Title: MULTIPLE LAYER ANTI-REFLECTIVE COATING

Abstract: A transparent substrate with an antireflection coating is provided that includes: at least six-layers in overlying contact on the surface, the six layers having at least one layer having a refractive index greater than about 2.15 at 632 nm and at least one layer having a lower refractive index of between 1.44 and 1.52 at 632 nm, where at least one of the lower refractive index layers is SiO₂ containing at least 0.25% hydrogen by atomic concentration. In a specific embodiment of the coating at least one layer having a refractive index greater than about 2.15 at 632 nm is TiO₂ containing at least 0.25% chlorine by atomic concentration.

**FIG. 1**
MULTIPLE LAYER ANTI-REFLECTIVE COATING

RELATED APPLICATIONS

[0001] This application claims priority benefit of US Provisional Application Serial Number 61/894,301 filed October 22, 2013; the contents of which are hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates in general to antireflection coatings, and in particular to a multiple layer vacuum deposited coatings that are produced by a highly uniform and stable plasma enhanced chemical vapor deposition (PECVD) process.

BACKGROUND OF THE INVENTION

[0003] Anti-reflective (AR) coatings on optically clear substrates have received both scientific and commercial attention for many years. Such coatings can enhance the performance and efficiency of products such as solar panels and cells, video display screens, automobile windscreens, building windows and touch displays. Unfortunately, AR coatings on such products have met with limited market penetration owing to the technological problems of depositing AR coatings of sufficient quality and performance. Owing to the practical difficulties, even those AR coatings that have been implemented have material attributes that are compromised when the manufacture of large substrates and high quantities is attempted.

[0004] The use of reactive sputtering technology to deposit AR coatings has proven difficult to control in production. Evidence of this is the lack of AR coatings on the aforementioned products. Some of the limitations of sputtering technology include deposition non-uniformity, process drift and instability and poor environmental durability.

[0005] Thus, there exists a need for multiple layer AR coatings with a high degree of spatially controlled optical thickness uniformity. There further exists a need to deposit coatings that are amorphous, dense and environmentally durable.

SUMMARY OF THE INVENTION

[0006] A transparent substrate with an antireflection coating is provided that includes: at least six-layers in overlying contact on the surface, the six layers having at least one layer having a refractive index greater than about 2.15 at 632 nm and at least one layer having a lower
refractive index of between 1.44 and 1.52 at 632 nm, where at least one of the lower refractive index layers is SiO₂ containing at least 0.25% hydrogen by atomic concentration. In a specific embodiment of the coating all of the at least one lower refractive index layer are SiO₂ containing at least 0.25% hydrogen by atomic concentration. In a specific embodiment of the coating at least one of the at least one layer has a refractive index greater than about 2.15 is TiO₂ containing at least 0.25% chlorine by atomic concentration. In a specific embodiment the substrate has at least one dimension larger than 150 mm. In a specific embodiment the substrate has at least one dimension larger than 300 mm. In a specific embodiment the inventive coating has an optical thickness variation of less than ± 1.5% over the substrate. In a specific embodiment the inventive coating has an optical thickness variation of less than ± 3% over the substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] FIG. 1 is a cross-section view schematically illustrating a six layer anti-reflection coating stack in accordance with the present invention with the extent of the individual layers being distorted for visual clarity;

[0008] FIG. 2 shows graphs of reflectance as a percentage vs. visible wavelength (nm) spectrum for 3 different coated samples. Each sample has a 6 layer AR coating of the present invention applied to both sides.

[0009] FIG. 3 compares graphs of reflectance as a percentage vs. the visible wavelength (nm) spectrum for a four layer AR coating and the 6 layer AR coating of the present invention.

DESCRIPTION OF THE INVENTION

[0010] As used herein, "large area" in the context of substrates is defined as having at least one dimension larger than 150 mm. This includes substrates that are individually coated as well as substrates that are combined on a carrier and passed through the coating process as, effectively, one larger substrate. These substrates can be flat like window glass or curved like an automotive windshield. They can be of any shape, square, round, etc. and can have holes or other features. They can also be flexible like a polymer film.

