the coated article, heating the entire coated article by placing it into a furnace, flash annealing only a surface of the transparent conductive oxide layer or passing an Eddy current through the transparent conductive oxide layer.

[0016] A coated article is a substrate having a coating stack. At least a portion of the substrate is coated with a functional coating. A protective layer is applied over at least a portion of the functional coating. The protective layer has a first protective film over at least a portion of the functional coating, and a second protective film over at least a portion of the functional coating. The second protective film is the last film within the coating stack, and includes titania and alumina. Optionally, a third protective film can be positioned between the first protective film and the second protective film, or between the first protective film and the functional coating.

[0017] A method of making a coated article including providing a substrate. A functional coating is applied over at least a portion of the substrate. A first protective film is applied over at least a portion of the functional coating. A second protective film that includes titania and alumina is applied over at least a portion of the first protective film. Optionally, a third protective film is applied between the first protective film and the second protective film, or between the first protective film and the functional coating.

[0018] A method of reducing the absorption, resistance or emissivity of a transparent conductive oxide layer. A substrate is provided. A transparent conductive oxide layer is applied over at least a portion of the substrate in an atmosphere that comprises between 0 % and 2.0 % oxygen.

[0018a] In one aspect, the present disclosure relates to a method of reducing a sheet resistance of a coated article comprising applying a coating to a substrate wherein the coating comprises a transparent conductive oxide layer at room temperature; and processing the transparent conductive oxide layer by flash annealing the transparent conductive oxide layer so that the transparent conductive oxide layer reaches a temperature of above 193°C (380°F) and no more than 470°C (878°F).

[0018b] In another aspect, the present disclosure relates to a method of making a coated article comprising the steps of applying a transparent conductive oxide layer over a substrate, raising a top surface of the transparent conductive oxide to above 193°C (380 °F) and not raising the top surface of the transparent conductive oxide above 470°C (878°F).

[0019] A coated article having reduced absorption, resistance or emissivity comprising a transparent conductive oxide layer made by the following steps. A substrate is provided. A transparent conductive oxide layer is applied over at least a portion of the substrate in an atmosphere that comprises between 0 % and 2.0 % oxygen.

BRIEF DESCRIPTION OF THE DRAWING(S)

[0020] The patent or application file contains at least one drawing executed in color. Copies of this patent or patent application publication with color drawing(s) will be provided by the Office upon request and payment of the necessary fee.

[0021] Figs. 1a, 1b, 1c and 1d are side views (not to scale) of coatings incorporating a feature of the invention;

60, and the second protective film 62 can be applied over the third protective film 64.

[00124] In a method for making a coated article, a functional coating 112 is applied over a substrate 10. A functional coating 112 can be applied over the substrate 10, or a substrate having a functional coating 112 can be provided. A protective layer 16 is applied over the functional coating 112. The protective layer 16 is applied by first applying a first protective film 60 over the transparent conductive oxide, and then applying a second protective film 62 over the first protective film 60. Optionally, a third protective film 64 can be applied over the first protective film 60, and the second protective film 62 can be applied over the third protective film 64.

[00125] Another exemplary method of the invention is a method of increasing the sheet resistance of a coated article. A coated article is provided. The coated article has a substrate and transparent conductive oxide layer over at least part of the substrate. The coated article is processed with a post-deposition process.

[00126] The post-deposition process can be tempering the coated article, flash annealing only a surface of the transparent conductive oxide layer, or passing an Eddy current through the transparent conductive oxide layer.

[00127] Tempering the coated article is done by heating the entire article so that the surface of the transparent conductive oxide layer reaches above 193ºC (380 ºF), at least 224ºC (435ºF), or at least 335ºC (635ºF) for at least 5, 10, 15, 20, 25 or 30 seconds, and at most 120, 90, 60, 55, 50, 45, 40, 35 or 30 seconds. The transparent conductive oxide layer should not be heated to more than 335ºC (635ºF) or 430ºC (806ºF). After the coated articled is heated, it is cooled rapidly to a normal temperature at a particular rate.

[00128] The coated article can be flash annealed to increase the sheet resistance. This is done by using a flash lamp to heat a surface of the coated article. The surface that is heated is the surface on which the transparent conductive oxide layer resides. The surface is heated to a temperature of above 193ºC (380 ºF), at least 224ºC (435ºF) or at least 335ºC (635ºF) for at least 5, 10, 15, 20, 25 or 30 seconds, and at most 120, 90, 60, 50, 55, 45, 40, 35 or 30 seconds. The surface should be heated to no more than 520ºC (968ºF), no more than 470ºC (878ºF), no more than 430ºC (806ºF) or no more than 335ºC (635ºF). After the surface is heated, it is cooled to a normal temperature.

