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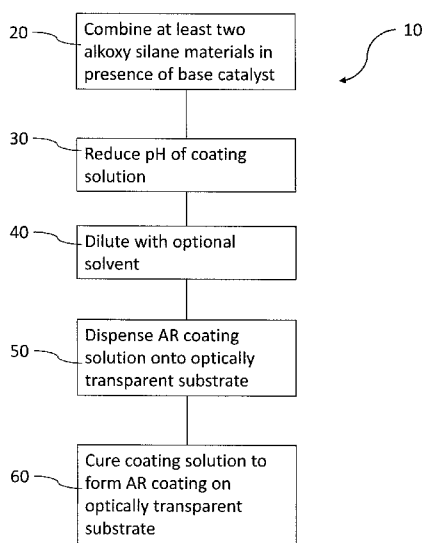


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- (71) **Applicant (for all designated States except US):** HONEYWELL INTERNATIONAL INC. [US/US]; 101 Columbia Road, Morristown, New Jersey 07962 (US).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** MUKHOPADHYAY, Sudip [IN/US]; Honeywell International Inc., Patent Services M/S AB/2B, 101 Columbia Road, P. O. Box 2245, Morristown, New Jersey 07962-2245 (US). PANDEY, Yamini [US/US]; Honeywell International Inc., Patent Services M/S AB/2B, 101 Columbia Road, P. O. Box 2245, Morristown, New Jersey 07962-2245 (US). DANKERS, Lea [US/US]; Honeywell International Inc., Patent Services M/S AB/2B, 101 Columbia Road, P. O. Box 2245, Morristown, New Jersey 07962-2245 (US).
- (74) **Agent:** BEATUS, Carrie; Honeywell International Inc., Law Department AB/2B, 101 Columbia Road, P.O. Box 2245, Morristown, New Jersey 07962-2245 (US).
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(54) **Title:** ANTI-REFLECTIVE COATINGS FOR OPTICALLY TRANSPARENT SUBSTRATES



(57) **Abstract:** Anti-reflective coatings and coating solutions, optically transparent elements and improved processes for preparing AR coatings and coating solutions are described. The anti-reflective coatings are formed from at least two different alkoxy silane materials in a base catalyzed reaction.

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*broadband antireflective coatings,*" Materials Science and Engineering B78 (2000), pp. 135-139. However, AR coatings formed from silicon dioxide coatings would benefit from improved hardness, adhesion, shelf-life and/or processing efficiency.

#### SUMMARY

5 **[0005]** Embodiments disclosed herein pertain to AR coatings and coating solutions, optically sensitive elements such as photovoltaic modules that employ AR coatings, and improved processes for preparing AR coatings and coating solutions.

**[0006]** A first example provides an optically transparent element comprising an optically transparent substrate; and an anti-reflective coating disposed on at least  
10 one surface of the optically transparent substrate, the anti-reflective coating comprising a polymer, the polymer comprising, at least one tetraalkoxy silane residue; and at least a second alkoxy silane residue selected from the group consisting of trialkoxy silanes, dialkoxy silanes, monoalkoxy silanes, and combinations thereof, wherein the polymer comprises at least 50 mole percent of the  
15 at least one tetraalkoxy silane residue based on the total moles of polymer and the coating comprises polymer particles having an average size of no more than 100nm.

**[0007]** A second example provides the optically transparent element of claim 1 wherein the at least one alkoxy silane residue is tetraethoxy silane. A third example provides the optically transparent element of any of examples 1-2, wherein the  
20 second alkoxy silane residue is selected from the group consisting of methyltriethoxy silane and vinyltriethoxy silane. A fourth example provides the optically transparent element of any of examples 1-3, wherein the at least one tetraalkoxy silane residue is tetraethoxy silane and the second alkoxy silane is methyltriethoxy silane.

**[0008]** A fifth example provides the optically transparent element of example 4,  
25 further comprising a vinyltriethoxy silane residue. A sixth example provides the optically transparent element of any of examples 1-5, wherein the polymer consists essentially of tetraethoxy silane residues and methyltriethoxy silane residues and has an average particle size of between 15 and 100 nm. A seventh example provides the optically transparent element of any of examples 1-6, wherein the  
30 polymer further comprises a metal alkoxide residue.

**[0009]** An eighth example provides the optically transparent element of any of examples 1-7, wherein the polymer further comprises a titanium isopropoxide residue. A ninth example provides the optically transparent element of any of examples 1-8, comprising at least about 20 mole percent of the second alkoxy silane residue. A tenth example provides the optically transparent element of any of examples 1-9, comprising between about 20 mole percent and 40 mole percent of the second alkoxy silane residue.

**[0010]** An eleventh example provides a photovoltaic module comprising at least one semiconductor layer; an optically transparent layer disposed over the at least one semiconductor layer; and an anti-reflective coating disposed on at least one surface of the optically transparent substrate, the anti-reflective coating comprising a polymer, the polymer comprising at least one tetraalkoxy silane residue; and at least a second alkoxy silane residue selected from the group consisting of trialkoxy silanes, dialkoxy silanes, monoalkoxy silanes, and combinations thereof, wherein the polymer comprises at least 50 mole percent of the at least one tetraalkoxy silane residue based on the total moles of polymer and the coating comprises polymer particles having an average size of no more than 100nm.

**[0011]** A twelfth example provides the photovoltaic module of example 11, wherein the at least one tetraalkoxy silane is tetraethoxy silane and the second alkoxy silane residue is selected from the group consisting of methyltriethoxy silane, vinyltriethoxy silane and combinations thereof.

**[0012]** A thirteenth example provides a method of producing a coating solution, comprising combining at least a first tetraalkoxy silane material, a second alkoxy silane material, a base catalyst and a solvent to form a coating, wherein the second alkoxy silane material is selected from the group consisting of trialkoxy silanes, dialkoxy silanes, monoalkoxy silanes and combinations thereof; maintaining the pH of the coating solution for a sufficient period of time at a sufficient temperature to form polymer particles having an average particle size between about 15 nm and about 100 nm; and reducing the pH of the coating solution to less than about 5.0.

