband transmittance through windows over a wide range of incident angles are disclosed. The improvements in transmittance result from coating the windows with a new class of materials consisting of porous nanorods. A high transmittance optical window comprises a transparent substrate coated on one or both sides with a multiple layer coating. Each multiple layer coating includes optical films with a refractive index intermediate between the refractive index of the transparent substrate and air. The optical coatings are applied using an oblique-angle deposition material synthesis technique. The coating can be performed by depositing porous SiO<sub>2</sub> layers using oblique angle deposition. The high transmittance window coated with the multiple layer coating exhibits reduced reflectance and improved transmittance, as compared to an uncoated transparent substrate.

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(21) Appl. No.: **12/946,580**(22) Filed: **Nov. 15, 2010****Related U.S. Application Data**

(60) Provisional application No. 61/293,469, filed on Jan. 8, 2010.



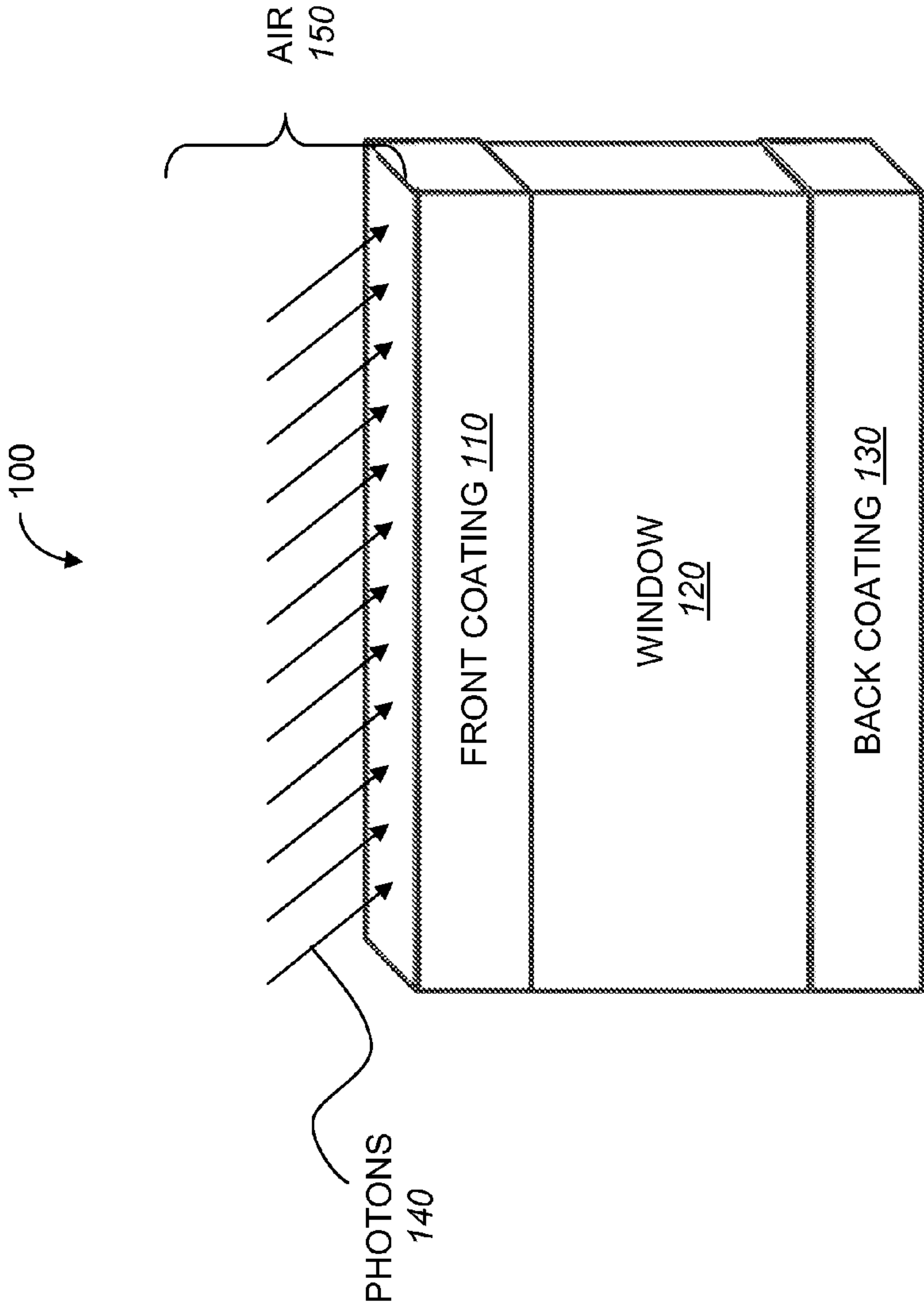


FIG. 1

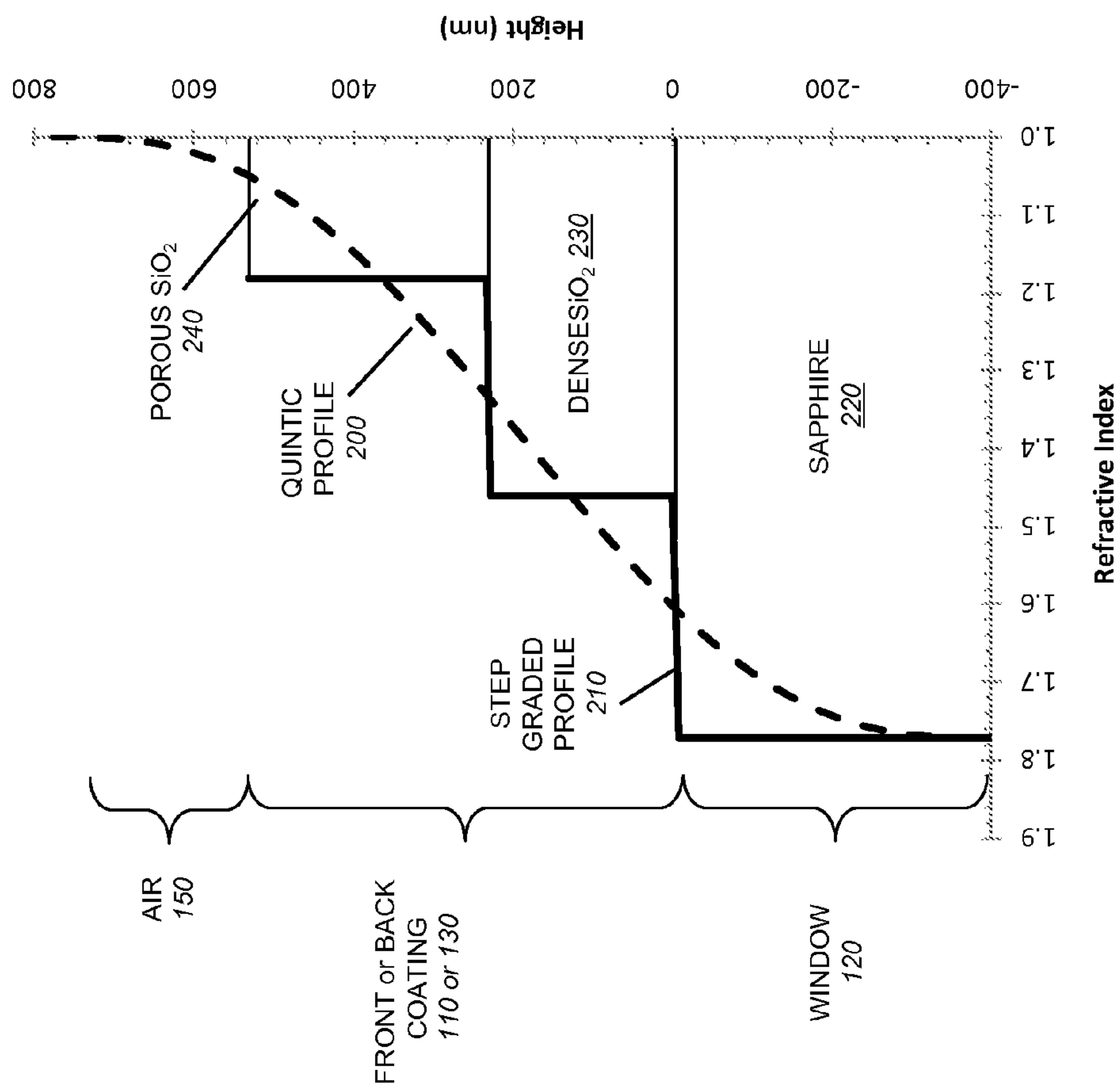


FIG. 2

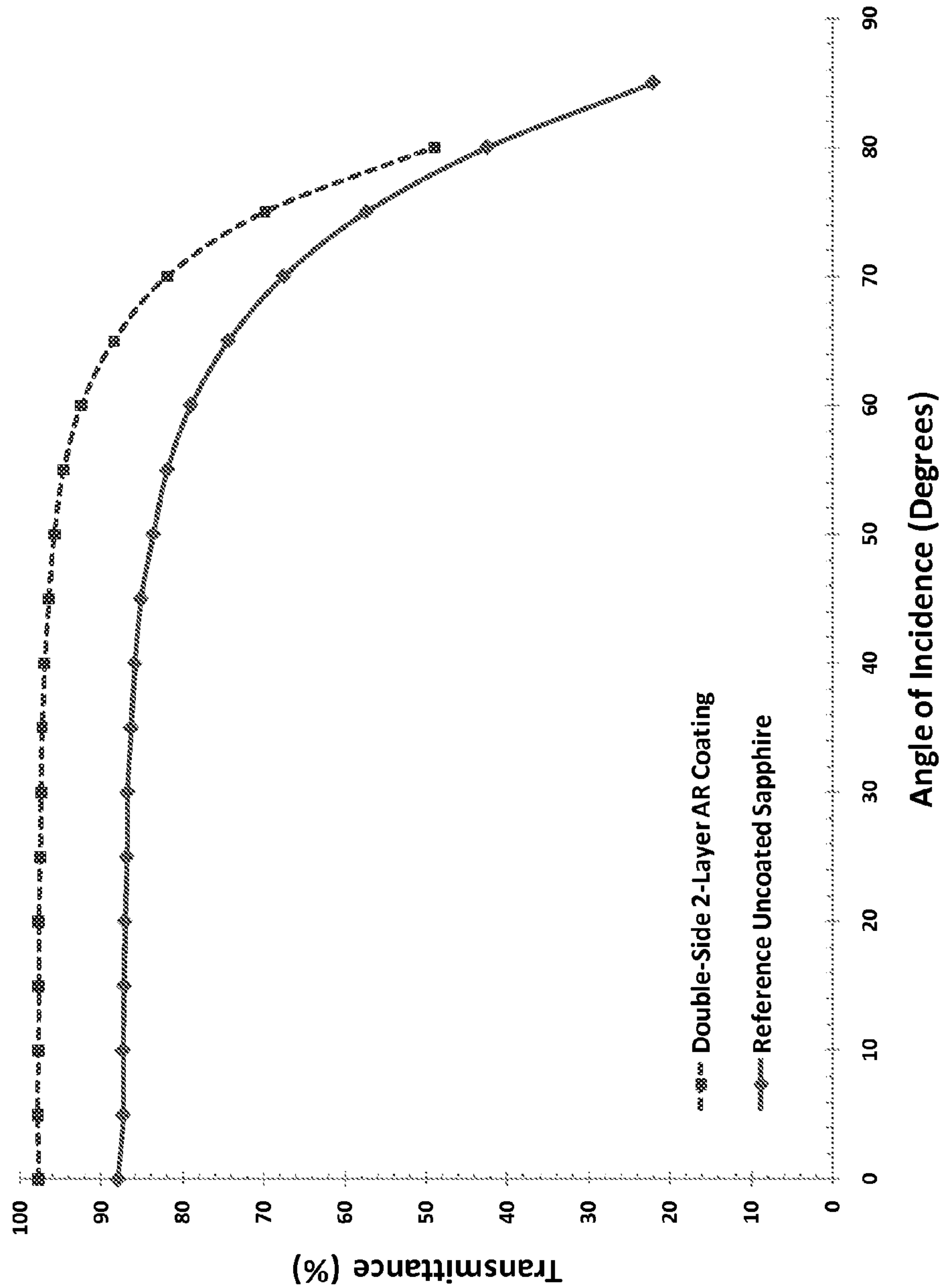


FIG. 3

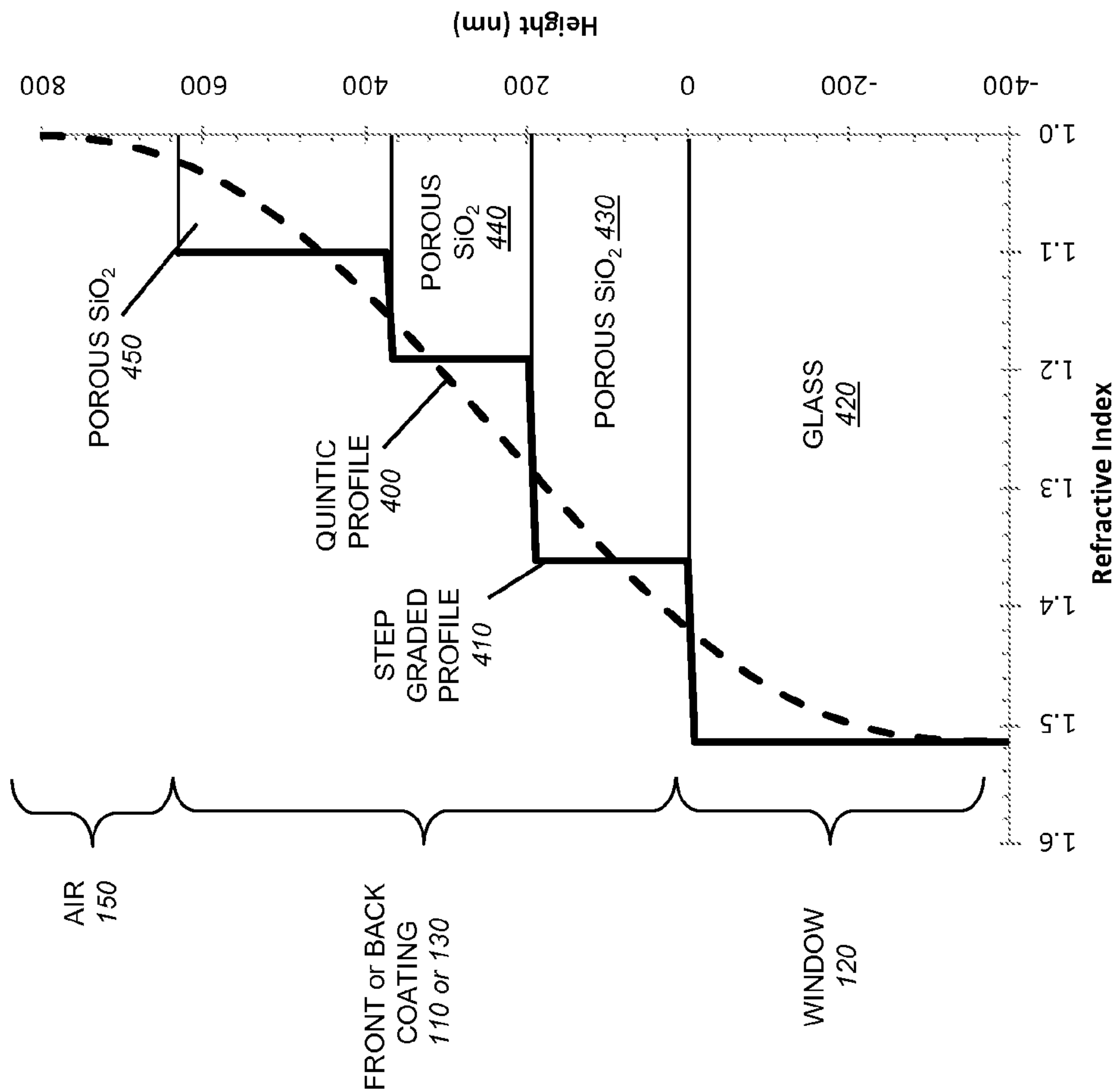


FIG. 4

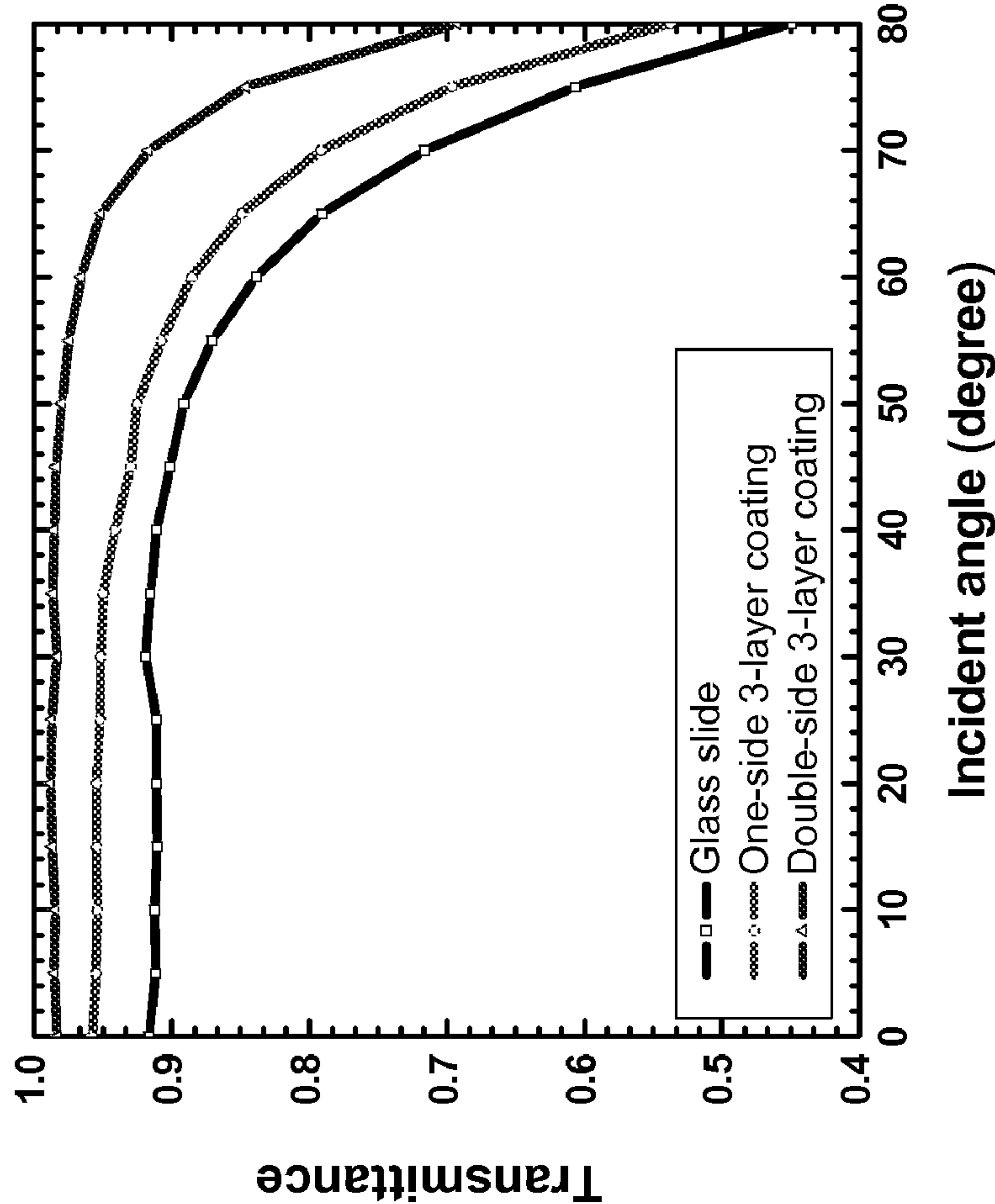


FIG. 5

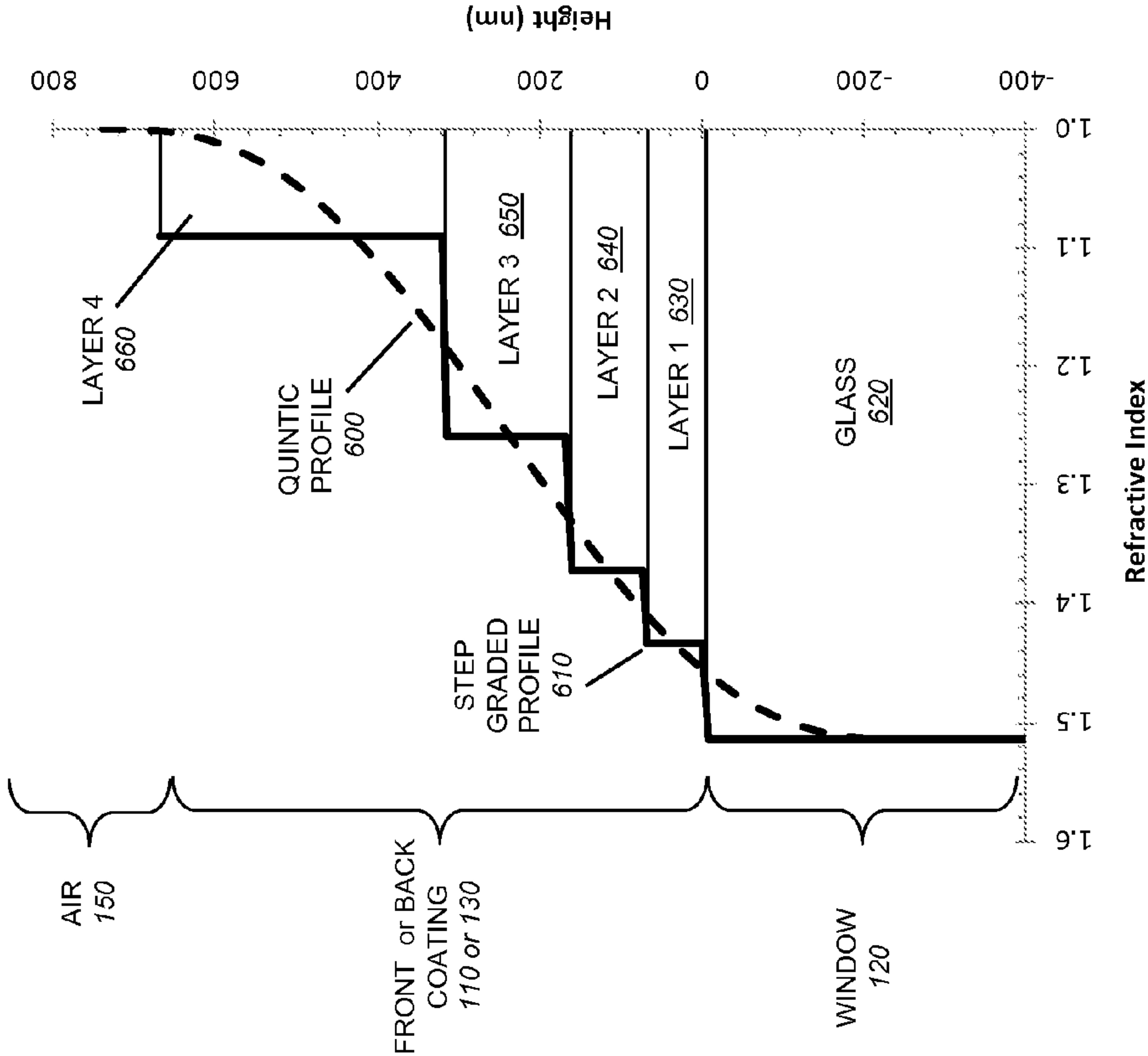


FIG. 6



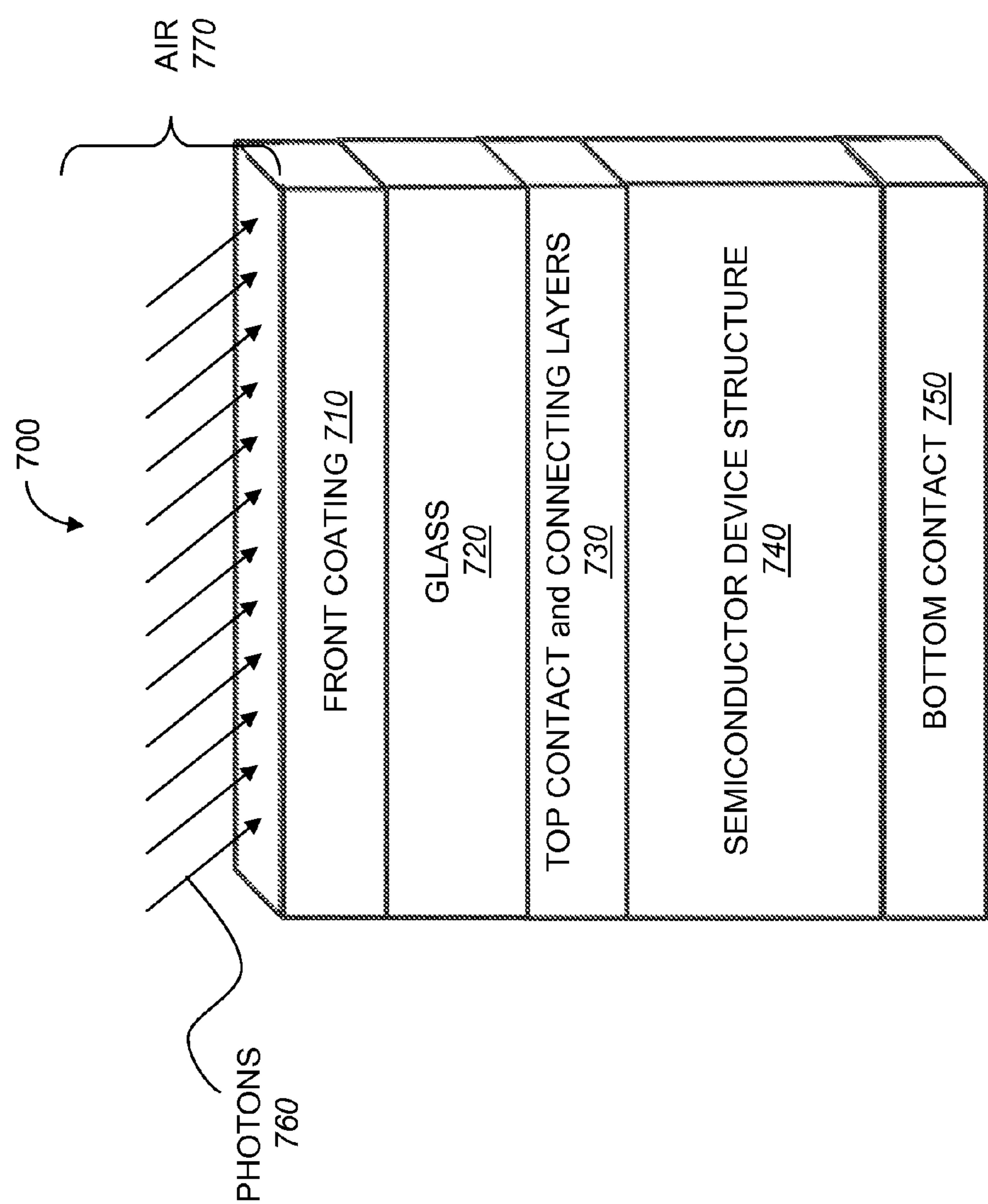


FIG. 7