[00129] Passing an Eddy current through the transparent conductive oxide ("TCO") can be done by exposing the transparent conductive oxide layer to a

[00140] The following samples were tested to establish the improved conductivity for each thickness of ITO.

Sample	ITO Thickness (nm)	ITO Surface Temp. (ºC(ºF))	Sheet Resistance (Ω/□)
1	96.8	Not flash annealed	68.4
2	96.8	224 (435)	23.6
3	96.8	335 (635)	24.8
4	96.8	430 (806)	21.8
5	96.8	470 (878)	21.2
6	96.8	520 (968)	20.2
8	105.2	Not flash annealed	67.2
8	105.2	224 (435)	23.0
9	105.2	335 (635)	23.6
10	105.2	430 (806)	21.2
11	105.2	470 (878)	20.6
12	105.2	520 (968)	19.6
13	111.6	Not flash annealed	67.2
14	111.6	224 (435)	21.8
15	111.6	335 (635)	23.6
16	111.6	430 (806)	20.6
17	111.6	470 (878)	20.0
18	111.6	520 (968)	19.0
19	114.9	Not flash annealed	67.2
20	114.9	224 (435)	21.2
21	114.9	335 (635)	22.4
22	114.9	430 (806)	18.9
23	114.9	470 (878)	18.9
24	114.9	520 (968)	17.9
25	127.9	Not flash annealed	61.3
26	127.9	224 (435)	18.9
27	127.9	335 (635)	20.0
28	127.9	430 (806)	17.7

29	127.9	470 (878)	17.1
30	127.9	520 (968)	14.9
31	133.1	Not flash annealed	60.2
32	133.1	224 (435)	17.7
33	133.1	335 (635)	19.5
34	133.1	430 (806)	17.1
35	133.1	470 (878)	15.9
36	133.1	520 (968)	14.3
37	147.9	Not flash annealed	58.4
38	147.9	224 (435)	17.7
39	147.9	335 (635)	18.9
40	147.9	430 (806)	16.5
41	147.9	470 (878)	15.3
42	147.9	520 (968)	13.1
43	160.3	Not flash annealed	56.6
44	160.3	224 (435)	16.5
45	160.3	335 (635)	18.3
46	160.3	430 (806)	15.3
47	160.3	470 (878)	14.1
48	160.3	520 (968)	13.1
49	170.8	Not flash annealed	54.3
50	170.8	224 (435)	15.3
51	170.8	335 (635)	16.5
52	170.8	430 (806)	14.1
53	170.8	470 (878)	14.1
54	170.8	520 (968)	12.0

[00141] As can be seen in Fig. 7, post-depositing heating of the ITO, regardless of the thickness, decreased the sheet resistance from about 55-70 Ω/□ to about 10-25 Ω/□. When the ITO thickness was at least than 96.8 nm thick, the sheet resistance was less than 25 Ω/□ regardless of the heating temperature. When the ITO thickness was at least 109.2, the sheet resistance was less than 20 Ω/□ if the ITO surface reached 520ºC (968ºF). At approximately 127.9 nm, the ITO had a sheet

resistance of less than 20 Ω/□ when heated to any temperature. The improvements in sheet resistance was unexpected. Similar results were obtained with other transparent conductive oxides, suggesting that the temperature, regardless of transparent conductive oxide, should be above 193°C (380°F), at least 224°C (435°F), or not above 430°C (806°F).

[00142] As shown in Fig. 8a-c, post deposition heating increased the crystallinity of the ITO layer. The samples that were tested are listed in Table 2, below.

Table 2: Samples for Example 1

Sample	Sample ID	Description
A	Uncoated Clear	Uncoated clear glass
B	PC-4042	Clear glass coated with ITO at 168.7 nm
C	PC-4042-40 AH	PC-4042 after heating
D	PC-4045	Clear glass coated with ITO at 141.7 nm
E	PC-4045-30 AH	PC-4045 after heating
F	PC-4046	Clear glass coated with ITO at 129.4 nm
G	PC-4046-30 AH	PC-4046 after heating

[00143] By focusing on the minimal surface temperature needed to increase the crystal formation of the ITO, a tremendous benefit by conserving energy is obtained.

