Abstract:
A method and apparatus of forming a transparent metal oxide layer on a conductive surface of a dielectric substrate involves exposing first and second conductive surface portions of the conductive surface of the dielectric substrate to first and second electrolytes respectively to form first and second electrochemical cells in which the first conductive surface is part of the first electrochemical cell and the second conductive surface is part of the second electrochemical cell and wherein the electrochemical cells are electrically connected together by the conductive surface of the dielectric substrate. An electric potential applied across first and second counter electrodes in the first and second cells respectively drives an electric current through the first and second electrolytes and causes metal ions and oxygen in the second electrolyte to form the transparent metal oxide layer on the second conductive surface portion when a current is passed through the first and second electrolytes. The transparent metal oxide layer may be made non-conductive or conductive or even semi-conductive through the absence or inclusion of dopant in the second electrolyte. A conductive surface of a dielectric substrate of any length can be uniformly plated with a transparent metal oxide layer by moving the dielectric substrate relative to the first and second electrolytes while exposing the first and second surface portions to the first and second electrolytes respectively.

FIG. 1

[Continued on next page]
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FORMING A TRANSPARENT METAL OXIDE LAYER ON A CONDUCTIVE SURFACE OF A DIELECTRIC SUBSTRATE

BACKGROUND OF THE INVENTION

1. Field of Invention

The present invention generally relates to forming a transparent metal oxide layer on a conductive surface of a dielectric substrate material such as glass, ceramic or polymer material, for example. The transparent metal oxide layer may be conductive, semi-conductive, or non-conductive.

2. Description of Related Art

Materials used to form conductive coatings generally fall into four categories: metals, metal oxides, conductive polymers, and nanomaterial. Metallic coatings exhibit the highest conductivity, particularly in nanomaterial form, however only ultra-thin continuous layers of about 5-10 nm thickness, for example, can be practically considered to be transparent. Metal oxides are generally orders of magnitude less conductive than metals but provide better transparency. Conductive plastics are also far less conductive than metals but offer greater flexibility, and sufficient transparency at lower cost. Nanomaterial coatings include metals and metal oxides, and at present are still at the lab scale of development. Transparent metal oxide layers are currently needed for industrial applications to provide transparent conductors in electronics such as in flat panel displays (FPDs), for example.

Transparent conductive oxides (TCO) are doped metal oxide films that have a poly- or micro-crystalline, or amorphous microstructure. These materials provide greater than 80% transmittance of incident light in the visible spectrum and have a resistivity of about $10^{-3} - 10^{-4}$ Ω·cm. A combination of two TCO layers each of about 30-50 nm thickness separated by an intermediate metallic layer of about 10-20 nm in thickness provides a composite structure having a tenfold reduction
in resistivity and an increased light transmittance of up to 95%. Recently, industrial applications of TCOs have expanded greatly. Rigid liquid crystal displays and other FPDs are the largest market for TCO coatings, but a variety of new market applications including touch screen displays, flexible displays, transparent displays, organic light emitting diode (OLED) displays, smart windows and solid state lighting are utilizing TCO coating as well. Although all of these technologies use TCO coatings to enable product functionality, technical requirements for TCOs in new applications are often different from those typical for a conventional LCD display.

Historically, the TCO market has been dominated by demands for Indium Tin Oxide (ITO). At the same time, sputtering has emerged as a dominant deposition technology for TCOs in general and for ITO coatings, in particular. While sputtering ITO has proven to be sufficient to satisfy industry needs up until now, both sputtering and ITO have a number of important drawbacks that are becoming increasingly apparent.

One such drawback is manufacturing costs. Indium is a scarce and expensive material and sputtering typically results in utilization of only approximately 30% of the indium with the remaining 70% of it being deposited on the walls of the sputtering chamber. Additionally, long down times are typically associated with vacuum based sputtering and this further contributes to the high overall cost of the ITO TCO process. Vacuum equipment such as magnetron sputtering is complex to operate and maintain. As a result, manufacturing lines utilizing this type of equipment generally require highly skilled labor and engineering staff in order to ensure stable line operation. In addition, magnetron sputtering technology requires pretreatment of the substrate surface by ion bombardment to provide adhesion of sputtered material. Finally, high temperatures are typically associated with the sputtering process or post-annealing treatment and this greatly restricts the application of ITO coating to substrates capable of
withstanding such temperatures. As a result, the use of ITO based TCO coatings on temperature sensitive substrates such as plastics is challenging.

Another issue is that there are currently no viable alternatives that will provide the electrical and optical characteristics of ITO coatings yet a growing number of market applications require greater conductivity and optical transparency.

The net result is that, at this time, there is a broad market opportunity for new, lower cost ITO deposition processes capable of replacing capital intensive and material wasteful sputtering for a number of existing market applications. There is also a market for a new "indium-free" TCO coating process that is capable of providing the market with a both lower cost and a better performance alternative to ITO in the mid-to long-term. For this reason, new TCO materials such as doped binary compounds, for example, aluminum doped zinc oxide (AZO), indium doped zinc oxide, yttrium doped zinc oxide, and cadmium doped zinc oxide, have been tested in several laboratories and have been proposed as alternative materials.

Alternative TCO deposition methods recently explored by industry and research communities include wet-process methods such as electrochemical methods. Electrochemical methods are based on electric current-driven deposition of metal or metal oxides primarily on the surfaces of substrates with sufficient bulk conductivity. However, there is a principle limitation in the use of such methods for coating dielectric substrates such as glass, ceramic and polymers, used in the production of consumable products. Conductive surfaces are needed to facilitate the use of electrochemical processes on these dielectric materials.

Thin layers of conductive metal oxides, for example FZnO fluoride doped zinc oxide FZnO, AZO or ITO can be deposited on glass and other dielectric substrates through various deposition methods, including for example metal
organic chemical vapor deposition (MOCVD), metal organic molecular beam deposition (MOMBD), and sputtering, thus making them potentially accessible to electrochemical processes.

US patent 5,316,697 "CONDUCTIVE, PARTICULATE, FLUORINE-DOPED ZINC OXIDE" 1994 to Palmer et al. describes a method for making a conductive, particulate, fluorine-doped, zinc oxide product using chemical vapour deposition. The process involves reacting vapour phase reactants in a vapour phase oxidation system at a temperature sufficient to form the conductive, particulate, fluorine-doped, zinc oxide product. Vapour phase reactants are used in the process and include elemental zinc vapour, at least one fluorine source, and at least one water source.

Glass sheets and polyester films coated with conductive metal oxides are commercially available, for example from Zhuhai Kaivo Electronic Components Co. Limited, No. 110, Yuanlinroad, Jida, Zhuhai, Guangdong-519015, China.