**[0013]** A fourteenth example provides the method of example thirteen wherein, the base catalyst comprises at least one quaternary ammonium.

**[0014]** A fifteenth example provides the method of any of examples 13-14, wherein the base catalyst comprises tetrabutylammonium hydroxide, tetramethylammonium hydroxide or a combination thereof. A sixteenth example provides the method of any of examples 13-15, wherein the coating solution is  
5 maintained at between about 35° C and about 70° C for between about 1 and about 5 hours prior to reducing the pH.

**[0015]** A seventeenth example provides the method of any of examples 13-16, wherein the solvent comprises water. An eighteenth example provides the method of any of examples 13-17, wherein the pH is reduced to no more than 2.0. A nineteenth  
10 example provides the method of any of examples 13-18, further comprising the step of storing the coating solution for at least about 24 hours. A twentieth example provides the method of any of examples 13-19, further comprising the step of freezing the coating solution.

**[0016]** A twenty-first example provides a method of forming an optically  
15 transparent element comprising dispensing a coating solution onto an optically transparent substrate, the coating solution formed by: combining at least a first tetraalkoxy silane material, a second alkoxy silane material, a base catalyst and a solvent, wherein the second alkoxy silane material is selected from the group consisting of trialkoxy silanes, dialkoxy silanes, monoalkoxy silanes and  
20 combinations thereof; maintaining the pH of the coating solution for a sufficient period of time at a sufficient temperature to form polymer particles having an average particle size between about 15 nm and about 100 nm, and reducing the pH of the coating solution to less than about 5.0; and curing the dispensed coating solution to form an anti-reflective coating on the optically transparent substrate.

**[0017]** A twenty-second example provides the method of example 21, wherein the  
25 coating solution is dispensed by spraying. A twenty-third example provides the method of any of examples 21-22, wherein prior to dispensing, the coating solution is changed from a frozen state to a liquid state. A twenty-fourth example provides an optically transparent element formed by the method of any of examples 21-23.

**[0018]** A twenty-fifth example provides an anti-reflective coating solution  
30 comprising a polymer comprising: at least one tetraalkoxy silane residue; and

at least a second alkoxy silane residue selected from the group consisting of trialkoxy silanes, dialkoxy silanes, monoalkoxy silanes, and combinations thereof, wherein the polymer comprises at least 50 mole percent of the at least one tetraalkoxy silane residue based on the total moles of polymer and the coating comprises polymer particles having an average size of no more than 100nm; a solvent, wherein the coating solution has a polymer particle concentration of up to about 25 wt% and a viscosity of no more than 2.0 cP, and wherein the coating solution has a viscosity of no more than 2.0 cP and a pH of no more than 5.0 for at least 24 hours at 25 ° C.

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10 **[0019]** A twenty-sixth example provides the anti-reflective coating solution of example 25 wherein the polymer consists essentially of tetraethoxy silane residues and methyltriethoxy silane residues.

#### BRIEF DESCRIPTION OF THE FIGURES

**[0020]** Figure 1 is a flow chart of a method of producing an optically transparent element including an AR coating in accordance with an embodiment of the invention.

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**[0021]** Figure 2 provides a schematic illustration of a photovoltaic cell including an AR coating in accordance with an embodiment of the invention.

**[0022]** Figure 3 is a schematic illustration of a portion of a polymer molecule in accordance with one embodiment of the present invention.

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#### DETAILED DESCRIPTION

**[0023]** Figure 1 is a flow chart illustrating a method 10 of forming an AR coating solution and optically transparent element according to one embodiment. According to the method 10, an AR coating solution is formed by combining at least two different alkoxy silane materials in a solvent and in the presence of a base catalyst under suitable reaction conditions to cause polymerization of the alkoxy silane materials (Block 20). The resulting AR coating solution includes a polymer having at least two different alkoxy silane residues.

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**[0024]** After combining the alkoxy silane materials, an acid may be added to the AR coating solution to adjust the solution pH (Block 30) and/or the AR coating

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solution may be further combined with at least one additional solvent (Block 40). In one embodiment, exemplary AR coating solutions are formed without the use of poragens such as polyethylene glycols or polyethylene oxides that evaporate during thermal processing steps to form pores. Additionally, the AR coating solutions are formed without having to filter the resulting polymer from the reaction solution or to remove components in the solution as required by other reaction methods.

**[0025]** The AR coating solution is dispensed onto an optically transparent substrate such as a glass substrate (e.g., sodalime glass, float glass, borosilicate and low iron sodalime glass), plastic cover, acrylic Fresnel lense or other optically transparent substrate (Block 50). The AR coating solution is then cured to form an AR coating on the optically transparent substrate (Block 60).

**[0026]** A variety of commercially available alkoxy silanes may be used to form the AR coating solution. Suitable alkoxy silanes that comprise the first of the at least two alkoxy silane materials include tetraalkoxy silanes, which may include one or more ethoxy, methoxy, and/or propoxy groups as well as hydrogen, methyl, ethyl or propyl groups. In one embodiment, at least one of the alkoxy silane materials is tetraethoxy silane (TEOS).