[00144] Example 2

[00145] A glass substrate was coated with a transparent conductive oxide layer. The transparent conductive oxide was gallium-doped zinc oxide ("GZO"). Several samples with different GZO thicknesses were prepared and the sheet resistance measured for samples to compare the effects of post-deposition processing to the sheet resistance of GZO as deposited. The post-deposition process was placing the coated article in a furnace. The sheet resistance of each sample was tested before and after flash annealing, and the results are shown in Fig. 9. The thickness and sheet resistance for the samples test are listed in Table 3, below.

Table 3: Samples from Example 2

Sample	**GZO Thickness (nm)**	**Sheet Resistance (as deposited)**	**Sheet Resistance (flash annealed)**
1	160	84.4	36.6
2	320	35.6	12.7

a thickness of 300 nm to 350 nm of AZO applied onto the substrate. The samples were tested to determine their emissivity, absorbance and/or sheet resistance. (Emissivity is a measure of conductivity.) These samples were heat treated by placing the coated article into a furnace for a period of time so that the transparent conductive oxide surface of the sample to reached at least 224°C (435°F) for about 30 seconds.

[00185] When coating a transparent article with a transparent conductive oxide, one wants a low absorbance and low sheet resistance (which corresponds to emissivity) article. Fig. 16 shows that as oxygen is added to the atmosphere, the absorption decreases. However, as shown by Fig. 17, the emissivity/sheet resistance of the article is highest when there is 0% oxygen in the atmosphere. Using Figs. 16 and 17, the ideal balance between absorption and emissivity is obtained when the sputtering atmosphere has between 0.75% and 1.25% oxygen in the atmosphere. As Fig. 17 shows, the sheet resistance of a heat-treated article coated with ITO is lower than non-heated articles coated with an ITO if the atmosphere has less than 2.0% oxygen. There is a significant increase in the sheet resistance when the atmosphere is 1.5% oxygen. Extrapolating from this data, it was concluded that the atmosphere in the coating chamber should be no more than 1.5% oxygen, preferably no more than 1.25%. In order to obtain some decrease absorption for ITO coated article, the atmosphere should contain at least 0.5% oxygen, preferably at least 0.75% oxygen.

[00186] **Example 9**

[00187] A glass substrate was coated with an aluminum-doped zinc oxide layer by a magnetron sputter vacuum deposition (“MSVD”) process. The target was a ceramic aluminum-doped zinc oxide, which contains a certain amount of oxygen in it. When using a MSVD process to deposit a material such as a transparent conductive oxide, the process causes the ceramic raw materials to disassociate, possibly causing some of the oxygen to escape. In order to ensure that the material deposited is oxidized, often oxygen is supplied to the coating chamber together with an inert gas. In this example, the AZO was deposited by MSVD in a coating chamber that had the oxygen content supplied to the chamber that was either 0%, 1%, 2%, 3%, 4%, 5% or 6%. The remainder of the atmosphere supplied to the coating chamber was argon, however, any inert gas could be used. The normalized absorption of the coating was determined. As shown in Fig. 18, the

normalized absorption at 550 nm was best when 0% oxygen was supplied to the coating chamber. It was acceptable when 1% oxygen was supplied to the coating chamber. Based on the data shown in Fig. 18, one would extrapolate that less than 0.5% oxygen in the coating chamber provides significantly better absorption than when 1% oxygen is used.

[00188] As shown in Fig. 19, the normalized absorption has a steep decline from 0% oxygen to 1% oxygen, and a minimal decline from 1% oxygen to 2% oxygen. This data further supports the conclusion that, by extrapolation, one would conclude that less than 1% oxygen, less than 0.5% oxygen, or less than 0.25% oxygen, or less than 0.1% oxygen, or 0% oxygen supplied to the coating chamber provides the best absorption.

[00189] **Example 10**

[00190] One problem with post-deposition heating of a coated article is the amount of energy wasted. As discussed above, post deposition heating of a transparent conductive oxide ("TCO") layer provides improved performance at smaller thicknesses. Placing a coated article into a furnace that heats the entire article wastes energy beyond the temperature necessary to crystalize the TCO layer. In order to determine the surface temperature needed to improve the performance of a transparent conductive oxide layer, a glass substrate was coated with indium-doped tin oxide at 115 nm or 171 nm thick. The samples had the surface of the ITO layer heated to temperatures listed in Tables 11 and 12. For the purpose of this experiment, the surfaces were heated by placing the entire coated article into a furnace, however, a flash lamp could be used as an alternative.