Another possibility for producing conductive layers on surfaces of dielectric substrates involves electroless deposition technology, also known as autocatalytic plating, which is capable of making conductive surfaces on non-conductive substrates. This is a non-galvanic plating method that involves several sequential electroless chemical reactions at an interface between aqueous electrolytes and non-conductive substrate surfaces which occur without the use of external electrical power. See, for example, US 6,464,762 B1 "Aqueous solution for the formation of indium oxide film by electroless deposition”, to Ara; US patent 6,387,542 B1 "ELECTROLESS SILVER PLATING" to Kozlov et al; US6,806,189 B2 "Method of silver (Ag) electroless plating on ITO electrode" to Kim et al.; US patent 6,527, 840 B1 "Silver alloy plating bath and method of forming a silver alloy film by means of the same" to Igarashi et al.; JP59143059 "Electroless plating apparatus" to ITSUPEI et al.; JP11152578A
Unfortunately, the quality of the conductive layers produced on dielectric substrates by the above presented methods is not sufficient for consumer electronic products due to low conductivity of the layers produced by electroless deposition, low thickness uniformity and low light transmittance from CVD and sputtering technologies. This has resulted in consideration of the use of a pre-coated surface on the dielectric substrate prior to forming a transparent conductive metal oxide layer using electrochemical processes.

Several research institutions have demonstrated the possibility of producing Cd-doped and Y-doped ZnO on conductive surfaces pre-formed on glass substrates but these results have only been demonstrated on small samples and were produced in conventional electrochemical chambers that are impractical to employ in mass production industrial processes.

PCT patent application No. CA2011/001013 "Electroplating Metal Oxides on Flat Conductive Surfaces" to Rubin et al. describes a method and apparatus for electrochemically forming an oxide layer on the flat conductive surface of semiconductor devices and photovoltaic (PV) cells. The method involves positioning a working electrode bearing the flat conductive surface in opposed parallel spaced apart relation to a flat conductive surface of a counter electrode. A volume of organic electrolyte solution containing chemicals for forming the oxide layer on the flat conductive surface of the working electrode is arranged to flood and to occupy the space defined between the flat conductive surface of the working electrode and the counter electrode. An electric current flows between substantially only the flat conductive surface of the counter electrode and substantially only the flat conductive surface of the working electrode, in the
organic electrolyte solution, for a period of time and at a magnitude sufficient to cause the chemicals to form the oxide layer on the flat conductive surface of the working electrode. The apparatus is specially designed so that the working and counter electrodes receive electrical power at their rear sides to protect their power input terminals from immediate contact with electrolyte which would damage them. Therefore, the use of this apparatus is well suited to use with substrates and counter electrodes that have bulk conductivity but the apparatus is not suitable for forming metal oxide layers on dielectric materials, even if their surfaces are pre-coated with a conductive layer.

Therefore there remains a challenge for forming high uniformity conductive metal oxide layers with high conductivity and high transparency over a large substrate area while keeping both electric terminals of the electrochemical apparatus protected from interaction with the electrolyte.

**SUMMARY OF THE INVENTION**

In accordance with one aspect of the invention, there is provided a method of forming a transparent metal oxide layer on a conductive surface of a dielectric substrate. The method involves exposing first and second conductive surface portions of the conductive surface of the dielectric substrate to first and second electrolytes respectively, and forming a first electrochemical cell comprised of the first conductive surface portion in contact with the first electrolyte and a first electrode in contact with the first electrolyte and spaced apart from the first conductive surface portion. The method further involves forming a second electrochemical cell comprised of the second conductive surface portion in contact with the second electrolyte and a second electrode in contact with the second electrolyte and spaced apart from the second conductive surface portion. The first and second electrochemical cells are electrically connected together in series by the conductive surface. The first electrolyte has first chemicals that facilitate conduction of electric current through the first electrolyte without
facilitating significant electrochemical reaction at the first electrode or at the first conductive surface portion. The second electrolyte has second chemicals that facilitate conduction of electric current through the second electrolyte, the second chemicals including a non-aqueous solvent, metal ions in a metal ion concentration at least sufficient to facilitate formation of the transparent metal oxide layer to a desired thickness and a source of oxygen suitable to facilitate formation of the transparent metal-oxide surface of the second conductive surface portion. The method further involves applying an electric potential between the first and second electrodes such that the second electrode has a positive polarity relative to the first electrode to cause an electric current to flow between the second electrode and the first electrode in series through the second electrolyte, the second conductive surface portion, the first conductive surface portion and the first electrolyte. The second electrode is at a sufficiently more positive potential than the second conductive surface portion to cause an electrochemical reaction to occur at the second conductive surface portion to form the transparent metal oxide layer on the second conductive surface portion.

The non-aqueous solvent may be protic or aprotic.

The method may involve releasing metal ions capable of forming the transparent metal oxide layer to be optically transparent in the visible region of the electromagnetic spectrum, from salts soluble the in non-aqueous solvent.

The method may involve causing the second electrolyte to include a dopant electrochemically embeddable into the transparent metal oxide layer to produce a conductive transparent metal oxide layer.

The method may involve admitting a chemical supplement into at least one of the first and second electrolytes.
The method may involve counting coulombs of charges in the electric current and ceasing the application of the electric potential when a coulomb charge count meets a charge count criterion associated with a desired thickness of the transparent metal oxide layer.

The method may involve interrupting the current when the metal ion concentration in the second electrolyte meets a metal ion concentration criterion, replacing the second electrolyte, and re-establishing the electric current.

The method may involve moving the substrate relative to the first and second electrolytes in a direction from the first electrolyte to the second electrolyte while the electric current is flowing, to cause the transparent metal oxide layer to be formed in a lengthwise direction along the conductive surface of the substrate.

Forming the first and second electrochemical cells may involve holding the first electrolyte in a first open-faced container and holding the second electrolyte in a second open-faced container.

The method may involve defining the first and second open-faced containers by an entrance wall, an interior wall, an exit wall, first end wall portions and a first bottom wall portion, such that the first open-faced container is defined between the entrance wall, the interior wall, the first end wall portions and the first bottom wall portion and such that the second open-faced container is defined between the interior wall, the exit wall, second end wall portions and a second bottom wall portion.

The method may involve causing the first electrode to extend through the entrance wall, a first end wall portion or the first bottom wall portion, at a first position in parallel spaced apart relation to the substrate and causing the second electrode to extend through the exit wall, a second end wall portion or the second
bottom wall portion, at a second position in parallel spaced apart relation to the substrate.

The method may involve admitting the dielectric substrate having the conductive surface through an entrance opening in the entrance wall and causing the substrate to extend over the first and second open-faced containers such that the conductive surface faces the first and second open-faced containers. The first conductive surface portion is a portion of the conductive surface that extends over the first container and the second conductive surface portion is a portion of the conductive surface that extends over the second open-faced container and the method may further involve causing a portion of the substrate to extend through an exit opening in an exit wall of the second open-faced container.