**[0027]** A second alkoxy silane material may be added to promote improved AR coating adhesion and/or other improved coating properties. Examples of these materials include trialkoxy silanes such as methyltriethoxy silane (MTEOS), aminopropyltriethoxy silane (APTEOS) and APTEOS-triflate, vinyltriethoxy silane (VTEOS), and diethylphosphatoethyltriethoxy silane. Examples also include dialkoxy silanes such as methyldiethoxy silane (MDEOS) dimethyldiethoxy silane (DMDEOS), and phenyldiethoxy silane (PDEOS). Suitable monoalkoxy silanes include trimethoxy silanes such as (3-glycidoxypropyl)-trimethoxy silane. Carbosilanes, mercapto silanes, hydridosilanes and silazanes such as dimethyldisilazane may also be suitable. Combinations of these second alkoxy silane materials may also be used. For example, MTEOS and/or VTEOS may be particularly suitable for improving adhesion and/or hardness. In one embodiment, the second alkoxy silane material or combination of materials may be combined with the first alkoxy silane material in an amount ranging from up to about 50 mol% to 40 mol% to 35 mol% to 25 mol% to 15 mol% based on the total moles of alkoxy silane material. In another

embodiment, the second alkoxy silane material may be added in an amount ranging from at least about 10 mol% to at least about 40 mol% based on the total moles of both alkoxy silane materials. The molar ratio of the first alkoxy silane to the second alkoxy silane material may range from 1:1 to 1000:1, more particularly from 10:1 to 500:1 and even more particularly from 25:1 to 100:1.

**[0028]** In addition to the alkoxy silane materials, at least one metal alkoxide may be included in the AR coating solution. Suitable metal alkoxides include metal isopropoxides and metal butoxides. Examples of metal isopropoxides include zirconium isopropoxide and titanium isopropoxide (TIPO). Examples of suitable metal butoxides include hafnium-n-butoxide and zirconium-n-butoxide. TIPO may be particularly suitable for improving AR coating hardness. In one embodiment, the AR coating solution includes less than 1 mol% metal alkoxide based on the total moles of metal alkoxide and alkoxy silane.

**[0029]** Combinations of the foregoing materials may be utilized to achieve desirable coating properties. In one embodiment, the AR coating solution includes TEOS and MTEOS. In another embodiment, the AR coating solution includes TEOS, MTEOS, VTEOS. In a further embodiment, the AR coating solution includes TEOS, MTEOS, VTEOS and TIPO.

**[0030]** Suitable base catalysts added to the AR coating solution include, for example, quaternary amine compounds of the formula  $R_1R_2R_3R_4N^+OH^-$  in which  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are each independently phenyl, hydrogen or a  $C_{1-16}$  alkyl. In some embodiments, suitable base catalysts include quaternary amine hydroxides such as tetrabutylammonium hydroxide and tetramethylammonium hydroxide. In some embodiments, suitable base catalysts include aqueous solutions of these components, and may optionally include additional distilled water beyond that found in the base catalyst aqueous solutions.

**[0031]** Examples of suitable solvents or diluents that may be used in the AR coating solution include but are not limited to acetone, water, propylene glycol methyl ether acetate (PGMEA), isopropyl alcohol (IPA), tetrahydrofuran (THF), ethanol, dipropylene glycol, tetraethylene glycol, ethyl acetate, PGME and combinations. In some embodiments, the solvent is free of acetone.



**[0032]** These components may be combined and reacted in, for example, a jacketed stirred tank reactor (STR) via a batch or semi-batch mode for a suitable reaction time in the range of about 1 to about 6 hours, more particularly 1 to 3.5 hours and at a suitable temperature in the range of about 35 °C to 70 °C.

5 **[0033]** Under the foregoing conditions, a hydrolysis reaction takes place to form a polymer in solution. Depending on the reaction conditions, the polymer contained in the solution may vary from linear or randomly branched chains, to porous matrices, to dense colloidal particles. In any case, the resulting polymer will include residues of at least two different alkoxy silane materials as described above and/or the  
10 optional metal alkoxide materials. The term "residue" as used herein is intended to refer to a portion of the polymer molecule derived from the alkoxy silane and/or metal alkoxide materials initially added to the AR coating solution. By way of example, it is generally known that tetraethoxy silane reacts under the foregoing conditions to form units of  $\text{SiO}_4$ , which would constitute one example of a tetraethoxy silane residue. It  
15 will also be appreciated that certain by-products may be formed and contained in the AR coating solution either as part of the polymer or as a separate component. For example, the hydrolysis of TEOS may result in the formation of ethanol as a by-product. Fig. 3 illustrates a depiction of an exemplary polymer molecule portion with certain residues circled.

20 **[0034]** In any case, the polymer includes at least two different alkoxy silane residues derived from the alkoxy silane materials discussed above. In one embodiment, the polymer includes at least one TEOS residue, at least one MTEOS residue or both. In another embodiment the polymer additionally includes at least one VTEOS residue. In a further embodiment, the polymer additionally includes at  
25 least one TIPO residue.

**[0035]** To further control the reaction conditions, the pH of the AR coating solution can be adjusted to between about 0 to about 4.0, more particularly, from about 0 to about 2.0 and even more particularly from about 0.5 to about 1.7 using an acid such as nitric acid after a suitable reaction time. This pH reduction may affect the  
30 polymerization condition, which in turn controls the polymer particle size contained in AR coating solution and subsequently cured coating. In one embodiment, the average particle size of the polymer in the AR coating solution may be less than 10

nm, more particularly, less than 1 nm. The average particle size of the AR coating after curing may be between about 15 and about 100 nm, more particularly, between about 25 and about 75 nm, and the polymer may have a molecular weight in the range of about 25,000 to about 150,000 Dalton. The AR coating may also be further  
5 diluted with a solvent that includes one or more of water, IPA, acetone and/or PGMEA. Additional acid may be added during dilution to maintain a desired pH.

**[0036]** The AR coating solution may be dispensed onto a surface of an optically transparent element by a variety of generally known coating methods including spin-  
on, slot die, spray, dip, roller and other coating techniques. The amount of solvent  
10 included in the initial reaction or added to the AR coating solution may be varied such that the solids concentration of the AR coating solution ranges from about 1 to about 25 weight percent depending upon the dispensing method. In some embodiments, there may be manufacturing advantages to forming a more concentrated batch in the STR, followed by diluting to a desired concentration. In  
15 alternate embodiments, dilution could occur prior to or during the initial mixing stage. For dip coating, a solids concentration of about 10 to 20 weight percent is desired. For other coating methods such as spin, slot die and spray, a lower solids concentration of about 1 to 6 weight percent may be desired. Embodiments of the present invention may be particularly suitable for spray application due to the  
20 relatively small polymer particle size achievable by the manufacturing process described above. The viscosity of the resulting coating solution may vary from between about 0.75 cP to about 2.0 cP.