[00191] After the post-deposition heating of the surface, the sheet resistance of each sample was measured (see Fig. 21, and Tables 11 and 12). The results show that at approximately 224°C (435°F), the layer reaches its lowest sheet resistance. Additionally heating the surface does not provide any additional reduction in sheet resistance. Therefore, in order to reduce the sheet resistance of a transparent conductive oxide layer, the post deposition heating should heat the surface of the transparent conductive oxide layer to above 193°C (380 °F), at least 224°C (435°F), between 224°C (435°F) and 430°C (806 °F), between 224°C (435 °F) and 335°C (635°F), or to 224°C (435°F).

Table 11: 115 nm Thick ITO Samples of Example 10

Max. Surface Temperature (°C (°F))	Sheet Resistance (Ω/□)
22 (72)	
93 (200)	69.7
149 (300)	67
158 (317)	68.9
177 (350)	65.3
193 (380)	62.6
224 (435)	21.2
335 (635)	22.4
430 (806)	18.9
470 (878)	18.9
520 (968)	17.9

Table 12: 171 nm Thick ITO Samples of Example 10

Max. Surface Temperature (°C (°F))	Sheet Resistance (Ω/□)
Room Temperature	
93 (200)	52.3
149 (300)	52.3
158 (317)	43.9
177 (350)	49
193 (380)	43.5
224 (435)	15.3
335 (635)	16.5
430 (806)	14.1
470 (878)	14.1
520 (968)	12

[00192] The invention is further described in the following numbered clauses.

[00193] Clause 1: A coated article comprising a substrate, an underlayer over said substrate, the underlayer comprising a first underlayer film wherein the first underlayer film comprises a high refractive index material, and a second underlayer film over the first layer wherein the second layer comprises a low

[00297] Clause 105: The method according to clauses 103 or 104 wherein the transparent conductive oxide layer has a thickness of at least 125 nm, particularly at least 150 nm, more particularly at least 175 nm, and at most 450 nm, at most 400 nm, at most 350 nm, at most 300 nm, at most 250 nm or at most 250 nm.

[00298] Clause 106: The method according to any of the clauses of 103 to 105 wherein the transparent conductive oxide layer comprises indium-doped tin oxide ("ITO"), and wherein the atmosphere comprises between 0.75% and 1.25% oxygen.

[00299] Clause 107: The method according to any of the clauses 103 to 106 wherein the transparent conductive oxide layer comprises a thickness of at least 95 nm and at most 225 nm.

[00300] Clause 108: The method according to any of the clauses 103 to 107 wherein the transparent conductive oxide layer comprises aluminum-doped zinc oxide ("AZO") and wherein the atmosphere comprises between 0% and 0.5% oxygen, particularly between 0% and 0.25% oxygen, more particularly between 0% volume and 0.1% volume oxygen, or more particularly 0% volume oxygen.

[00301] Clause 109: The method according to clause 108 wherein the transparent conductive oxide layer comprises a thickness of at least 225 nm and at most 440 nm.

[00302] Clause 110: The method according to any of the clauses 103 to 109 further comprising applying a functional coating over at least a portion of the substrate wherein the function coating is positioned between the substrate and the transparent conductive oxide layer.

[00303] Clause 111: The method according to any of the clauses 103 to 110 further comprising applying a first protective film over at least a portion of the transparent conductive oxide layer, wherein the first protective film comprises titania, alumina, zinc oxide, tin oxide, zirconia, silica or mixtures thereof, and a second protective film over at least a portion of the first protective film wherein the second protective film comprises titania and alumina, wherein the second protective film is an outermost film.

[00304] Clause 112: A method of reducing a sheet resistance of a coated article comprising applying a coating to a substrate wherein the coating comprises a transparent conductive oxide layer at room temperature; and heating a top surface of the transparent conductive oxide layer to above 193°C (380°F) or at least 224°C (435°F) for at

[00313] Clause 121: The method according to any of the clauses 112 to 120, wherein the heating step does not raise the top surface of the transparent conductive oxide above 335°C (635°F).

[00314] Clause 122: The method according to any of the clauses 112 to 121, wherein the substrate is glass and the transparent conductive oxide has an absorption not greater than 0.3.

[00315] Clause 123: The method according to any of the clauses 112 to 122, wherein the substrate is glass and the transparent conductive oxide has an absorption at least as high as 0.05.

[00316] Clause 124: The method according to any of the clauses 112 to 123, wherein the coated article is a refrigerator door.

[00317] Clause 125: The method according to any of the clauses 112 to 124, wherein the applying step is done in an atmosphere that has an oxygen content supplied to the atmosphere of between 0% and 1.5%.