[0011] As used herein, "optical thickness" is defined as the physical thickness of a layer multiplied by the refractive index (RI) of that layer at 632 nm. Visible light is generally accepted, and defined herein, as being light within a wavelength range between about 425 and 675 nm.
[0012] It is to be understood that in instances where a range of values are provided that the range is intended to encompass not only the end point values of the range but also intermediate values of the range as explicitly being included within the range and varying by the last significant figure of the range. By way of example, a recited range of from 1 to 4 is intended to include 1-2, 1-3, 2-4, 3-4, and 1-4.

[0013] The PECVD layers of the present invention are enabled by the AC ion source sold by General Plasma, Inc. in Tucson Arizona and detailed in WO2010077659. This source couples two electrodes across an AC power supply. The electrodes span the width of the substrate (inclusive of carriers holding many small substrates) and the substrate(s) is moved past the electrodes. During a PECVD coating process, a plasma and ion beam deposition zone is formed along the length of the source (the width of the substrate) between the substrate and source. Highly uniform coatings are deposited across the substrate width, to within ±1.5% optical thickness variation, as the substrate passes through this deposition zone. Constant conveyance speed through the deposition zone produces equally uniform coating along the substrate length. Two other aspects of the AC ion source to make the inventive 6 layer AR coating possible: 1) highly stable and repeatable deposition process over days and weeks and 2) The deposited films are dense and amorphous and are environmentally durable.

[0014] A PECVD process with AC ion sources is generally conducted in the sequence and according to the guidelines below. These illustrative steps are for an SiO2 coating process. The process steps for other materials are similar other than precursor and gas changes. While helpful as starting points, the process settings given will vary according to product requirements and substrate materials.

[0015] 1) Place a substrate to be coated into the vacuum coating chamber and evacuate the chamber to base pressure of approximately 0.05Pa or less.

[0016] 2) Flow oxygen gas into the deposition zone to the process flow setting. A common flow requirement is 3000 liter 0.2 per meter of substrate width. The deposition zone process pressure should be in the range of 0.2Pa to 2Pa.

[0017] 3) Turn on the plasma power supply and adjust the output to the process setting

[0018] 4) Flow precursor vapor into the deposition zone. For depositing SiO2 with trimethyldisiloxane (TMDSO), the precursor flow to oxygen flow ratio should be about 1:10.

[0019] 5) Move the substrate through the deposition zone at a constant rate. For one set of process precursor, gas and power supply settings, the substrate travel rate through the deposition zone then determines the coating thickness. Due to the repeatability of the AC ion source
PECVD process, the process settings for one AR layer can be determined by single layer deposition runs. When the multilayer AR stack is deposited, with a series of 6 deposition runs without breaking vacuum, the previously determined settings for each layer are used and the optical thickness of each layer is accurately repeated in the stack.

[0020] Note that PECVD coating chambers can be configured to accommodate different substrate sizes and production quantity requirements. For instance, to coat glass 150mm x 100mm pieces with a six layer AR where the annual production quantity is many millions of pieces, the chamber can be designed with 6 AC ion sources. The glass pieces can be mounted in a carrier so about 150 pieces are on one carrier. In this case, the AC ion source deposition zone spans the width of the carrier such that all the glass pieces are uniformly coated. The carrier is moved past the 6 AC ion sources at a constant speed. The process settings of each AC ion source are adjusted so the layer thickness and film properties are correct for the constant speed shared by all the layers. Many other configurations will be evident to those skilled in the art. These will include roll to roll batch systems, large single sheet glass coating systems and smaller, rotating drum configurations. In all configurations, the substrate is moved past the AC ion source to effect PECVD coating uniformity.