The method may involve causing the entrance opening and the exit opening to be sealed against the conductive surface of the dielectric substrate to prevent leakage of the first and second electrolytes respectively from the entrance and exit openings respectively.

The method may involve causing the interior wall to be sealed against the conductive surface of the dielectric substrate to prevent exchange of the first and second electrolytes at the interior wall.

The method may involve moving the substrate relative to the first and second electrolytes in a direction from the first electrolyte to the second electrolyte while the electric current is flowing, to cause the transparent metal oxide layer to be formed in a lengthwise direction along the conductive surface of the substrate.

Moving may involve moving the substrate while holding the first and second open-faced containers stationary.
The method may involve causing the first and second open-faced containers to be placed open-face down on the conductive surface of the dielectric substrate such that the substrate extends under the entrance wall, the interior wall, the exit wall, and the first and second end wall portions such that the first and second conductive surfaces of the dielectric substrate face the first and second open-faced containers. The first conductive surface portion is a portion of the conductive surface that extends under the first open-faced container and the second conductive surface portion is a portion of the conductive surface that extends under the second open-faced container and the method may further involve causing a portion of the conductive surface of the dielectric substrate to extend under the exit wall of the second open-faced container.

The method may involve holding the substrate with the conductive surface face-up in a container holding an initial electrolyte and causing the first and second open-faced containers to be placed open-face down on the conductive surface of the dielectric substrate. This may involve causing the first and second open-faced containers to be substantially submerged in the initial electrolyte and causing the entrance wall, the exit wall, and the first and second end wall portions to be sealed against the substrate to contain a first volume of the initial electrolyte in the first open-faced container and to contain a second volume of the initial electrolyte in the second open-faced container.

The method may involve causing the interior wall to be sealed against the conductive surface of the dielectric substrate to prevent leakage of the first and second electrolytes respectively under the interior wall.

The method may involve moving the substrate relative to the first and second electrolytes in a direction from the first electrolyte to the second electrolyte while the electric current is flowing, to cause the transparent metal oxide layer to be formed in a lengthwise direction along the conductive surface of the substrate.
Moving may involve moving the first and second open-faced containers while holding the substrate stationary.

In accordance with another aspect of the invention, there is provided a method of forming a transparent metal oxide layer on a first conductive surface of a first dielectric substrate. The method involves pressing the first conductive surface of a first dielectric substrate against a space-defining frame gasket on a second conductive surface of a second dielectric substrate such that the frame defines a sealed space between the first conductive surface and the second conductive surface. The method further involves admitting an electrolyte having chemicals that facilitate conduction of electric current through the electrolyte into the sealed space through an opening in the frame gasket, the chemicals including a non-aqueous solvent, metal ions in a metal ion concentration at least sufficient to facilitate formation of the transparent metal oxide layer to a desired thickness and a source of oxygen suitable to facilitate formation of the transparent metal-oxide surface of the second conductive surface. The method further involves applying an electric potential between the first and second conductive surfaces such that the second conductive surface has a negative polarity relative to the first conductive surface to cause an electric current to flow between the first conductive surface and the second conductive surface through the electrolyte to cause an electrochemical reaction to occur at the first conductive surface to form the transparent metal oxide layer on the first conductive surface.

The non-aqueous solvent may be protic or aprotic.

The method may involve releasing metal ions capable of forming the transparent metal oxide layer to be optically transparent in the visible region of the electromagnetic spectrum, from salts soluble in the non-aqueous solvent.
The method may involve causing the second electrolyte to include a dopant electrochemically embeddable into the transparent metal oxide layer to produce a conductive transparent metal oxide layer.

The method may involve admitting a chemical supplement into the electrolyte.

The method may involve counting coulombs of charges in the electric current and ceasing the application of the electric potential when a coulomb charge count meets a coulomb charge count criterion associated with a desired thickness of the transparent metal oxide layer.

The method may involve interrupting the current when a metal ion concentration in the electrolyte meets a metal ion concentration criterion, replacing the electrolyte, and re-establishing the electric current.

The pressing may involve pressing sufficiently to compress the space-defining frame gasket to sufficiently seal the sealed space to prevent leakage of the electrolyte from the sealed space.

Applying an electric potential may involve fastening first and second conductive clamps on first and second opposite edges respectively of the first substrate to make electrical contact with the first conductive surface at opposite edges of the first substrate and fastening third and fourth of conductive clamps on third and fourth edges of the dielectric substrate to make electrical contact with the second conductive surface on the dielectric substrate and connecting the first and second clamps to a positive terminal of a current source and connecting the third and fourth clamps to a negative terminal of the current source.

In accordance with another aspect of the invention, there is provided an apparatus for forming a transparent metal oxide layer on a conductive surface of
a dielectric substrate. The apparatus includes provisions for holding a first electrolyte and a first electrode in contact with the first electrolyte, and provisions for holding a second electrolyte and a second electrode in contact with the second electrolyte. The apparatus further includes provisions for simultaneously exposing first and second conductive surface portions of the conductive surface of the dielectric substrate to the first and second electrolytes respectively, such that the first and second conductive surface portions are spaced apart from the first and second electrodes respectively to form first and second electrochemical cells respectively and whereby the first and second electrochemical cells are electrically connected together in series by the conductive surface of the dielectric substrate. The first electrolyte has first chemicals that facilitate conduction of electric current through the first electrolyte without facilitating significant electrochemical reaction at the first electrode or at the first conductive surface portion. The second electrolyte has second chemicals that facilitate conduction of electric current through the second electrolyte, the second chemicals including a non-aqueous solvent, metal ions in a metal ion concentration at least sufficient to facilitate formation of the transparent metal oxide layer to a desired thickness and a source of oxygen suitable to facilitate formation of the transparent metal-oxide layer on the second conductive surface portion. The apparatus further includes provisions for applying an electric potential between the first and second electrodes such that the second electrode has a positive polarity relative to the first electrode to cause an electric current to flow between the second electrode and the first electrode in series through the second electrolyte, the second conductive surface portion, the first conductive surface portion and the first electrode. The second electrode is at a sufficiently more positive potential than the second conductive surface portion to cause an electrochemical reaction to occur at the second conductive surface portion to form the transparent metal oxide layer on the second conductive surface portion.

The non-aqueous solvent may be protic or aprotic solvent.
The apparatus may include releasing metal ions capable of forming the transparent metal oxide layer to be optically transparent in the visible region of the electromagnetic spectrum, from salts soluble in non-aqueous solvent.

The apparatus may include causing the second electrolyte to include a dopant electrochemically embeddable into the transparent metal oxide layer to produce a conductive transparent metal oxide layer.