## HIGH TRANSMITTANCE OPTICAL WINDOWS AND METHOD OF CONSTRUCTING THE SAME

### RELATED APPLICATIONS

**[0001]** This application claims the benefit of co-pending U.S. Provisional Patent Application Ser. No. 61/293,469, filed on Jan. 8, 2010 entitled EFFICIENT SOLAR CELL EMPLOYING MULTIPLE ENERGY-GAP LAYERS AND LIGHT-SCATTERING STRUCTURES AND METHODS FOR CONSTRUCTING THE SAME, which is expressly incorporated herein by reference.

### GOVERNMENT SUPPORT

**[0002]** This invention was supported in part by Small Business Innovative Research (SBIR) contract # W31P4Q-08-C-0300 from the Defense Advanced Research Projects Agency (DARPA) to Magnolia Optical Technologies, Inc., 52 B Cummings Park, Suite 314, Woburn, Mass. 01801. The government may have certain rights in this invention.

### FIELD OF THE INVENTION

**[0003]** This invention relates to transparent optical windows for detectors, sensors, and other optical devices; and to semiconductor-based photovoltaic energy converters, also known as “solar cells,” and to the design and fabrication of the same.

### BACKGROUND OF THE INVENTION

**[0004]** Transparent windows are employed in a wide range of military and commercial applications, including optical lenses and photovoltaic cover glass. Glass, sapphire, and quartz are well-known materials used to form high transmittance optical windows for a wide range of applications. Because these materials have very low absorption coefficients over a wide range of photon energies, optical transmittance through glass, sapphire, and quartz windows