**[0037]** Unlike other methods of forming AR coating materials, the AR coating solution of the present invention is ready for use without removing the particles from  
25 solution. Additionally, the AR coating solutions formed by embodiments of the present invention may remain stable for an extended period of time. As used herein, stability refers to the optical and/or mechanical performance characteristics of the coating solution including, without limitation, light transmittance, viscosity, adhesion and/or pH. At room temperature, coating solutions of the present invention may  
30 remain stable for at least 24 hours, more particularly, about one week, even more particularly, about 4 weeks. Additionally, coating solutions of the present invention may be stored in a -20° C to -40° C freezer for up to at least six months without

materially impacting the optical or mechanical properties desired for glass coatings. The ability to preserve AR coatings for an extended period of time may provide a significant manufacturing advantage, particularly if the coating solution is transported to an off-site location and/or stored for a period of time prior to use.

5 **[0038]** After application, the AR coating solution is cured onto the optically transparent substrate. When applied to glass substrates, the AR coating solution can be subjected to a high temperature heat tempering step, ranging from about 600°C to about 750°C depending on the glass composition, for between about 1 minute and about 1 hour to cure the coatings. It will be appreciated that the various  
10 alkoxysilane and/or metal alkoxide residues described above may be further modified during the curing process. However, these additional derivative residues still constitute alkoxysilane and/or metal alkoxide residues for the purposes of the present application.

**[0039]** AR coated optically transparent elements according to embodiments of the  
15 present invention may possess improved light transmittance characteristics. For example, the AR coating may have a refractive index in the range of about 1.15 to about 1.3, resulting in up to about a 4.26 percent transmission gain in the visible portion (350 to 800 nanometers) of the light spectrum and/or up to about a 3 percent transmission gain in the infrared portion (800 to 2500 nanometers) of the light  
20 spectrum.

**[0040]** If both sides of an optically transparent substrate are coated, up to about an 8-9 percent transmission gain in the visible portion of the light spectrum and up to about a 5-7 percent transmission gain in the infrared portion of the light spectrum may be obtained. Exemplary data relating to these properties are presented in the  
25 Examples section set forth below. In some embodiments, the absolute gain in transmittance is independent of the coating methods used as long as the thickness of the AR film is tuned to the incident light wavelength (the AR film thickness is about 1/4th the wavelength of the incident light).

**[0041]** As further demonstrated in the Examples, AR coatings of the present  
30 invention may also have improved adhesion and/or hardness compared to conventional sol gels. Additionally, AR coatings that include TIPO may have self-cleaning properties due to the generation of hydroxyl radicals in the presence of

water and solar UV light. The hydroxyl radicals may oxidize water insoluble organic dirt on the glass surface to form highly water-soluble compounds that are washed out during rain. The self-cleaning properties could be optimized according to the amount of TIPO added. In some embodiments, a TIPO content of about 0.0005 moles to about 0.003 moles is exemplary.

**[0042]** FIG. 2 is a cross-sectional view of a photovoltaic module (e.g., solar cell) for converting light to electricity, according to an embodiment of this invention. Incoming or incident light from the sun or the like is first incident on AR coating 1, passes therethrough and then through glass substrate 2 and front transparent electrode 3 before reaching the photovoltaic semiconductor (active film) 4 of the module. The module may also include, but does not require, a reflection enhancement oxide and/or EVA film 5, and/or a back metallic contact and/or reflector 6 as shown in FIG. 2. Other types of photovoltaic devices may of course be used, and the FIG. 2 module is merely provided for purposes of example and understanding. It will also be understood that a module may include a single AR coated optically transparent substrate that covers multiple photovoltaic cells connected in series.

**[0043]** As explained above, the AR coating 1 reduces reflections of the incident light and permits more light to reach the thin film semiconductor film 4 of the photovoltaic module thereby permitting the device to act more efficiently. While certain of the AR coatings 1 discussed above are used in the context of the photovoltaic devices/modules, this invention is not so limited. AR coatings according to this invention may be used in other applications. Also, other layer(s) may be provided on the glass substrate under the AR coating so that the AR coating is considered disposed on the glass substrate even if other layers are provided therebetween.

#### EXAMPLES 1-16

**[0044]** In Examples 1-16, 122 grams of isopropanol and 62 grams of acetone were charged into a reactor. In Examples 1-10, 0.09 moles of tetraethoxy silane (TEOS) and 0.01 moles of methyltriethoxy silane (MTEOS) were added to the reactor while stirring with an agitator. In Examples 12-16, the molar ratio of TEOS to

MTEOS was varied. The total moles of all monomers were kept at a constant total of 0.1 moles to simplify kinetics measurements. Table 1 below sets forth the specific component amounts used for each Example.

**[0045]** Tetrabutylammonium hydroxide (TBAH) (0.002 moles of 40% aq. solution) or tetramethylammonium hydroxide (TMAH) (0.002 moles of 25% aq. solution) was added as a base catalyst and the reaction mixture was then heated to 35-70° C for 1-3.5 h. The reaction mixture was then cooled and nitric acid was added to the reaction mixture in a semi-batch fashion to adjust the pH of the reaction mixture to 0.5-1.7. The reaction mixture was then cooled and diluted with IPA, Acetone and/or PGMEA. The molecular weight was measured by Gel permeation chromatography and it ranged from about 25,000-150,000 Dalton depending on reaction conditions. After dilution and pH control the polymer formulation was stored in a -20° C to -40° C freezer.