The apparatus may include provisions for counting coulombs of charges in the electric current and means, in communication with the means for counting coulombs, for ceasing the application of the electric potential when a coulomb charge count indicated by the means for counting coulombs meets a coulombs count criterion associated with a desired thickness of the transparent metal oxide layer.

The apparatus may include provisions for interrupting the current when a metal ion concentration in the second electrolyte meets a metal ion concentration criterion, means for replacing the second electrolyte, and means for re-establishing the electric current after second electrolyte has been replaced.

The apparatus may include provisions for moving the substrate relative to the first and second electrolytes in a direction from the first electrolyte to the second electrolyte while the electric current is flowing, to cause the transparent metal oxide layer to be formed in a lengthwise direction along the conductive surface of the substrate.

The means for holding the first electrolyte and the first electrode may include a first open-faced container and the means for holding the second electrolyte and the second electrode may include a second open-faced container.
The first open-faced container may include an entrance wall and an interior wall, a pair of first end walls and a first bottom wall portion and the second open-faced container may comprise the interior wall and an exit wall and a pair of second end walls and a second bottom wall portion the first and second open-faced containers have first and second end wall portions.

The first electrode may extend through the entrance wall, at least one of the first end wall portions or the first bottom wall portion, at a first position in parallel spaced apart relation to the substrate and the second electrode may extend through the exit wall, at least one of the second end wall portions or the second bottom wall portion, at a second position in parallel spaced apart relation to the conductive surface of the dielectric substrate.

The means for simultaneously exposing the first and second surface portions of the conductive surface of the substrate may include an entrance opening in the entrance wall and an exit opening in the exit wall, for receiving and positioning the dielectric substrate to cause the dielectric substrate to extend over the first and second open-faced containers such that the first conductive surface portion faces the first open-faced container and such that the second conductive surface portion faces the second open-faced container.

The apparatus may include entrance and exit seals operably configured to seal the entrance opening and the exit opening against the conductive surface of the dielectric substrate to prevent leakage of the first and second electrolytes respectively from the entrance and exit openings respectively.

The apparatus may include an interior wall seal operably configured to seal the interior wall against the conductive surface of the dielectric substrate to prevent exchange of the first and second electrolytes at the interior wall.
The apparatus may include provisions for moving the substrate relative to the first and second electrolytes in a direction from the first electrolyte to the second electrolyte while the electric current is flowing, to cause the transparent metal oxide layer to be formed in a lengthwise direction along the conductive surface of the substrate.

The provisions for moving may include provisions for moving the substrate and provisions for holding the first and second open-faced containers stationary while the substrate is being moved.

The apparatus may further include provisions for positioning the first and second open-faced containers face down on the conductive surface of the dielectric substrate such that the substrate extends under the entrance wall, the interior wall, the exit wall, and the first and second pairs of end walls such that the first and second conductive surfaces of the dielectric substrate face the first and second open-faced containers.

The apparatus may include provisions for holding a volume of an initial electrolyte, provisions for holding the dielectric substrate with the conductive surface face-up in the initial electrolyte, and the provisions for positioning the first and second open-faced containers face down on the conductive surface of the dielectric substrate may comprise provisions for causing the first and second open-faced containers to be substantially submerged in the initial electrolyte. The apparatus may further include provisions for sealing the entrance wall, the exit wall, and the first and second end wall portions against the substrate to contain a first volume of the initial electrolyte in the first open-faced container and to contain a second volume of the initial electrolyte in the second open-faced container.
The apparatus may include provisions for sealing the interior wall against the conductive surface of the dielectric substrate to prevent leakage of the first and second electrolytes respectively at the interior wall.

The apparatus may include provisions for moving the substrate relative to the first and second electrolytes in a direction from the first electrolyte to the second electrolyte while the electric current is flowing, to cause the transparent metal oxide layer to be formed in a lengthwise direction along the conductive surface of the substrate.

The provisions for moving may include provisions for moving the first and second open-faced containers and provisions for holding the substrate stationary while the first and second open-faced containers are being moved.

In accordance with another aspect of the invention, there is provided an apparatus for forming a transparent metal oxide layer on a first conductive surface of a first dielectric substrate. The apparatus includes a space-defining frame gasket positioned on the conductive surface of the dielectric substrate. The gasket has an inner wall defining a space bounded by the inner wall and a portion of the conductive surface of the dielectric substrate. The apparatus further includes provisions for pressing a second conductive surface of a second dielectric substrate against the space-defining frame gasket to cause the space to be a sealed space, and an opening in the frame gasket for admitting into the sealed space an electrolyte having chemicals that facilitate conduction of electric current through the electrolyte. The chemicals include non-aqueous solvent, metal ions and a source of oxygen suitable to facilitate formation of the transparent metal-oxide layer on the conductive surface of the first dielectric substrate. The apparatus further includes provisions for applying an electric potential between the second conductive surface of the second dielectric substrate and the first conductive surface of the first substrate such that the first
conductive surface of the first substrate has a negative polarity relative to the second conductive surface of the second dielectric substrate to cause an electric current to flow between the second conductive surface and the first conductive surface, through the electrolyte to cause an electrochemical reaction to occur at the first conductive surface to form the transparent metal oxide layer on the first conductive surface.

The non-aqueous solvent may be protic or aprotic solvent.

The apparatus may include releasing metal ions capable of forming the transparent metal oxide layer to be optically transparent in the visible region of the electromagnetic spectrum, from salts soluble in non-aqueous solvent.

The apparatus may include causing the second electrolyte to include a dopant electrochemically embeddable into the transparent metal oxide layer to produce a conductive transparent metal oxide layer.

The apparatus may include provisions for counting coulombs of charges in the electric current and means in communication with the means for counting coulombs for ceasing the application of the electric potential when a coulomb charge count indicated by the means for counting coulombs meets a coulomb count criterion associated with a desired thickness of the transparent metal oxide layer.

The apparatus may include provisions for interrupting the current when a metal ion concentration in the electrolyte meets a metal ion concentration criterion, provisions for replacing the electrolyte, and provisions for re-establishing the electric current after the electrolyte has been replaced.
The provisions for pressing may be operably configured to press sufficiently to compress the space-defining frame gasket to sufficiently seal the sealed space to prevent leakage of the electrolyte from the sealed space.

The provisions for applying an electric potential may include first and second conductive clamps on first and second opposite edges respectively of the first substrate in electrical contact with the first conductive coating at opposite side edges of the first substrate and third and fourth conductive clamps on third and fourth opposite edges of the dielectric substrate in electrical contact with the second conductive surface of opposite side edges of the dielectric substrate. The first and second clamps are operably configured to be connected to a negative terminal of a current source and the third and fourth clamps are operably configured to be connected to a positive terminal of the current source.