[0001] Turning now to the drawings, FIG. 1 schematically illustrates an anti-reflection coating in accordance with the present invention. Coating 20 is a structure of six layers. A first layer 34, adjacent to the substrate, has an RI greater than 2.15 at a wavelength of about 632 nm. A specific material for layer 34 is titanium oxide (TiO$_2$). The second layer 32 is a layer of a non-absorbing material having a refractive index between about 1.44 and 1.52. A specific material for this layer is silicon dioxide (SiO$_2$). Additional layers 28 and 24 are formed of materials with the same refractive index as layer 34, namely, greater than 2.15 at a wavelength of about 632 nm; or such layers are each independently formed of a material of a different refractive index to achieve a desired reflectivity coating 20. Layers 26 and 22 are formed of materials with the same refractive index as layer 32, namely, between 1.44 and 1.52. Alternatively, such layers are each independently formed of a material of a different refractive index to achieve a desired reflectivity coating 20. In certain inventive embodiments layers 34, 28, and 24 are all TiO$_2$ and layers 32, 26, and 22 are all SiO$_2$.

[0002] The precursor used to make the TiO$_2$ layer is TiCl$_4$. TiCl$_4$ vapor is delivered to the deposition zone with oxygen during the coating process. Using the AC ion source described above, a dense, amorphous TiO$_2$ layer with an RI of greater than 2.36 measured at 632nm with no measureable absorbion is deposited on the substrate. The TiO$_2$ film is highly durable,
passing grid and tape adhesion tests after boiling in water for 10 minutes and after immersion in a heated salt bath for 24 hours. The TiO_2 film is composed of titanium, oxygen and a small amount of chlorine. The function of the chlorine in the deposition process is not known. However, based upon the final film properties, its presence in the plasma process and the in the layer must be considered important.

[0003] The precursor used to make the SiO_2 layer 32 is trimethyldisiloxane (TMDSO). This precursor is vaporized and combined with oxygen in the deposition zone during the coating process and a dense, amorphous SiO_2 film is deposited. The film has an RI of about 1.46 and has no measureable absorption. The SiO_2 film is highly durable, passing grid and tape adhesion tests after boiling in water for 10 minutes and after immersion in a heated salt bath for 24 hours. The SiO2 film is composed of silicon, oxygen and small amounts of hydrogen and carbon.

[0004] Silane (SiH_4) gas has been used in place of TMDSO to make SiO_2 layers of equally good quality and performance. These films have been made using the same AC ion source. Because good PECVD films can be made without the inclusion of carbon, as is the case with silane, only hydrogen is considered mandatory for correct film formation.

[0005] Evidence of the process stability and repeatability of the linear PECVD plasma source can be seen in FIG. 2 and Example 1. To achieve the repeatability shown in the graphs, the optical thickness of each layer must remain constant over time. With reactive sputtering, due to process instability and drift, only 4 layer AR stacks are commercially made.

[0006] A 4 layer AR stack design has a narrower bandwidth than a 6 layer AR stack (reference FIG. 3 and Example 2). With a narrower bandwidth, higher reflectance at the low and high wavelengths are detected by the human eye and the overall perceived reflectance is higher. The advantage of a 4 layer stack over a 6 layer design is variation of the overall perceived reflectance color is reduced for a given layer optical thickness error. If a process is capable of ±3% optical thickness uniformity in production, the color variation from substrate to substrate will be acceptable for a 4 layer AR stack. If a 6 layer design is attempted with the same process, given the overall wider low reflection bandwidth, the reflectance variations at the high and low wavelengths are much more visible and result in unacceptable color variation to the user.

[0007] To make a 6 layer AR stack in production with acceptable color variation, the process optical thickness accuracy and repeatability must be better than ±3%. The PECVD process using AC ion sources is capable of stable, drift free operation over days and weeks with optical thickness variation less than ±1.5%.
EXAMPLES

[0008] The present invention is further detailed with respect to the following examples.