**[0046]** After storing in a frozen state, these formulations were then deposited on glass or transparent substrates. Dip, slot, die, roller and spin coating techniques were attempted. In almost all cases the desired coating thicknesses of 125nm was obtained by curing at 200-700° C, more favorably at 600-750° C, in air or nitrogen after 3 minutes to 1 hour. A broadband spectroscopy tool available from n&k Technology, Inc. was used for coating thickness measurements. Average polymer particle size in the coating was determined to be between 10 and 100 nm by SEM analysis.

**[0047]** Transmittance data were measured by UV-Visible spectral measurement that measures wavelengths from 300-2500 nm. A broadband spectroscopy tool available from n&k Technology, Inc. was used for refractive index measurements. Tables 1 and 2 provide composition and performance data for Examples 1-16.

**[0048]** A Pencil Hardness test was used as an indicator of scratch resistance/hardness and was performed by attempting to scratch the AR coating with pencils of various hardness (e.g., 3B, 4B, etc.). An Adhesion Tape Test was used as an indicator of coating adhesion and was performed by forming cross-hatches in the coating, pressing an adhesive-backed tape material to the coated substrate, pulling the tape away from the coating and then studying the effect the tape had on the cross-hatched portions of the coating. A Contact Angle Test was used to determine

the contact angle of the AR coated substrate using a VCA 2500 instrument available from AST Products, Inc. The results of these tests are shown in Table 2.

TABLE ONE

Example	Mole TEOS	Mole MTEOS	Mole TBAH	Mole TMAH	Reaction Time (h)
1	0.09	0.01	0.0005	0	3.5
2	0.09	0.01	0.001	0	3.5
3	0.09	0.01	0.002	0	3.5
4	0.09	0.01	0.004	0	2.5
5	0.09	0.01	0.005	0	2
6	0.09	0.01	0.007	0	Gelled
7	0.09	0.01	0	0.0005	3.5
8	0.09	0.01	0	0.001	3.5
9	0.09	0.01	0	0.002	2.5
10	0.09	0.01	0	0.003	Gelled
11	0.09	0.01	0.002	0	3.5
12	0.08	0.02	0.002	0	3.5
13	0.07	0.03	0.002	0	3.5
14	0.06	0.04	0.002	0	3.5
15	0.05	0.05	0.002	0	3.5
16	0.064	0.036	0.002	0	3.5

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TABLE TWO

Example	Thickness (nm)	RI at 550 nm	% T Gain at 550 nm	Pencil Hardness	Adhesion Tape Test	Contact Angle
1	125	1.2	4	3B	Poor	<10
2	125	1.2	4	3B	Poor	<10
3	125	1.19	4	3B	Acceptable	<10
4	125	1.18	4	3B	Acceptable	<10
5	125	1.16	3.8	2B	Acceptable	<10
6	-	-	-	-	-	-
7	125	1.16	4	4B	Excellent	<10
8	125	1.17	4	4B	Excellent	<10
9	125	1.18	3.8	4B	Excellent	<10
10	-	-	-	-	-	-
11	125	1.2	4	3B	Poor	<10
12	125	1.2	4	3B	Poor	<10
13	125	1.2	4	3B	Acceptable	<10
14	125	1.2	4	3B	Acceptable	>10
15	125	1.2	3.8	2B	Acceptable	>10
16	125	1.23	3.2-3.5	1H-3H	Excellent	<10

**[0049]** It was observed that about 0.0005 to about 0.003, or more particularly, about 0.002 mole of TBAH resulted in an optimized rate of reaction. Lower amounts of TBAH slowed the rate of reaction, whereas, higher amounts increased the reaction rate to gel formation level.

5 **[0050]** It was determined that Examples 1-16 all had refractive indices near 1.23 and percent transmission gains (over uncoated substrates) of up to 4%. Pencil hardness results generally indicated an acceptable scratch resistance, with Example 16 having particularly high scratch resistance. Examples 3-5, 7-9 and 16 also exhibited acceptable to excellent coating adhesion using the Adhesion Tape Test.

10 **[0051]** Example 11 was also modified to include 0.00015 mole of diethylphosphatoethyltriethoxy silane (while maintaining 1 mole total monomer), in the reaction solution. This improved hardness and adhesion, however, the refractive index of the coated film increased from 1.2 to 1.3. Certain examples were also treated with a 50-50 mixture of ethanol and water before curing in order to remove  
15 TBAN (tetrabutyl ammonium nitrate) that would otherwise be present on the film as a result of reaction between the TBAH and the nitric acid. It was found that this washing step further improved the hardness of the films. In some cases a hardness of 3H could be achieved by this treatment prior to the curing step.

**[0052]** Example 16 was further subjected to several durability tests as set forth in  
20 Table 3 below to determine whether adhesion or transmittance was lost.

TABLE THREE

Parameter	Test Conditions	Result
<b>Salt spray test(DIN50021)</b>	in salt (5% NaCl) chamber at 35° C for 96 h and then in DI water rinse and air dry	Pass
<b>Climate variable test (IEC1215)</b>	-40 to +85° C, 100 cycle	Pass
<b>Damp test (IEC61250)</b>	130° C, 85% humidity, 96h	Pass
<b>Boiling DI water test</b>	submerge in boiling water for 30 min and then rub coating with a paper soaked in n-propanol	Pass

<b>Abrasion resistance (ISO-9211-3-1-02)</b>	linear abraiser, 500 g weight, 500 rubs	Pass
<b>UV stability</b>	exposed under UV light @ 254 nm at room temperature for 1 h	Pass
<b>Acid test (DIN50018)</b>	0.67% sulfuric/sulfurous acid, 40 °C, 20 cycle of 2.5 min each	Pass
<b>Base test</b>	same as acid test but with 0.67% aq. NaOH	Pass

**[0053]** A “pass” indicated less than 0.02 loss of transmittance and no detectable change in adhesion. As shown above, Example 16 passed all durability tests.

**[0054]** Samples of Example 16 was further tested to confirm stability after approximately ten days at room temperature. As shown in Table Four below, coating solution samples were formed having varying molar concentrations of polymer material.