is typically limited by reflection losses. Fresnel reflection losses in optical windows arise from the difference in index of refraction between air ( $n \sim 1$ ) and the window material ( $n \sim 1.4-1.8$ ). Although Fresnel reflection losses are typically relatively low at normal incidence, they can become quite substantial for off-angle light incidence. For example, Fresnel reflection from uncoated glass generally varies from over 4% at normal incidence to as much as 40% at an incident angle of 75°.

**[0005]** Reducing optical reflection from surfaces is highly desirable to many applications in optics. Reducing reflection is commonly achieved through coating or texturing the surface of interest. Numerous applications involving dielectric or semiconducting materials use the light that is transmitted through the material's surface. Examples of such an application are optical lenses, windows, photovoltaic devices, and photodetectors. Glass (amorphous  $\text{SiO}_2$ ) is an example of a dielectric material widely used in a variety of optical applications (e.g. lenses, windows) and as a cover or encapsulation for semiconductor optoelectronic devices.

**[0006]** Glass is completely transparent for wavelengths longer than 400 nm. However, due to Fresnel reflection, it reflects about 4% of the incident light from its surface (–8% from two surfaces). This reflection is undesirable in many applications as it can degrade the efficiency of the underlying device (e.g. efficiency of a solar photovoltaic cell), reduce signal-to-noise ratio (e.g. in a photodetector), and cause glare

(e.g. from LCD screens, computer monitors, and televisions). For these applications, it is desirable not only to reduce reflectance but also to improve transmittance through the surface, which is achieved through a coating material that is non-absorbing and a coating surface that is specular.

**[0007]** Conventionally, a single-layer coating with optical thickness equal to one quarter of the wavelength ( $\lambda/4$ ) of interest has been used as an AR coating. Preferably, such single-layer  $\lambda/4$  AR coating should have a refractive index,  $n_{\lambda/4}$  as given by

$$n_{\lambda/4} = \sqrt{n_{\text{substrate}} \times n_{\text{air}}}$$

Often due to unavailability of materials with the desired, exact value of the refractive index, the performance of such  $\lambda/4$  AR coatings deviates from the optimum. This is especially the case for low-index substrates, such as glass. An ideal single-layer  $\lambda/4$  AR coating on glass surface in an air ambient would require a material with refractive index of  $(1.46)^{1/2} \approx 1.2$ . There is no conventional inorganic material that has such a low refractive index. Also, fundamentally, these single-layer  $\lambda/4$  AR coatings can minimize reflection only for one specific wavelength at normal incidence and they are inherently unable to exhibit spectrally broadband reduction in reflectance over wide range of angles-of-incidence.