Other aspects and features of the present invention will become apparent to those ordinarily skilled in the art upon review of the following description of specific embodiments of the invention in conjunction with the accompanying figures.

**BRIEF DESCRIPTION OF THE DRAWINGS**

In drawings which illustrate embodiments of the invention,

Figure 1 is a perspective view of an apparatus according to a first embodiment of the invention;

Figure 2 is a cross-sectional/perspective view of the apparatus shown in Figure 1 with the cross-sectional view taken along line II-II in Figure 1;

Figure 3 is a schematic diagram of an electrical circuit formed by the apparatus shown in Figures 1 and 2;
Figure 4 is a schematic representation of a system according to a second embodiment of the invention including the apparatus shown in Figures 1 and 2 with provisions for moving a substrate relative to the apparatus to cause a transparent metal oxide layer to be formed on a long substrate;

Figure 5 is a schematic representation of an apparatus according to a third embodiment of the invention where a polymeric dielectric substrate having a conductive surface is rolled on a spool and fed into the apparatus shown in Figures 1 and 2 and is then wound on a take up spool after processing through the apparatus shown in Figures 1 and 2;

Figure 6 is an apparatus according to a fourth embodiment of the invention employing a variation of the apparatus shown in Figures 1 and 2 in an inverted orientation with provisions for moving the apparatus relative to a fixed tray containing an initial electrolyte;

Figure 7 is a cross-sectional/fragmented view of the apparatus shown in Figure 6 with the cross-section taken along lines VII-VII in Figure 6;

Figure 8 is a perspective/schematic view of an apparatus according to a fifth embodiment of the invention employing only a single electrochemical cell;

Figure 9 is an exploded view of an electrochemical cell portion of the apparatus shown in Figure 8.

DETAILED DESCRIPTION

Referring to Figure 1, an apparatus for forming a transparent metal oxide layer on a conductive surface 32 of a dielectric substrate 34, according to a first embodiment of the invention is shown generally at 10. The dielectric substrate in
this embodiment may be glass or ceramic material having a thickness of about 0.3mm to about 4mm or polymeric material having a thickness of about 0.05mm to about 1 mm and the transparent conductive surface 32 may be for example a fluoride-doped ZnO layer having a thickness of between about 20nm to about 1000 nm and a sheet resistance of about 500 ohm/sq. to about 5 ohm/sq. The dielectric substrate 34 may be several meters long.

In this embodiment, the apparatus includes provisions shown generally at 12 for holding a first electrolyte 14 and a first electrode 16 in contact with the first electrolyte 14. The apparatus 10 further includes provisions shown generally at 18 for holding a second electrolyte 20 and a second electrode 22 in contact with the second electrolyte. The apparatus 10 also includes provisions shown generally at 24 and 26 for simultaneously exposing first and second conductive surface portions 28 and 30 of the conductive surface 32 of the dielectric substrate 34 to the first and second electrolytes 14 and 20 respectively. The first and second conductive surface portions 28 and 30 are spaced apart from the first and second electrodes 16 and 22 respectively to form first and second electrochemical cells 36 and 38 respectively such that the first and second electrochemical cells 36 and 38 are electrochemically connected together in series by the conductive surface 32 of the dielectric substrate 30.

The main function of the first electrolyte 14 is to conduct electric current between the first conductive surface portion 28 and the first electrode 16. The chemical composition of the first electrode can be quite simple and may include merely only a solvent and dissolved potassium chloride salt, for example. With this simple chemical composition there will be no significant chemical reaction at the first electrode or at the first conductive surface portion that will significantly degrade either of these entities. The second electrolyte 20 has a chemical composition that is much more complex. The chemical composition of the second electrolyte 20 is configured to facilitate conducting electric current
between the second electrode 22 and the second conductive portion 30 and to facilitate electrochemical formation of the desired transparent metal oxide layer on the second conductive surface portion 30 of the dielectric substrate 34. The chemicals in the second electrolyte 20 include a non aqueous solvent, metal ions in a concentration at least sufficient to facilitate formation of the transparent metal oxide layer to a desired thickness on the second conductive surface portion 30 and a source of oxygen suitable to facilitate formation of the transparent metal oxide layer on the second conductive surface portion 30. The apparatus 10 further includes provisions for applying an electric potential between the first and second electrodes 16 and 22 such that the second electrode 22 has a positive polarity relative to the first electrode 16 to cause an electric current to flow between the second electrode 22 and the first electrode 16, in series, through the second electrolyte 20, the second conductive surface portion 30, the first conductive surface portion 28 and the first electrolyte 14. This creates an electric circuit wherein the second electrode 22 is at a sufficiently more positive potential than the second conductive surface portion 30 to cause an electrochemical reaction to occur at the second conductive surface portion 30, to form the transparent metal oxide layer on the second conductive surface portion 30.

Referring to Figure 2, the provisions 12 for holding the first electrolyte 14 and the provisions 18 for holding the second electrolyte 20 are comprised first and second open-faced containers 50 and 52 respectively. The first and second open-faced containers 50 and 52 are formed by a body 53 having an entrance wall 54 an interior wall 56, an exit wall 62, a first pair of side walls, only one of which is shown at 58 in Figure 2, a second pair of side walls, only one of which is shown at 59 and first and second bottom wall portions 60 and 66. The entrance wall 54, interior wall 56, first pair of side walls (58) and first bottom wall portion 60 define the first open-faced container 50. The second open faced container 52 is defined by the interior wall 56, the exit wall 62, the second pair of side walls (64) and the second bottom wall portion 66.
The body 53 may be produced from Teflon® reflowed anodized aluminium, Teflon®, organic glass or other chemically and mechanically stable materials. The length of the body 53 may be defined between outer surfaces of the entrance and exit walls 54 and 62 and may be from about 10cm to about 200cm. The width of the body 53 may be defined between outer surfaces of the respective pairs of side walls 58 and 59 and may be about 10cm to about 200cm. The width may be determined, based on the width of the dielectric substrate 34 on which the transparent metal oxide layer is to be formed. The height of the body 53 may be between about 4cm to about 50cm. The height, of course, defines the depth of the first and second open-faced containers 50 and 52 respectively and may be set within the above indicated range to provide for a suitable spacing of the first and second electrodes from the first conductive surface portion 28 and the second conductive surface portion 30 respectively and to provide for a sufficient volume of first and second electrolytes 14 and 20 to provide a suitable supply of chemicals for forming the transparent metal oxide to a desired thickness. For example, the first and second open-faced containers 50 and 52 may have depths from about 3cm to about 47cm and widths from about 20cm to about 190cm but their lengths may be different. For example, the first open-faced container 50 may have a length of about 10cm to about 50cm and the second open-faced container 52 may have a length of about 2cm to about 150cm.