[00318] Clause 126: The method according to any of the clauses 112 to 125, wherein the substrate is glass and the transparent conductive oxide has an absorption not greater than 0.2 and at least as high as 0.05.

[00319] Clause 127: A method of making a coated article comprising applying a transparent conductive oxide layer over a substrate, raising a top surface of the transparent conductive oxide to above 193°C (380°F), or at least 224°C (435°F) and not raising the top surface of the transparent conductive oxide above 430°C (806 °F) (or particularly 335°C (635°F)) for at least 5 second, at least 10 second, at least 15 seconds, at least 20 seconds, at least 25 seconds, at least 30 seconds, and no more than 120 second, 90 second, 60 second, 55 second, 50 seconds, 45 seconds, 40 second or 35 seconds.

[00320] Clause 128: The method according to clause 127 further comprising not heating the coated article above 335°C (635°F).

[00321] Clause 129: The method according to any of the clauses 127 to 128, wherein the transparent conductive oxide layer comprises tin-doped indium oxide having a thickness of at least 96 nm and at most 171 nm and a sheet resistance of less than 25 Ω/□.

[00322] Clause 130: The method according to any of the clauses 1127to 129 further comprising applying a protective layer over the transparent conductive oxide wherein the protective layer comprises titania and alumina.

THE INVENTION CLAIMED IS

1. A method of reducing a sheet resistance of a coated article comprising applying a coating to a substrate wherein the coating comprises a transparent conductive oxide layer at room temperature; and processing the transparent conductive oxide layer by flash annealing the transparent conductive oxide layer so that the transparent conductive oxide layer reaches a temperature of above 193ºC (380ºF) and no more than 470ºC (878ºF).

2. The method according to claim 1 wherein the transparent conductive oxide layer is at least 125 nm and at most nm to 950 nm.

3. The method according to claim 1 wherein the transparent conductive oxide layer comprises tin-doped indium oxide and is at least 105 nm and at most 171 nm, and wherein the sheet resistance of the coated article after the processing step is less than 20 Ω/□.

4. The method according to claim 1, wherein the transparent conductive oxide layer comprises gallium-doped zinc oxide having a thickness of at least 320 nm and at most 480 nm and wherein the sheet resistance of the coated article after the processing step is less than 20 Ω/□.

5. The method according to claim 1, wherein the transparent conductive oxide layer comprises alumina-doped oxide having a thickness of at least 344 nm and at most 880 nm, and wherein the sheet resistance of the coated article after the processing step is less than 20 Ω/□.

6. The method according to claim 1, wherein the applying the coating step comprises a magnetron sputtered vacuum deposition process.

7. The method according to claim 1 wherein the transparent conductive oxide is heat at least to 224ºC (435ºF).

8. The method according to claim 1 further comprising applying a first protective film over at least a portion transparent conductive oxide layer, wherein the first protective film comprise titania, alumina, zinc oxide, tin oxide, zirconia, silica or mixtures thereof, and applying a second protective film over at least a portion of the transparent conductive oxide layer wherein the second protective film comprises titania and alumina,

and wherein the applying the first protective film and applying the second protective film occurs before or after the processing step.

9. The method according to claim 1 wherein the heating step does not raise the top surface of the transparent conductive oxide above 335ºC (635ºF).

10. The method according to claim 1 wherein the substrate is glass and the transparent conductive oxide has an absorption not greater than 0.3.

11. The method according to claim 1 wherein the substrate is glass and the transparent conductive oxide has an absorption at least as high as 0.05.

12. The method according to claim 1, wherein the coated article is a refrigerator door.

13. The method according to claim 1, wherein the applying step is done in an atmosphere that has an oxygen content supplied to the atmosphere of between 0% and 1.5%.

14. The method according to claim 1 wherein the substrate is glass and the transparent conductive oxide has an absorption not greater than 0.2 and at least as high as 0.05.

15. A method of making a coated article comprising the steps of applying a transparent conductive oxide layer over a substrate, raising a top surface of the transparent conductive oxide to above 193ºC (380ºF) and not raising the top surface of the transparent conductive oxide above 470ºC (878°F).

16. The method according to claim 15 further comprising not heating the coated article above 335ºC (635°F).

17. The method according to claim 15 wherein the transparent conductive oxide layer comprises tin-doped indium oxide having a thickness of at least 96 nm and at most 171 nm and a sheet resistance of less than 25 Ω/□.

18. The method according to claim 15 further comprising applying a protective layer over the transparent conductive oxide wherein the protective layer comprises titania and alumina.