**[0008]** In 1880, Lord Rayleigh mathematically demonstrated that graded-refractive-index layers have broadband antireflection properties. Multi-layer stacks of materials with different refractive indices have been used in order to achieve broadband reduction in reflection. Anti-reflection (AR) coatings with specular surface made of multiple discrete layers of non-absorbing materials can exploit thin film interference effects to reduce the reflectance while improving transmittance.

**[0009]** Optimization of multi-layer AR coatings is a difficult challenge because of the extremely large and complex dimensional space of possible solutions. Analytical methods to optimize AR coatings are not feasible due to the complexity of the problem. Heuristic methods such as needle-optimization, jump-elimination, and genetic algorithm are commonly used. It is desirable to provide a computational genetic algorithm method to achieve optimization of the coatings.

**[0010]** Theoretically, it has been known for some time that Fresnel reflection losses can be minimized between two media by varying the index of refraction across the interface. Until recently, however, the unavailability of materials with desired refractive indices, particularly materials with very low refractive indices below  $n=1.2$ , prevented the implementation of high-performance step graded refractive index designs. Recently, however, Prof. Fred Schubert and his group at Rensselaer Polytechnic Institute (RPI) have created a new class of materials comprising porous nanorods. In particular, the RPI group has demonstrated that oblique-angle deposition can be used to tailor the refractive index of a wide variety of thin film materials. Therefore it is desirable to apply this new material synthesis technique to the formation of coatings that can minimize reflection losses and maximize the transmittance through a wide variety of optical windows.

### SUMMARY OF THE INVENTION

**[0011]** This invention overcomes the disadvantages of the prior art by providing antireflection structures and a method of manufacturing the antireflection structures to increase the transmittance through a variety of different optical windows for a variety of applications. The various illustrative embodi-



ments reduce reflection losses, thus maximizing transmittance through optical windows. The various illustrative embodiments utilize multiple layer optical coatings in which the refractive index is varied between that of the window material and air in discrete steps. It is possible to design antireflection (AR) coatings that, due to interference effects, have a lower reflectivity than a continuously graded AR coating. In one embodiment, the optical antireflection coating comprised of at least two layers, up to any plurality of layers, which have a similar chemical composition but a different porosity and thus a different refractive index. In another embodiment, the optical antireflection coating contains (i) at least one layer of the AR coating comprising a single dense material, (ii) at least one layer of the AR coating comprising a solid solution of two different dense materials (that is a mixture of two dense materials), and (iii) at least one layer of the AR coating comprising a porous material. In yet another embodiment, a pore-closure layer is employed that covers the top surface and prevents moisture, or particles, from infiltrating the porous film. The pore-closure layer is very thin (much smaller than  $\lambda$ ) so as to be applied without influencing the reflectivity of the AR coating. More particularly, the pore closure layer is constructed and arranged to avoid negatively affecting the reflectivity.

**[0012]** In the illustrative embodiment, a high transmittance window comprises a transparent substrate coated on both sides with a multiple layer coating, such that each multiple layer coating comprises a plurality of optical films. The multiple layer coating defines a refractive index intermediate between the refractive index of the transparent substrate and air. The window can comprise, but is not limited to, glass, quartz, and sapphire materials. The multiple layer coating can comprise a plurality of various optical thin film materials, including but not limited to,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{BaF}_2$ ,  $\text{CdTe}$ , and diamond like carbon materials. Conductive, transparent coatings can be formed by using transparent conductive oxide (TCO) materials such as indium tin oxide (ITO) and zinc oxide (ZnO). The individual layers in the optical coating can comprise a single material of varying porosity, or of a solid solution of two different, dense materials, or any combination thereof. In a specific embodiment, the window material comprises sapphire and the index of refraction in each coating is varied from 1.5 to 1.1 over two steps, with the plurality of deposited layers defining approximately 230 nm of dense  $\text{SiO}_2$  ( $n \sim 1.46$ ) and approximately 300 nm of porous  $\text{SiO}_2$  ( $n \sim 1.18$ ).

**[0013]** In another illustrative embodiment, a plurality of antireflection layers of transparent refractive thin film are deposited on the front, sun-facing surface of a photovoltaic device. The purpose of the antireflection layers is to maximize the number of incident photons that are directed into the active region of an underlying semiconductor solar cell device. The antireflection structure is formed of multiple layers of optical thin film material on top of a transparent cover glass, while having an index of refraction intermediate between that of the glass and air. In the illustrative embodiment, the profile is characterized by a step-graded profile that may or may not follow a quintic profile to provide maximum photon transmission through the antireflection layers. The exact thickness and index of refraction of each of the layers in the antireflection layer can be adjusted to further minimize reflection losses over a broad spectrum of photon wavelengths and angles of incidence. The antireflection coating can be built using a variety of different materials, either in

combination or with various degrees of porosity, including but not limited to,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{BaF}_2$ ,  $\text{CdTe}$ , ITO or other TCO materials, and diamond like carbon materials. In a specific embodiment, the index of refraction in the topmost coating is varied from 1.5 to 1.1 over three steps, with the plurality of deposited layers defining approximately 192 nm of porous  $\text{SiO}_2$  ( $n \sim 1.36$ ), approximately 179 nm of porous  $\text{SiO}_2$  ( $n \sim 1.19$ ), and approximately 260 nm of porous  $\text{SiO}_2$  ( $n \sim 1.10$ ).

**[0014]** A method of constructing the improved antireflection structures described herein comprises coating the top and sometimes also the bottom surfaces of a transparent window with nanostructured optical coatings. The nanostructured optical coatings can be applied using the oblique angle deposition material synthesis technique. According to the illustrative embodiment, a transparent substrate is provided having a front surface and a back surface. The transparent substrate is then coated on at least one surface with a multiple layer ("multi-layer") coating comprising a plurality of optical films, and the multi-layer coating defining a refractive index intermediate between the refractive index of the transparent substrate and the refractive index of air. The coating can be performed by depositing porous  $\text{SiO}_2$  layers using oblique-angle deposition. The coating can also be performed by depositing layers comprising  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{BaF}_2$ ,  $\text{CdTe}$  and diamond like carbon materials using oblique angle deposition. In further embodiments, the coating is applied to the front surface after forming a thin film solar cell device on the back surface of the transparent substrate.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0015]** The invention will be readily understood by the following detailed description in conjunction with the accompanying drawings, wherein like reference numerals designate like structural elements, and in which:

**[0016]** FIG. 1 is a schematic side cross-sectional view of a double-side coated optical window, according to an illustrative embodiment;

**[0017]** FIG. 2 is a graph showing index of refraction versus position for a two-layered step-graded antireflection coating structure on a sapphire window to enhance optical transmission into or out of the window, according to the illustrative embodiment;

**[0018]** FIG. 3 is a graph showing measured transmittance through an uncoated sapphire window and through a sapphire window coated on both sides with a 2-layer AR structure, according to the illustrative embodiment;

**[0019]** FIG. 4 is a graph showing index of refraction versus position for a three-layered step-graded antireflection coating structure on a glass window to enhance optical transmission into or out of the window, according to the illustrative embodiment;

**[0020]** FIG. 5 is a graph showing measured transmittance through an uncoated glass slide and through a glass side coated on one and both sides with a 3-layer AR structure, according to the illustrative embodiment;

**[0021]** FIG. 6 is a graph showing index of refraction versus position for a four-layered step-graded antireflection coating structure on a glass window to enhance optical transmission into or out of the window, according to the illustrative embodiment; and

**[0022]** FIG. 7 is a schematic side cross sectional view of a photovoltaic device employing a step-graded antireflection coating on the top side of a glass window covering a semi-



conductor device structure, configured and arranged to face the sun to enhance optical transmission of photon energies into the active regions of the underlying solar cell, according to an illustrative embodiment.