Example 1

[0009] Three (3) pieces of 300 mm x 600 mm glass borosilicate glass substrate having a thickness of 0.6 mm are coated on both sides with a 6 layer AR stack. The pieces are coated sequentially, one at a time. FIG. 3 shows graphs of percent reflectance over the visible light spectrum for each coated piece. The coating process is as follows: One piece is loaded into a single-ended, vertical coater PECVD chamber. It is appreciated that a PECVD apparatus that only has a single AC ion source deposits PECVD layers one at a time. The first TiO\textsubscript{2} layer is deposited (RI 2.366, physical thickness 13.33 nm). The precursor is TiCl\textsubscript{4}. Oxygen gas is delivered with the precursor vapor to the plasma source as the substrate is moved past the source. The ratio between oxygen and precursor vapor is 2:1. After this coating step, the precursor is changed to TMDSO and oxygen flow is changed to effect a ratio of 02:1 02:TMDSO. Once the precursor and gas flows have stabilized and the plasma power and conveyor speed settings are made, the substrate is moved past the AC ion source to make SiO\textsubscript{2} (RI 1.465, physical thickness 37.90 nm). These steps are repeated to make the other alternating layers as follows: TiO\textsubscript{2} (RI 2.366, physical thickness 46.16 nm) then SiO\textsubscript{2} (RI 1.465, physical thickness 17.71 nm) then TiO\textsubscript{2} (RI 2.366, physical thickness 38.71 nm) then SiO\textsubscript{2} (RI 1.465, physical thickness 96.58 nm). No metrology is performed inside the vacuum chamber. Prior to the complete stack deposition, the individual layer thickness and RI are measured using a Filmetric F20 spectrophotometer and a Metricone 2010/M Prism coupler respectively. Once the precursor and oxygen gas flow, AC plasma power and conveyor speed settings are determined for each layer, the complete stack is made by repeating these settings to make each layer. SIMS (Secondary Ion Mass Spectrometry) analysis was done on individual layers to determine the material constituents. For the TiO\textsubscript{2} layer, the atomic concentration of chlorine was 0.478%. For the SiO\textsubscript{2} layer, the atomic concentration of hydrogen was 1.29%. The SIMS analysis was done on a Cameca IMS-4f double focusing, magnetic sector ion micro-analyzer.

[0010] After one side of the glass is coated, the sheet is turned over and the second side is coated with the same 6 layer AR stack, and by the same method as above. As is apparent from the overlaying graphs in FIG. 2, the coating repeatability is excellent.

Example 2

[0011] A 4 layer AR coating is designed using the same materials as Example 1 (two layers of TiO\textsubscript{2} and two of SiO\textsubscript{2}) and a glass sheet is coated on both sides using the same PECVD
coating chamber and the AC ion source. The reflectance curve over the visible spectrum for this four layer AR coating and 6 layer AR coating are shown in FIG. 3. As is apparent, a 6 layer AR coating has significantly lower overall reflection and the AR bandwidth is wider. The increase in bandwidth is especially important as the human eye detects light from 425nm to 675nm. With a 4 layer AR, while the reflectance minimum can be made low, the higher reflectance at the low and high wavelengths, still detectable by the human eye, cause a higher overall perceived reflectance.

The foregoing description is illustrative of particular embodiments of the invention, but is not meant to be a limitation upon the practice thereof. The following claims, including all equivalents thereof, are intended to define the scope of the invention.
CLAIMS

1. A transparent substrate with an antireflection coating comprising:
   at least six-layers in overlying contact on the surface, said six layers having at least one
   layer having a refractive index greater than about 2.15 at 632 nm and at least one layer having a
   lower refractive index of between 1.44 and 1.52 at 632 nm;
   wherein at least one of said lower refractive index layers is SiO₂ containing at least
   0.25% hydrogen by atomic concentration.

2. The coating of claim 1 wherein all of said at least one lower refractive index layer are
   SiO₂ containing at least 0.25% hydrogen by atomic concentration.

3. The coating of claim 1, wherein at least one of said at least one layer having a
   refractive index greater than about 2.15 is TiO₂ containing at least 0.25% chlorine by atomic
   concentration.