TABLE FOUR

Item	Samples of Example 16				Comments (condition: RT)
	2%	3%	4%	16%	
Density(g/ml)	0.814	0.814	0.815	0.819	Weight 20ml solution
Solid content(%)	0.81	1.25	1.72	6.68	ASTM D1644, 150C 30min
Viscosity(cP)	0.76	0.80	0.83	1.81	ASTM D446, Cannon-Fenske viscometer tube
PH value	~4	~4	~4	~3	PH test paper

**[0055]** The results shown in Table 4, indicate that the samples maintained a viscosity of less than 2.0 cP and a pH of about 3-4 after storage, which confirmed stability of the coating solution.

#### 15 EXAMPLES 17-42

**[0056]** Tables 5-6 provide composition and performance data for Examples 17-42, in which different types and amounts of one or more adhesion promoting materials were added. In Examples 17-40, 122 grams of isopropanol and 62 grams



of acetone were charged into a reactor. In Examples 41-42, 366 grams of isopropanol and 250 grams of acetone were charged in a reactor.

**[0057]** In each example, tetraethoxy silane (TEOS) and/or methyltriethoxy silane (MTEOS) were added to the reactor while stirring with an agitator. At least one of VTEOS, DMDEOS, MDEOS and/or TIPO was also added.

**[0058]** In Examples 17-40, TBAH (0.002 moles of 40% aq. solution) was used as the base. In Examples 41 and 42, 0.006 moles of TBAH was added as a base catalyst, and additional water was also added.

**[0059]** The reaction mixture was then heated to 35-70° C for 3.5 h. The reaction mixture was then cooled to 45° C and nitric acid was added to the reaction mixture in a semi-batch fashion to adjust the pH of the reaction mixture to 0.5-1.7. The reaction mixture was then cooled and diluted with IPA, Acetone, PGMEA, and/or water. In Examples 41 and 42, the reaction mixture was diluted with a combination of 14 weight percent PGMEA, 46.472 weight percent IPA, 37.38 weight percent acetone and 1.87 weight percent water.

**[0060]** After dilution and pH control the polymer formulation was stored in a -20° C to -40° C freezer. The molecular weight was measured by GPC and it was around 25,000-150,000 Dalton depending on reaction conditions.

**[0061]** These formulations were then deposited on glass substrates by spin coating. In almost all cases the desired coating thicknesses of 125nm was obtained after cure at 200-700° C, more favorably at 600-750° C, in air or nitrogen after 3 minutes to 1 hour.

**[0062]** The same tests performed on Examples 1-16 were performed on Examples 17-40 and are set forth in Table 6. Examples 41 and 42 included slightly different tests, including average light transmission gain from 350 to 1200 nm and a Surface Roughness (RMS) Test, as set forth in Table 7, which was measured by scanning force microscopy. The Scratch Test was measured pursuant to EN-1096-2.

TABLE FIVE

Example	TEOS (moles)	MTEOS (moles)	DMDEOS (moles)	MDEOS (moles)	Water (moles)	VTEOS (moles)	TIPO (moles)
17	0.095	0	0.005	0	0	0	0

Example	TEOS (moles)	MTEOS (moles)	DMDEOS (moles)	MDEOS (moles)	Water (moles)	VTEOS (moles)	TIPO (moles)
18	0.09	0	0.01	0	0	0	0
19	0.085	0	0.015	0	0	0	0
20	0.08	0	0.02	0	0	0	0
21	0.089	0.01	0	0.001	0	0	0
22	0.088	0.01	0	0.002	0	0	0
23	0.087	0.01	0	0.003	0	0	0
24	0.086	0.01	0	0.004	0	0	0
25	0.085	0.01	0	0.005	0	0	0
26	0.087	0.005	0.005	0.003	0	0	0
27	0.0885	0.01	0	0	0	0.0015	0
28	0.087	0.01	0	0	0	0.003	0
29	0.0855	0.01	0	0	0	0.0045	0
30	0.085	0.01	0	0	0	0.005	0
31	0.0891	0.01	0	0	0	0.0009	0
32	0.089	0.01	0	0	0	0.001	0
33	0.0899	0.01	0	0	0	0	0.0001
34	0.0897	0.01	0	0	0	0	0.0003
35	0.0895	0.01	0	0	0	0	0.0005
36	0.088	0.01	0	0	0	0	0.0002
37	0.087	0.01	0	0	0	0	0.0003
38	0.087	0.01	0	0.0015	0	0.0015	0
39	0.084	0.01	0	0.003	0	0.0003	0
40	0.0865	0.005	0.005	0.0015	0	0.0015	0.0005
41	0.37	0.21	0	0	0.712	0.006	0
42	0.37	0.21	0	0	0.712	0.006	0.001

TABLE SIX

Example	Thickness (nm)	RI at 550 nm	% T Gain at 550 nm	Pencil Hardness	Adhesion Tape Test	Contact Angle
17	125	1.18	4	6B	Acceptable	<10
18	125	1.18	4	6B	Acceptable	<10
19	125	1.18	4	6B	Acceptable	<10
20	125	1.18	4	6B	Acceptable	>10
21	125	1.19	4	HB	Excellent	<10
22	125	1.19	4	HB	Excellent	<10
23	125	1.19	4	HB	Excellent	<10
24	125	1.19	3.8	HB	Excellent	<10
25	125	1.19	3.6	HB	Excellent	<10
26	125	1.18	4	HB	Excellent	<10
27	125	1.21	4	H	Excellent	<10
28	125	1.21	4	H	Excellent	>10

29	125	1.21	3.8	H	Excellent	<10
30	125	1.22	3.6	H	Excellent	<10
31	125	1.23	3.5	2H	Excellent	>10
32	125	1.24	2.9	2H	Excellent	>10
33	125	1.25	4	H	Excellent	<10
34	125	1.2	4	H	Excellent	<10
35	125	1.2	3.8	H	Excellent	>10
36	125	1.2	2.9	H	Poor	>10
37	125	1.2	3.5	H	Poor	>10
38	125	1.21	4	2H	Excellent	>10
39	125	1.24	3.6	3H	Excellent	>10
40	125	1.25	3.5	3H	Excellent	>10

TABLE SEVEN

Example	Thickness (nm)	Average % T Gain (350-1200 nm)	Scratch Test	Adhesion Tape Test	Surface Roughness (RMS)
41	125	3.1	pass	pass	<1 Å
42	125	3.0	pass	pass	<1 Å

5 **[0063]** Examples 17-42 indicate that the addition of VTEOS, DMDEOS, MDEOS and TIPO improved certain physical characteristics of the AR coatings, including scratch resistance/hardness and/or adhesion. VTEOS, in particular, appeared to improve film hardness and uniformity.