[0023] The drawings are not necessarily to scale with emphasis instead being placed upon illustrating embodiments of the present invention.

#### DETAILED DESCRIPTION

[0024] Ultra-high, broadband transmittance through coated glass windows is demonstrated over a wide range of incident angles. The measured improvements in transmittance result from coating the windows with materials consisting of porous nanorods. The use of porous nano-materials fabricated by, for example, oblique-angle deposition, enables a tunable refractive index, flexibility in choice of material, simplicity of a physical vapor deposition process, and the ability to optimize the coating for any substrate-ambient material system. A multi-layer coating adapted for a glass substrate, is fabricated and characterized as described below. For multi-layer AR coatings, according to an illustrative embodiment, the refractive index of the layers is step-graded (i.e. decreased in discrete steps), from the substrate value, 1.46, to a value of 1.18, according to the various illustrative embodiments.

[0025] FIG. 1 details a cross-sectional view illustrating a high transmittance window structure **100** comprising a transparent optical window **120** having an antireflection structure **110** and **130** coated, respectively, on the front and back sides. According to the illustrative embodiment, the front coating **110** is deposited on a device window **120** configured and arranged to face a light source, which provides a readily available source of photons **140**. The front coating **110** is a multiple-layer coating comprising a plurality of optical films, and the multiple-layer coating defines an index of refraction between air **150** and the window **120**. The multi-layer coating can comprise two, three, or more layers, up to a plurality of layers, defining refractive indices as appropriate to achieve the desired transmittance. Refer to FIGS. 2, 4 and 6, showing examples of the refractive index profile. A back coating **130** is applied to the back side of the window **120** and comprises materials possessing indices of refraction between that of the window **120** and air **150**. Although photons **140** are illustratively shown as a series of a single direction of photon stream, it should be clear to those skilled in the art that the various, illustrative, and alternate embodiments will function with various varying degrees and/or amount of incident of light or source of photon energies.

[0026] In various embodiments, front coating **110** and back coating **130** are configured and arranged with transparent antireflection coating structures to reduce the reflection of incident photons at the material interface between air **150** and the window **120**. In the various embodiments, front coating **110** and back coating **130** are implemented in accordance with industry standard processes and materials known to those skilled in the art. Transparent antireflection coating structures can comprise a single layer or multiple layers of materials having an index of refraction intermediate between the window **120** and the media in which the incident photons are delivered, which by way of example is illustrated as air **150** in FIG. 1. Single-layer transparent antireflection coating structures are generally characterized by enhanced transmittance around a single wavelength of light when the light is at normal incidence to the transparent antireflection coating

structure surface. In alternate embodiments, graded-index coatings with variable-index profiles are utilized. By way of example, a quintic profile is illustrated at near optimum profile for a graded-index antireflection coating (see, for example, by way of useful background information, U.S. Pat. No. 4,583,822, entitled QUINTIC REFRACTIVE INDEX PROFILE ANTIREFLECTION COATINGS, by W. H. Southwell, the teachings of which are expressly incorporated herein by reference as useful background information). The various illustrative and alternate embodiments utilize optical materials with very low refractive indices that closely match the refractive index of air, which historically have not been utilized.

[0027] Oblique-angle deposition is utilized as an effective technique for tailoring the refractive index of a variety of thin film materials (see for example, by way of useful background, J.-Q. Xi, M. F. Schubert, J. K. Kim, E. F. Schubert, M. Chen, S.-Y. Lin, W. Liu, and J. A. Smart, *Optical Thin-Film Materials with Low Refractive Index for Broad-Band Elimination of Fresnel Reflection*, Nat. Photon., vol. 1, pp. 176-179, 2007). Oblique-angle deposition is a method of growing nanostructured, porous thin films, and hence thin films with low-refractive index (low-n), enabled by surface diffusion and self-shadowing effects during the deposition process. In oblique-angle deposition, random growth fluctuations on the substrate produce a shadow region that incident vapor flux cannot reach, and a non-shadow region where incident flux deposits preferentially, thereby creating an oriented rod-like structure with high porosity. The deposition angle, defined as the angle between the normal to the sample surface and the incident vapor flux, results in the formation of nanorod structures that are tilted relative to the sample surface. Given that the gaps between the nanorods can be much smaller than the wavelength of visible and infrared light, the nanostructured layers act as a single homogeneous film with a refractive index intermediate between air and the nanorod material, decreasing in refractive index with increasing porosity.

[0028] Both conducting and non-conducting graded-index antireflection coatings that are broadband and Omni-directional have been demonstrated using this deposition technique. As taught by Cho et al. in U.S. Pat. No. 7,483,212, by way of background, both oblique angle deposition and co-sputtering are material synthesis techniques that can be used to construct multiple layer, graded refractive index coatings to minimize reflection losses. The teachings of this patent are expressly incorporated herein by reference as useful background information. It is contemplated in illustrative embodiments that these processes can be adapted to minimize reflection losses for optical windows.

[0029] The refractive index of a front coating **110** and/or a back coating **130** on a window **120** is shown in the graph of FIG. 2 according to an illustrative embodiment. One example of step graded profile **210** is shown, along with a continuously varying quintic profile **200** of the index of refraction approximated as taught in U.S. Pat. No. 4,583,822, which is incorporated by reference as useful background information. In particular, the index of refraction, herein referred to as "n", is varied from that of the window **120**, which in this case is composed of transparent sapphire material **220** having a reflection value "n" of approximately 1.77, to that of air **150**, which is shown by way of example to be approximately 1. Fresnel reflection from one surface of uncoated sapphire generally varies from approximately 8% at normal incidence to up to approximately 50% at an incident angle of 75°. While



dense  $\text{SiO}_2$  is an optically transparent material, it has an index of refraction comparable to common silicon encapsulants ( $n \sim 1.47$ ). Thus, in conventional implementations,  $\text{SiO}_2$  is not typically used to reduce reflection losses. However, according to the illustrative embodiment, oblique angle deposition is employed to produce porous  $\text{SiO}_2$  layer with lower index of refraction. More particularly, the index of refraction of the front coating **110** is varied from 1.77 to 1 over two discrete steps which can comprise a first approximately 230 nm layer **230** of dense  $\text{SiO}_2$  material ( $n \sim 1.46$ ) and a second approximately 300 nm layer **240** of porous  $\text{SiO}_2$  material ( $n \sim 1.18$ ).

[0030] Notably, all layers of a multi-layer AR coating are constructed from a single material, porous silica (porous  $\text{SiO}_2$ ), according to the illustrative embodiment. Silica is particularly adept for use as AR coating on a glass, quartz, or sapphire substrate, as it is native, stable and robust.

[0031]  $\text{SiO}_2$  coatings are well known for their long-term stability and high transmittance over a wide spectral range. Conventional, dense  $\text{SiO}_2$  has a refractive index of approximately 1.46, and thus is not an effective antireflection material for glass windows with a refractive index of approximately 1.5. However, the refractive index of porous  $\text{SiO}_2$  can be reduced to values of 1.1 or lower by increasing the porosity. Oblique angle deposition enables the creation of a wide variety of step graded refractive index structures.

[0032] This particular combination of index of refraction and layer thicknesses illustratively provides an appropriate approximation of the quintic profile **200**, as shown in the graph of FIG. 2. During an operational embodiments of a design-optimization process, the thickness as well as the porosity of each layer in the multi-layer graded index AR coating is permitted to vary. In an embodiment, the coatings are optimized in the wavelength range of 400 nm to 2500 nm, and the angle of incidence ranges from  $0^\circ$  to  $40^\circ$ . The thickness and refractive index values of each coating can be measured using any conventional technique known to those of ordinary skill, including variable angle spectroscopic ellipsometry and scanning electron microscopy, among others. It should be clear to those skilled in the art that the number of discrete steps and the illustrated refraction index are only shown for illustrative purposes and that the number of discrete steps and various values of refractive index can be varied according to the various embodiments. Furthermore, discrete antireflection coatings can surpass the performance of continuously graded coatings by taking of advantage of interference effects, which continuously graded coatings are expressly designed to avoid, as taught by Martin F. Schubert et al. in Appl. Phys. Express, volume 3, article no. 082502.