Still referring to Figure 2, the first electrode 16 extends through the entrance wall 54 at a first position, in parallel spaced apart relation to the first conductive surface portion 28 and the second electrode 22 extends through the exit wall 62 at a second position, in parallel spaced apart relation to the second conductive surface portion 30. To facilitate this, the entrance wall 54 is provided with an elongated entrance opening 70 having upper and lower wall portions 72 and 74 on which are secured first upper and lower elastomeric seals 76 and 78.
respectively. The first upper and lower elastomeric seals 76 and 78 may be made from soft elastic rubber material for example Vitom™ available from E. I. du Pont de Nemours and Company of the USA.

The first electrode 16 is a planar electrode comprising a dielectric substrate 80 such as glass having a thickness of about 0.3 - 4mm for example, having a conductive surface 82 disposed on one broad face thereof. The conductive surface 82 may be produced from chemically stable materials, for example, fluoride doped zinc oxide having a thickness of about 300nm to about 1500nm and a sheet resistance from about 20Q/sq to about 0.1Q/sq. This conductive layer may be produced on the dielectric substrate 80 by CVD or sputtering techniques, for example. The first electrode 16 is inserted through the entrance opening 70 such that an end portion 84 of the first electrode rests adjacent a first surface 86 of the interior wall 56. A support (not shown) may be provided to position the end portion 84 such that the first electrode will be parallel with the first conductive surface portion 27. The first upper and lower elastomeric seals 76 and 78 bear upon the conductive surface 82 and a non-conductive surface 88 of the first electrode 16 to prevent the first electrolyte 14 from leaking out through the entrance opening 70. The first electrode 16 further has an outer edge 90 that extends outside of the first open-faced container 50 and to which is secured a first conductive clamp 92 comprising a contact element 94 and a C-shaped channel 96 having first and second opposite legs 98 and 100. The contact element 94 is received between the first leg 98 and the conductive surface 82 of the first electrode 16 so as to make contact therewith. The contact element 94 is made from soft sufficiently conductive metal such as silver or indium, for example. Screws such as shown at 102 are provided to press the contact element 94 solidly against the conductive surface 82 to make good electrical contact therewith. The clamp 92 is connected to a wire 104 which in turn is connected to a negative terminal 106 of a power supply 108.
Similarly, the exit wall 62 is provided with an elongated opening 110 having upper and lower wall portions 112 and 114 to which are secured second upper and lower elastomeric seals 116 and 118 respectively. The second electrode 22 is the same as the first electrode 16 and has a substrate 120 having a lower non-conductive surface 122 and an upper conductive surface 124. The second electrode 22 is inserted into the opening 110 until an end portion 126 thereof is adjacent a second surface 128 of the interior wall 56. A support (not shown) may be provided to position the end portion 126 such that the second electrode will be parallel with the second conductive surface portion 30. The second upper and lower elastomeric seals 116 and 118 are the same as those described in connection with the first electrode (76 and 78) and bear against the conductive and non-conductive surfaces 124 and 122 respectively to seal the opening 110 to prevent leakage of the second electrolyte 20 through the opening 110. The second electrode is provided with a second conductive clamp 130 the same as the conductive clamp 92 used on the first electrode 16 and a wire 132 is connected to the second conductive clamp 130 to connect it to a positive terminal 134 of the power supply 108.

The first electrode 16 and the first conductive surface portion 28 may be spaced apart by about 1mm to about 50mm. The second electrode 22 and the second conductive surface portion 30 may be spaced apart by the same distance.

The provisions for simultaneously exposing the first and second conductive surface portions 28 and 30 of the conductive surface 32 on the substrate 34 to the first and second electrolytes respectively include an entrance opening 150 in the entrance wall 54 and an exit opening 152 in the exit wall 62, for receiving and positioning the dielectric substrate 34 to cause the dielectric substrate to extend over the first and second open faced containers 50 and 52 such that the first conductive surface portion 28 faces the first open-faced container 50 and such that the second conductive surface portion 30 faces the second open-faced
container 52. The entrance opening 150 has respective upper and lower entrance walls 154 and 156 to which are attached upper and lower entrance seals 158 and 160 respectively. The upper and lower entrance seals 158 and 160 are the same as the elastomeric seals 76 and 78. The upper entrance seal 58 bears upon the uncoated surface of the dielectric substrate 34 while the lower entrance seal 160 bears upon the conductive surface 32 of the substrate and thus seals the entrance opening to prevent leakage of the first electrolyte 14 from the entrance opening 150.

Similarly, the exit opening 152 has upper and lower walls 162 and 164 to which are connected upper and lower exit seals 166 and 168 respectively, the same as the elastomeric seals 116 and 118. The upper exit seal 166 bears upon the uncoated surface of the substrate 34 while the lower exit seal 168 bears upon the second conductive surface portion 30 of the dielectric substrate 34 to seal the exit opening 152 to prevent leakage of the second electrolyte 20 from the exit opening 152. The entrance and exit openings 150 and 152 are disposed in a common substrate plane which is parallel to and spaced apart from an electrode plane in which the first and second electrodes 16 and 22 lie. The substrate plane and the electrode plane are disposed so that the first and second electrolytes 14 and 20 contact the entire first and second conductive surface portions 28 and 30 of the conductive surface 32 respectively. In the embodiment shown, the interior wall 56 is disposed mid-way between the entrance and exit walls 54 and 62 and has an upper portion 170 that is disposed slightly below the substrate plane. An interior wall seal 172 is disposed on the upper portion 170 so as to contact the conductive surface 32 of the dielectric substrate 34. The interior wall seal 172 has a thickness about the same thickness of the lower entrance seal 160. This sufficiently prevents ion exchange between the first electrolyte 14 and the second electrolyte 20. If the thickness of the interior seal 172 is lower than the thickness of the entrance seal 160, a space between the conductive surface 32 of the substrate 34 and the entrance seal 172 is formed, resulting in an ion exchange
path between the first electrolyte 14 and the second electrolyte 20 (not shown). The creation of such an ion exchange path between the first and second electrodes 16 and 22 through the first and the second electrolytes 14 and 20 may result in undesirable metal oxide plating on the first electrode 16.

Each of the entrance wall 54 and the interior wall 56 and the exit wall 62 have elongated openings 180, 182 and 184 respectively in which are received respective heater elements 186, 188, and 190 respectively, seen best in Figure 1, for heating the first and second open faced containers 50 and 52 and for ultimately heating the first and second electrolytes 14 and 20 to a temperature of between about 15 degrees Celsius to about 120 degrees Celsius. Referring back to Figure 2, in the embodiment shown, the first, second and third elongated openings 180, 182 and 184 are disposed in a plane approximately mid-way between the substrate plane and the electrode plane.