10 **[0064]** It was also determined that the reactions described herein can be scaled up to 100 to 1000 liter batch sizes without difficulty or losses in the resulting optical and mechanical properties of the resulting film.

15 **[0065]** Various modifications and additions can be made to the exemplary embodiments discussed without departing from the scope of the present invention. For example, while the embodiments described above refer to particular features, the scope of this invention also includes embodiments having different combinations of features and embodiments that do not include all of the described features. Accordingly, the scope of the present invention is intended to embrace all such alternatives, modifications, and variations as fall within the scope of the claims, together with all equivalents thereof.

## CLAIMS

1. An optically transparent element comprising:  
an optically transparent substrate; and  
an anti-reflective coating disposed on at least one surface of the optically  
5 transparent substrate, the anti-reflective coating comprising a polymer, the polymer  
comprising:  
at least one tetraalkoxy silane residue; and  
at least a second alkoxy silane residue selected from the group consisting of  
trialkoxo silanes, dialkoxo silanes, monoalkoxo silanes, and combinations thereof,  
10 wherein the polymer comprises at least 50 mole percent of the at least one  
tetraalkoxy silane residue based on the total moles of polymer and the coating  
comprises polymer particles having an average size of no more than 100nm.
2. The optically transparent element of claim 1 wherein the at least one  
15 alkoxy silane residue is tetraethoxy silane.
3. The optically transparent element of any of claims 1-2 wherein the  
second alkoxy silane residue is selected from the group consisting of methyltriethoxy  
silane and vinyltriethoxy silane.  
20
4. The optically transparent element of any of claims 1-3 wherein the at  
least one tetraalkoxy silane residue is tetraethoxy silane and the second alkoxy  
silane is methyltriethoxy silane.
- 25 5. The optically transparent element of claim 4 further comprising a  
vinyltriethoxy silane residue.
6. The optically transparent element of any of claims 1-5 wherein the  
polymer further comprises a metal alkoxide residue.  
30
7. The optically transparent element of any of claims 1-6 comprising at  
least about 20 mole percent of the second alkoxy silane residue.

8. The optically transparent element of any of claims 1-7 further comprising at least one semiconductor layer disposed adjacent to the optically transparent element.

5 9. A method of forming an optically transparent element comprising:  
dispensing a coating solution onto an optically transparent substrate,  
the coating solution formed by:

combining at least a first tetraalkoxy silane material, a second alkoxy  
silane material, a base catalyst and a solvent, wherein the second  
10 alkoxy silane material is selected from the group consisting of trialkoxy  
silanes, dialkoxy silanes, monoalkoxy silanes and combinations  
thereof;

maintaining the pH of the coating solution for a sufficient period of time  
at a sufficient temperature to form polymer particles having an average  
15 particle size between about 15 nm and about 100 nm, and  
reducing the pH of the coating solution to less than about 5.0; and  
curing the dispensed coating solution to form an anti-reflective coating  
on the optically transparent substrate.

20 10. The method of claim 9, wherein the base catalyst comprises at least  
one quaternary ammonium.

11. The method of any of claims 9-10, wherein the base catalyst comprises  
tetrabutylammonium hydroxide, tetramethylammonium hydroxide or a combination  
25 thereof.

12. The method of any of claims 9-11 wherein the coating solution is  
maintained at between about 35° C and about 70° C for between about 1 and about  
5 hours prior to reducing the pH.

30 13. The method of any of claims 9-12 wherein the pH is reduced to no  
more than 2.0.

14. The method of any of claims 9-13 further comprising the step of storing the coating solution in a liquid or frozen state for at least about 24 hours prior to dispensing.

5 15. The method of any of claims 9-14 wherein the coating solution is dispensed by spraying.