[0033] FIG. 3 shows a graph that compares the measured transmittance of an uncoated sapphire (without AR) to sapphire coated on two sides with a two-layered, nanostructured  $\text{SiO}_2$  AR coating. The samples were prepared in an electron-beam evaporator using two different deposition angles ( $\sim 0^\circ$  and  $60^\circ$ ). In order to quantify the thickness and refractive index of each individual layer, a sacrificial silicon substrate was placed alongside the sapphire windows during each deposition step. The thickness and refractive index of the single layer films on silicon were measured with an ellipsometry-based measurement system. The transmittance of the coated and uncoated glass slides was then measured using an angle and wavelength dependent transmittance measurement setup. The measurement setup for characterizing transmittance versus wavelength includes a Xenon lamp light source and an Ando AQ6315A optical spectrum analyzer. The spec-

trum analyzer is calibrated to detect transmitted photons over a broadband spectrum (400 nm-1800 nm).

[0034] The measured peak transmittance of the uncoated glass slide is approximately 88%, in-line with the expected approximate 6-7% reflection loss at each glass/air interface. The peak transmittance increases to over 98% for the double-sided coated samples. As shown in the graph of FIG. 3, the transmittance of the double-sided two-layer antireflection coating is also significantly higher than the sample without antireflection coating across a wide range of incident angles. While the transmittance of the uncoated sapphire falls to below 80% at an incident angle of approximately  $60^\circ$ , the sapphire with the double-sided coating still maintains at a transmittance above 92%. The measured average transmittance of the sample with double-sided 2-layer antireflection coatings is 97% (between  $0^\circ$  and  $75^\circ$  and between 400 nm and 1600 nm), which represents tremendous increase over the 86% average transmittance of the uncoated reference sample.

[0035] The refractive index of a front coating **110** or a back coating **130** on a window **120** is shown in the graph of FIG. 4 according to an illustrative embodiment in which the window material is glass and the coating comprises  $\text{SiO}_2$  of varying porosity. One example of step graded profile **410** is shown, along with a continuously varying quintic profile **400** of the index of refraction approximated as taught in U.S. Pat. No. 4,583,822, which is incorporated by reference as useful background information. In particular, the index of refraction, herein referred to as “n”, is varied from that of the window **120**, which in this case is composed of transparent glass material **420** having a reflection value “n” of approximately 1.5, to that of air **150**, which is shown by way of example to be approximately 1. The Fresnel reflection from one surface of uncoated glass generally varies from approximately 4% at normal incidence to up to approximately 40% at an incident angle of  $75^\circ$ . According to the illustrative embodiment, oblique angle deposition is employed to produce a porous  $\text{SiO}_2$  layer with a lower index of refraction. More particularly, the index of refraction of front coating **110** is varied from 1.5 to 1 over three discrete steps, which can comprise one 192 nm layer optical material **430** having a refractive index of  $n \sim 1.36$ , a second 179 nm layer of optical material **440** having a refractive index of  $n \sim 1.19$ , and a third 260 nm layer of optical material **450** having a refractive index of  $n \sim 1.10$ . This particular combination of index of refraction and layer thicknesses illustratively provides an appropriate approximation of the quintic profile **200**, as shown in the graph of FIG. 2. It should be clear to those skilled in the art that the number of discrete steps and the illustrated refraction index are only shown for illustrative purposes and that the number of discrete steps and various values of refractive index can be varied according to the various embodiments.

[0036] FIG. 5 shows a graph that compares the measured transmittance of an uncoated glass slide to the measured transmittance of glass slides coated on either one side, or two sides, with a three-layered, nanostructured  $\text{SiO}_2$  coating. The samples were prepared in an electron-beam evaporator using three different deposition angles ( $\sim 60^\circ$ ,  $72^\circ$ , and  $80^\circ$  respectively). In order to quantify the thickness and refractive index of each individual layer, a sacrificial silicon substrate was placed alongside the glass slides during each deposition step. The thickness and refractive index of the single layer films on silicon were measured with an ellipsometry-based measurement system, yielding layers with  $n \sim 1.10$ , 1.22, and 1.36 at a wavelength of 460 nm. The transmittance of the coated and



uncoated glass slides was then measured using an angle and wavelength dependent transmittance measurement setup. The measurement setup for characterizing transmittance versus wavelength includes a Xenon lamp light source and an Ando AQ6315A optical spectrum analyzer. The spectrum analyzer is calibrated to detect transmitted photons over a broadband spectrum (400 nm-1800 nm).

[0037] The measured broadband transmittance of the uncoated glass slide is approximately 92% at normal incidence, which is expected given the approximate 4% reflection loss at each glass/air interface. The broadband transmittance at normal incidence increases to over 96% and 98%, respectively, for the single- and double-sided coated samples. These results are dramatically better than previous efforts to improve the transmittance through glass by reducing reflection losses (for example, as shown in U.S. Pat. No. 7,642,199 by Paul Meredith and Michael Harvey). The transmittance of the double-sided three-layer antireflection coating is also significantly higher than the sample without antireflection coating across a wide range of incident angles, as shown in FIG. 5. While the transmittance of the uncoated glass slide falls to below 80% at an incident angle of 65°, the glass slide with the double-sided coating still maintains a transmittance above 95%. The measured average transmittance of the sample with double-sided double-layer antireflection coatings is 97% (between 0° and 75° and between 400 nm and 1600 nm), which represents tremendous increase relative to the 86% average transmittance of the uncoated reference sample.

[0038] In the illustrative embodiments discussed above, SiO<sub>2</sub> materials have been employed for the coating material because of its high transmission and stability. Window material can include quartz, glass, and sapphire. Additional optical material can also be employed in step graded AR coatings on optical windows, including SiO<sub>2</sub>, TiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, BaF<sub>2</sub>, CdTe, and diamond like carbon materials. Conductive, transparent coatings can be formed by using transparent conductive oxide (TCO) materials such as indium tin oxide (ITO). The individual layers in the optical coating can comprise a single material of varying porosity, or of a solid solution of two different, dense materials, or any combination thereof. A variety of different index profiles can be employed, using two, three, four, or more index steps. While in some cases these index steps and individual layer thickness can be adjusted to approximate a continuous graded profile, in further embodiments the index versus thickness profile can deviate from that of a continuously graded profile in order to take advantage of interference phenomena. Moreover, the index step profile can be altered to minimize reflections and maximize transmittance through the optical window over specific spectral regions or incidence angles.

[0039] The refractive index of a front coating 110 or a back coating 130 on a window 120 is shown in the graph of FIG. 6, according to another illustrative embodiment. One example of step graded profile 610 is shown, along with a continuously varying quintic profile 600 of the index of refraction approximated as taught in U.S. Pat. No. 4,583,822, which is incorporated by reference as useful background information. In particular, the index of refraction, herein referred to as “n”, is varied from that of the window 120, which in this case is composed of transparent glass material 220 having a reflection value “n” of approximately 1.5, to that of air 150, which is shown by way of example to be approximately 1. FIG. 6 depicts a profile for a four-layered coating in which Layer 1 630 comprises a 70 nm layer having a refractive index of

n~1.43, Layer 2 640 comprises a 90 nm layer having a refractive index of n~1.37, Layer 3 650 comprises a 150 nm layer having a refractive index of n~1.26, and Layer 4 660 comprises a 350 nm layer having a refractive index of n~1.09. In another embodiment, the index of refraction of front coating 110 is varied from 1.5 to 1 over four discrete steps, which can comprise one 75 nm layer optical material 630 having a refractive index of n~1.35, a second 100 nm layer of optical material 640 having a refractive index of n~1.29, third 160 nm layer of optical material 650 having a refractive index of n~1.20, and a forth 210 nm layer of optical material 660 having a refractive index of n~1.09. It should be clear to those skilled in the art that the number of discrete steps and the illustrated refraction index are only shown for illustrative purposes and that the number of discrete steps and various values of refractive index can be varied according to the various embodiments.