Still referring to Figure 2, the first and second bottom wall portions 60 and 66 have electrolyte admittance openings 192 and 194 respectively and electrolyte drain openings 196 and 198 respectively. The electrolyte admittance openings 192 and 194 may be connected to respective conduits (not shown) for supplying volumes of the first and second electrolytes 14 and 20 respectively. The drain openings 196 and 198 may be connected a common drain (not shown) or to reclamation apparatus for reclaiming and/or recycling the first and second electrolytes 14 and 20.

Ideally, the first and second electrodes 16 and 22 and dielectric substrate 34 are positioned as shown in Figure 2 before any electrolyte is admitted into the first or second open-faced containers 50 or 52. Once the first and second electrodes 16 and 22 have been positioned, volumes of the first and second electrolytes 14 and 20 are dispensed into the first and second open-faced containers 50 and 52 through the electrolyte admittance openings 192 and 194 until the first electrolyte
14 touches the first conductive surface portion 28 of the dielectric substrate 34 and until the second electrolyte 20 touches the second conductive surface portion 30. Entrance and exit gutters 200 and 202, for example may be employed adjacent the entrance and exit openings 150 and 152 to collect any electrolyte that may leak past the seals at the entrance or exit openings 150, 152.

The first and second electrolytes 14 and 20 have chemicals that facilitate conduction of electric current therethrough and may include protic non-aqueous solvents that include at least one of methanol, ethanol, propanol, isopropanol, ethylene glycol, glycerol and tetrahydrofurfuryl alcohol.

Alternatively, they may include aprotic non-aqueous solvents that include at least one of N-Methylacetamide, dimethylformamide, acetonitrile, dimethylsulfoxide (DMSO) and propylene carbonate.

As described above, the first electrolyte 14 may, for example, be very simple and include merely a non-aqueous solvent and at least one salt, for example potassium chloride, to provide for conductivity.

At least the second electrolyte 20 has a chemical composition that includes a source of oxygen sufficient to permit the transparent metal oxide layer to be formed to a desired thickness. The source of oxygen may include dissolved oxygen or at least one oxygen precursor such as at least one of dissolved nitrate, nitrite, peroxy compounds, ozone, and traces of water. The concentration of dissolved oxygen ready for use in the electrochemical process of forming the transparent metal oxide layer should be selected such that at least enough source oxygen is provided in the volume of second electrolyte 20 dispensed into the second open-faced container 52 to facilitate formation of a metal oxide layer of a desired thickness.
The chemical composition of the second electrolyte 20 also includes an ionic source of metal sufficiently soluble in the selected solvent and that will facilitate formation of the metal transparent oxide layer to a desired thickness and such that the transparent metal oxide layer has an optical transparency from about 85% to about 95% in a spectral region having wavelengths from about 380 nm to about 750 nm.

Using the apparatus described, where a transparent zinc oxide layer is to be formed, the chemicals in the second electrolyte will include an ionic source of metal such as at least one dissolved zinc salt or at least one zincate or a combination of the at least one dissolved zinc salt and the at least one zincate. The at least one dissolved zinc salt may be nitrate, chloride, perchlorate or sulphate, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L (gram equivalent/litre) to 0.1 Eq/L of zinc or from 0.0001 Eq/L of zinc to a saturation concentration to produce a zinc oxide film having a thickness of about 10nm to about 500nm, for example.

Where a transparent non-conductive aluminum oxide layer is intended to be formed, the ionic source of metal may include at least one dissolved aluminum salt or at least one aluminate or a combination of the at least one dissolved aluminum salt or at least one aluminate. The dissolved aluminium salt may be nitrate, chloride, perchlorate or sulphate, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L (gram equivalent/litre) to 0.1 Eq/L of aluminum or from 0.0001 Eq/L of aluminum to a saturation concentration to produce an aluminum oxide film having a thickness of about 10nm to about 500nm, for example.

Where a transparent non-conductive indium oxide layer is to be formed, the ionic source of metal may include at least one dissolved indium salt. The at least one dissolved indium salt may be nitrate, chloride or sulphate, for example. The
organic solvent electrolyte solution may contain from 0.0001 Eq/L to 0.1 Eq/L of indium or from 0.0001 Eq/L of indium to a saturation concentration to produce an indium oxide film having a thickness of about 10nm to about 500nm, for example.

Where a transparent non-conductive cadmium oxide layer is to be formed, the ionic source of metal may include at least one dissolved cadmium salt. The at least one dissolved cadmium salt may be nitrate, chloride, perchlorate or sulphate, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L to 0.1 Eq/L of cadmium or from 0.0001 Eq/L of cadmium to a saturation concentration to produce a cadmium oxide film having a thickness of about 10nm to about 500nm, for example.

Where a transparent non-conductive magnesium oxide layer is to be formed, the ionic source of metal may include at least one dissolved magnesium salt. The at least one dissolved magnesium salt may be nitrate, chloride or perchlorate, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L to 0.1 Eq/L of magnesium or from 0.0001 Eq/L of magnesium to a saturation concentration to produce a magnesium oxide film having a thickness of about 10nm to about 500nm, for example.

Where a transparent non-conductive silver oxide layer is to be formed, the ionic source of metal may include at least one dissolved silver salt. The at least one dissolved silver salt may be nitrate or perchlorate, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L to 0.1 Eq/L of silver or from 0.0001 Eq/L of silver to a saturation concentration to produce a silver oxide film having a thickness of about 10nm to about 500nm, for example.

Where a transparent non-conductive yttrium oxide layer is to be formed, the ionic source of metal may include at least one dissolved yttrium salt. The at least one dissolved yttrium salt may be nitrate, chloride, perchlorate or sulphate, for
example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L (gram equivalent/litre) to 0.1 Eq/L of yttrium or from 0.0001 Eq/L of yttrium to a saturation concentration to produce an yttrium oxide film having a thickness of about 10nm to about 500nm, for example.

Where a transparent non-conductive scandium oxide layer is to be formed, the ionic source of metal may include at least one dissolved scandium salt. The at least one dissolved scandium salt may be nitrate, chloride, perchlorate or sulphate, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L (gram equivalent/litre) to 0.1 Eq/L of scandium or from 0.0001 Eq/L of scandium to a saturation concentration to produce a scandium oxide film having a thickness of about 10nm to about 500nm, for example.

Where a transparent non-conductive oxide layer of a lanthanide is to be formed, the ionic source of lanthanide may include at least one dissolved lanthanide salt. The at least one dissolved lanthanide salt may be nitrate, chloride, perchlorate or sulphate, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L to 0.1 Eq/L of lanthanide or from 0.0001 Eq/L of lanthanide to a saturation concentration to produce a lanthanide oxide film having a thickness of about 10nm to about 500nm, for example.