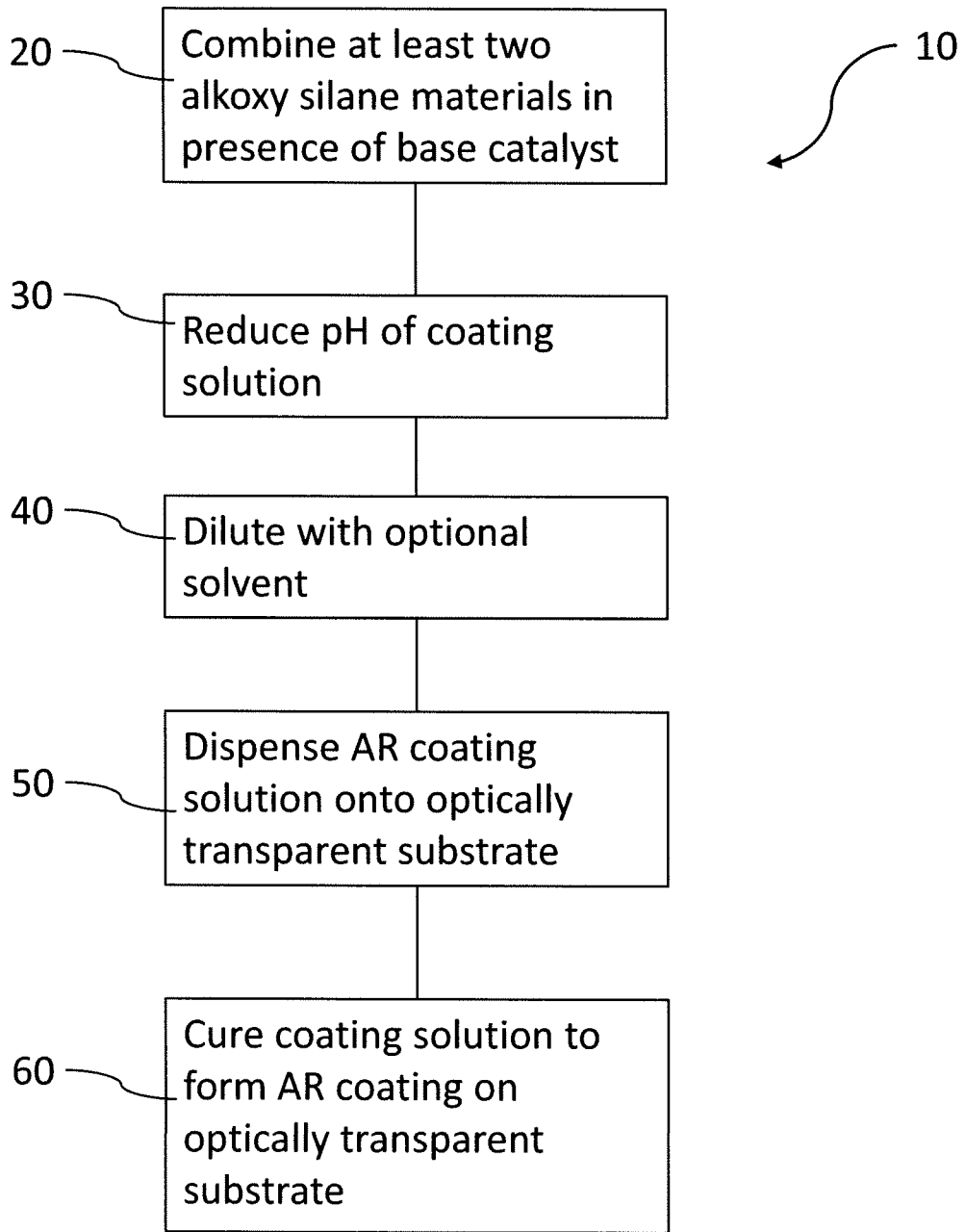


FIGURE 1

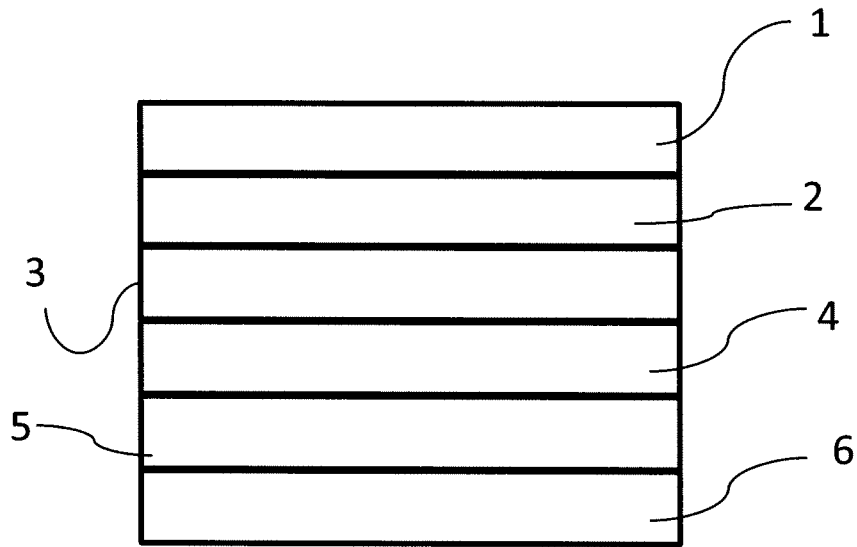


FIGURE 2



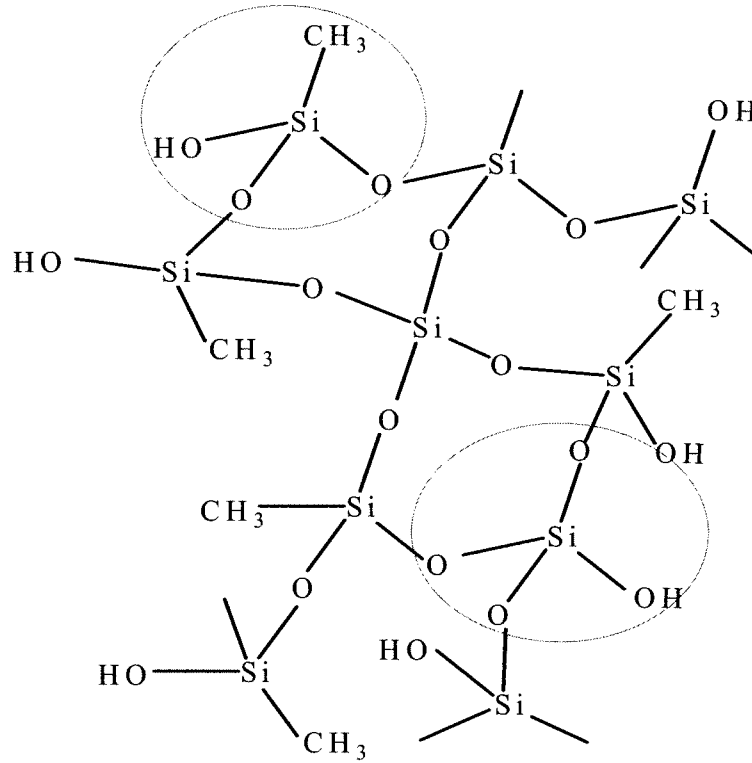


FIGURE 3