[0040] In yet another embodiment, a pore-closure layer is employed that covers the top surface and does not allow moisture, or particles, to enter the porous film. The pore-closure layer is very thin (much smaller than  $\lambda$ ) so that it does not influence the AR coating in terms of its reflectivity. That is, the pore closure layer does not affect the reflectivity in a negative way. For example, the topmost, low-index layer in the AR coating can be capped with a thin (~10 nm), dense layer of SiO<sub>2</sub>.

[0041] Double coated windows as described hereinabove can be applicable to a variety of different optical systems used for both defense and commercial applications. Optical windows coated on a single side are also of interest for a variety of applications, including photovoltaic solar cells. FIG. 7 details a cross sectional view illustrating a partial photovoltaic structure 700 comprising a semiconductor solar cell device structure 740 with a bottom contact 750. An intermediate layer 730 connects the semiconductor device structure 740 to a glass cover 720. The photovoltaic structure 700 includes an antireflection structure 710 to enhance photon absorption within the active region of the semiconductor structure 740. According to the illustrative embodiment, a front coating 710 is deposited on a device covered by a glass window 720 configured and arranged in a photovoltaic (PV) system arranged to face the sun, which provides a readily available source of photon energies 760 to the PV system. The front coating 710 is comprised of materials possessing optical characteristics having index of refractions between air 770 and the glass window 720. Refer to FIGS. 4 and 6 showing examples of the refractive index. Although photons 760 are illustratively shown as a series of a single direction of photon stream, it should be clear to those skilled in the art that the various, illustrative, and alternate embodiments will function with various varying degrees and/or amount of incident of light or source of photon energies.

[0042] It should now be apparent that a multi-layer, broadband, omnidirectional AR coating made of a single material having tailored-refractive-index layers on a glass substrate reduced reflectance while improving optical transmittance. The availability of the nanostructured low-n material and tunable-n materials deposited by using oblique-angle deposition has allowed the fabrication of highly effective AR coatings for low index substrates such as glass. Antireflection coatings consisting of three layers of nanostructured SiO<sub>2</sub> have been shown to significantly increase the transmittance of optical glass windows. Double-sided coatings have achieved average transmittance values in excess of 98% over a broad



spectrum and range of incident angles, which has benefits for a wide variety of specialized commercial and military optical window applications. In addition, single-sided, step graded-refractive index coatings can benefit from crystalline silicon or thin film photovoltaic systems which employ either a top cover glass or a glass superstrate.

**[0043]** The many features and advantages of the illustrative embodiments described herein are apparent from the above written description and thus it is intended by the appended claims to cover all such features and advantages of the invention. Further, because numerous modifications and changes will readily occur to those skilled in the art, it is not desired to limit the invention to the exact construction and operation as illustrated and described. For example, the illustrative embodiments can include additional layers to perform further functions or enhance existing, described functions. Likewise, while not shown, the electrical connectivity of the cell structure with other cells in an array and/or an external conduit is expressly contemplated and highly variable within ordinary skill. More generally, while some ranges of layer thickness and illustrative materials are described herein. It is expressly contemplated that additional layers, layers having differing thicknesses and/or material choices can be provided to achieve the functional advantages described herein. In addition, directional and locational terms such as “top”, “bottom”, “center”, “front”, “back”, “above”, and “below” should be taken as relative conventions only, and not as absolute. Furthermore, it is expressly contemplated that various semiconductor and thin films fabrication techniques can be employed to form the structures described herein. Accordingly, this description is to be taken only by way of example and not to otherwise limit the scope of the invention.

What is claimed is:

1. A high transmittance optical window comprising:  
a transparent substrate coated on both sides with a multiple layer coating; and  
the multiple layer coating comprising a plurality of optical films, and the multiple layer coating defining a refractive index intermediate between the refractive index of the transparent substrate and air.
2. The high transmittance window of claim 1 wherein the transparent substrate comprises at least one of glass, quartz, and sapphire materials.
3. The high transmittance window of claim 1 wherein the multiple layer coating comprises at least one of  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{BaF}_2$ ,  $\text{CdTe}$ , and diamond like carbon materials.
4. The high transmittance window of claim 1 wherein the multiple layer coating comprises a transparent conductive oxide including at least one of indium tin oxide and zinc oxide.
5. The high transmittance window of claim 1 wherein the multiple layer coating is deposited by oblique-angle deposition.
6. The high transmittance window of claim 1 wherein the multiple layer coating comprises at least two layers having a similar chemical composition but a different porosity and thus a different refractive index.
7. The high transmittance window of claim 6 wherein the transparent substrate comprises sapphire and the index of refraction for each of the plurality of optical films is varied from 1.5 to 1.1 over two steps, with the plurality of deposited

layers defining approximately 230 nm of dense  $\text{SiO}_2$  ( $n \sim 1.46$ ) and approximately 300 nm of porous  $\text{SiO}_2$  ( $n \sim 1.18$ ).

8. The high transmittance window of claim 1 wherein the multiple layer coating contains one of (i) at least one layer of the AR coating comprises a single dense material, (ii) at least one layer of the AR coating comprises a solid solution of two different dense materials, and (iii) at least one layer of the AR coating comprises a porous material.

9. The high transmittance window of claim 6 further comprising a pore closing coating.

10. A photovoltaic device comprising:

a glass window coated on a top, sun-facing surface with a multiple layer coating comprising a plurality of optical films, and the multiple layer coating defining a refractive index intermediate between the refractive index of the glass window ( $n \sim 1.5$ ) and air ( $n \sim 1$ ); and  
an underlying semiconductor solar cell device.

11. The photovoltaic device of claim 10 wherein the glass window forms a cover glass that is attached to the underlying semiconductor device with transparent epoxy.

12. The photovoltaic device of claim 10 wherein the glass window forms a transparent superstrate upon which a semiconductor thin film solar cell structure is deposited.

13. The photovoltaic device of claim 10 wherein the multiple layer coating comprises at least two layers having a similar chemical composition but a different porosity and thus a different refractive index.

14. The photovoltaic device of claim 13 wherein the index of refraction in the topmost coating is varied from 1.5 to 1.1 over three steps, with the plurality of optical films defining approximately 192 nm of porous  $\text{SiO}_2$  ( $n \sim 1.36$ ), approximately 179 nm of porous  $\text{SiO}_2$  ( $n \sim 1.19$ ), and approximately 260 nm of porous  $\text{SiO}_2$  ( $n \sim 1.10$ ).

15. The photovoltaic device of claim 13 further comprising a pore closing coating covering the topmost layer in the antireflection coating.

16. A method of manufacturing a thin film solar cell comprising:

providing a transparent substrate having a front surface and a back surface; and  
coating the transparent substrate on at least one side with a multiple layer optical coating comprising a plurality of optical films, and the multiple layer optical coating defining a refractive index intermediate between the refractive index of the transparent substrate and the refractive index of air.

17. The method of claim 16 wherein the step of coating the transparent substrate comprises the deposition of porous  $\text{SiO}_2$  layers using oblique-angle deposition.

18. The method of claim 16 wherein the step of coating the transparent substrate comprises the deposition of porous  $\text{TiO}_2$  layer using oblique-angle deposition.

19. The method of claim 16 wherein the step of coating the transparent substrate comprises the depositing of a porous layers consisting of  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{BaF}_2$ ,  $\text{CdTe}$ , and diamond like carbon materials using oblique-angle deposition.

20. The method of claim 16 wherein the multiple layer optical coating is applied on the front surface after forming a thin film solar cell device on the back surface of the transparent substrate.

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