4. The coating of claim 1, wherein all of said at least one layer having a refractive index
   greater than about 2.15 are TiO₂ containing at least 0.25% chlorine by atomic concentration.

5. The coating of one of claims 1 to 4, wherein the substrate has at least one dimension
   larger than 150mm.

6. The coating of one of claims 1 to 4, wherein the substrate has at least one dimension
   larger than 300mm.

7. The coating of one of claims 1 to 4, wherein the optical thickness variation is less than
   ± 1.5% over the substrate.

8. The coating of one of claims 1 to 4, wherein the optical thickness variation is less than
   ± 3%, over the substrate.

9. A process of making a coating of any one of claims 1 to 4 comprising:
inserting the substrate into a plasma enhanced chemical vapor deposition (PECVD) apparatus;
energizing an AC ion source in the PECVD apparatus in the presence of a first precursor and oxygen to form a first layer of said coating; and
5 depositing at least five more layers of said coating.
INTERNATIONAL SEARCH REPORT

PCT/US2014/061816

A. CLASSIFICATION OF SUBJECT MATTER

G02B 1/11(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)

G02B 1/11; C23C 14/34; G02B 5/28; H01L 21/4763; G02B 1/10; B32B 17/06; H01L 21/461

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: antireflection, coating, substrate, SiO2, T1O2, refractive index, multiple layer, hydrogen, chlorine, dimension and PECVD

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 5362552 A (AUSTIN, R. RUSSEL) 08 November 1994 See claim 1; column 3, line 49-column 4, line 15; and figure 1.</td>
<td>1-8</td>
</tr>
<tr>
<td>A</td>
<td>US 6368470 B1 (WOODARD, FLOYD E.) 09 April 2002 See abstract and claim 1.</td>
<td>9</td>
</tr>
<tr>
<td>A</td>
<td>US 5147125 A (AUSTIN, R. RUSSEL) 15 September 1992 See column 4, line 49-column 12, line 11 and figures 1-11.</td>
<td>1-9</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier application or patent but published on or after the international filing date
  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed
  "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  "&" document member of the same patent family

Date of the actual completion of the international search
10 February 2015 (10.02.2015)

Date of mailing of the international search report
11 February 2015 (11.02.2015)

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongna-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. +82 42 472 3473

Authorized officer
KIM, Jin Ho
Telephone No. +82-42-481-8699

Form PCT/ISA/210 (second sheet) (January 2015)
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CN 1420943 AO</td>
<td>28/05/2003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 1268871 Al</td>
<td>02/01/2003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HK 1053675 Al</td>
<td>11/11/2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>KR 10-0721731 Bl</td>
<td>28/05/2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 01-48261 Al</td>
<td>05/07/2001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 01-48261 A9</td>
<td>08/11/2001</td>
</tr>
<tr>
<td>US 5147125 A</td>
<td>15/09/1992</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>US 2008-0002260 Al</td>
<td>03/01/2008</td>
<td>AU 2007-264948 Al</td>
<td>03/01/2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 2007-264948 B2</td>
<td>31/01/2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BR PI0714043 A2</td>
<td>18/12/2012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 2655480 Al</td>
<td>03/01/2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 101512389 A</td>
<td>19/08/2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 101512389 B</td>
<td>23/03/2011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 2033019 A2</td>
<td>11/03/2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>KR 10-1410433 Bl</td>
<td>01/07/2014</td>
</tr>
<tr>
<td></td>
<td></td>
<td>KR 10-2009-0021188 A</td>
<td>27/02/2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 7692855 B2</td>
<td>06/04/2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2008-000841 A2</td>
<td>03/01/2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2008-000841 A3</td>
<td>14/02/2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2002-0022359 Al</td>
<td>21/02/2002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 6294459 Bl</td>
<td>25/09/2001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 6541843 B2</td>
<td>01/04/2003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 6673713 B2</td>
<td>06/01/2004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 6784094 B2</td>
<td>31/08/2004</td>
</tr>
</tbody>
</table>