Where a transparent non-conductive gallium oxide layer is to be formed, the ionic source of metal may include at least one dissolved gallium salt. The at least one dissolved gallium salt may be nitrate, chloride, perchlorate or sulphate, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L to 0.1 Eq/L of gallium or from 0.0001 Eq/L of gallium to a saturation concentration to produce a gallium oxide film having a thickness of about 10nm to about 500nm, for example.
Where it is desired to form a transparent non-conductive oxide layer comprised of a transition metal of Sub-Group IVA of the periodic table, such as titanium, zirconium or hafnium, the ionic source of such transition metal may include at least one dissolved metal salt. The at least one dissolved metal salt may be chloride or sulphate, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L to 0.1 Eq/L of the transition metal or from 0.0001 Eq/L of the transition metal to a saturation concentration to produce a transparent metal oxide film having a thickness of about 10nm to about 500nm, for example.

Where it is desired to form a transparent non-conductive oxide layer comprised of a metal of Sub-Group IVB of the periodic table, such as germanium, tin or lead, the ionic source of the appropriate metal may include at least one dissolved metal salt. The at least one dissolved metal salt may be chloride or sulphate, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L to 0.1 Eq/L of metal or from 0.0001 Eq/L of metal to a saturation concentration to produce a metal oxide film having a thickness of about 10nm to about 500nm, for example.

Where it is desired to form a transparent non-conductive oxide layer comprised of a transition metal of Sub-Group VA of the periodic table, such as vanadium, niobium or tantalum, the ionic source of such transition metal may include at least one dissolved transition metal salt. The at least one dissolved transition metal salt may be nitrate or chloride, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L to 0.1 Eq/L of metal or from 0.0001 Eq/L of metal to a saturation concentration to produce a metal oxide film having a thickness of about 10nm to about 500nm, for example.

Where it is desired to form a transparent non-conductive oxide layer comprised of a transition metal of Sub-Group VIA of the periodic table such as chromium, molybdenum, or tungsten, the ionic source of such transition metal may include
at least one dissolved transition metal salt. The at least one dissolved transition metal salt may be chloride or sulphate, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L to 0.1 Eq/L of metal or from 0.0001 Eq/L of metal to a saturation concentration to produce a metal oxide film having a thickness of about 10nm to about 500nm, for example.

Where it is desired to form a transparent non-conductive oxide layer of a transition metal of Sub-Group VIIA of the periodic table such as manganese or rhenium, the ionic source of such transition metal may include at least one dissolved transition metal salt. The at least one dissolved transition metal salt may be chloride or sulphate, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L to 0.1 Eq/L of metal or from 0.0001 Eq/L of metal to a saturation concentration to produce a metal oxide film having a thickness of about 10nm to about 500nm, for example.

Where it is desired to form a transparent non-conductive oxide layer of metals of Group VIII of the period table, such as iron, cobalt, nickel or ruthenium, the ionic source of the appropriate metal may include at least one dissolved metal salt. The at least one dissolved metal salt may be chloride or sulphate, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L to 0.1 Eq/L of metal or from 0.0001 Eq/L of metal to a saturation concentration to produce a metal oxide film having a thickness of about 10nm to about 500nm, for example.

Where it is desired to form a transparent non-conductive oxide layer of a metal of Sub-Group VB of the periodic table, such as antimony or bismuth, the ionic source of the appropriate metal may include at least one dissolved metal salt. The at least one dissolved metal salt may be nitrate, chloride or sulphate, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L to 0.1 Eq/L of metal or from 0.0001 Eq/L of metal to a saturation concentration to
produce a metal oxide film having a thickness of about 10nm to about 500nm, for example.

The second electrolyte 20 may include a dopant at a concentration that causes the transparent metal oxide layer to be conductive. The dopant and a concentration of its precursor in the second electrolyte 20 is selected such that a doped transparent conductive metal oxide is formed on the second conductive surface 30, to have a sheet resistance in the range of 1000-10000 Ω/sq, and a transmittance in the visible wavelength range in the range from 60% to 100%.

Dopants may include at least one element from the group comprising halogens, zinc, cadmium, magnesium, copper, silver, gold, boron, aluminum, gallium, indium, scandium, yttrium, germanium, tin, lead, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, cobalt, nickel, ruthenium, arsenic, antimony, bismuth, Pt-group of metals, and lanthanides, for example.

Where a transparent conductive aluminum-doped zinc oxide layer is to be formed, the ionic source of metal may include at least one dissolved zinc salt and at least one dissolved aluminum salt. The dissolved zinc salt may be nitrate, chloride, perchlorate or sulphate, for example. The dissolved aluminum salt may be selected from nitrate, chloride, perchlorate or sulphate for example. The organic solvent electrolyte solution may contain gram equivalents of zinc and aluminum in the ratio of between about 10000:1 to 5:1 to produce an aluminum-doped zinc oxide film having a thickness of about 10nm to about 500nm, for example.

Where an yttrium-doped zinc oxide layer is to be formed, the ionic source of metal may include at least one dissolved zinc salt and at least one dissolved yttrium salt. The dissolved zinc salt may be selected from nitrate, chloride, perchlorate or sulphate for example. The dissolved yttrium salt may be selected
from nitrate, chloride, perchlorate or sulphate, for example. The organic solvent electrolyte solution may contain gram equivalents of zinc and yttrium in the ratio of between about 10000:1 to 5:1 to produce an yttrium-doped zinc oxide film having a thickness of about 10nm to about 500nm.

Where a transparent conductive indium-doped zinc oxide layer is to be formed, the ionic source of metal may include at least one dissolved zinc salt and at least one dissolved indium salt. The dissolved zinc salt may be nitrate, chloride, perchlorate or sulphate for example, and the at least one dissolved indium salt, may be nitrate, chloride, perchlorate or sulphate, for example. The organic solvent electrolyte solution may contain gram equivalents of zinc and indium in the ratio of between about 10000:1 to 5:1 to produce an indium-doped zinc oxide film having a thickness of about 10nm to about 500nm, for example.

Where a transparent conductive cadmium-doped zinc oxide layer is to be formed, the ionic source of metal may include at least one dissolved zinc salt and at least one dissolved cadmium salt. The dissolved zinc salt may be nitrate, chloride, perchlorate or sulphate for example, and the at least one dissolved cadmium salt, may be nitrate, chloride, perchlorate or sulphate, for example. The organic solvent electrolyte solution may contain gram equivalents of zinc and cadmium in the ratio of between about 10:1 to 1:10 to produce a cadmium-doped zinc oxide film having a thickness of about 10nm to about 500nm, for example.

Where a transparent conductive chlorine-doped zinc oxide layer is to be formed, the ionic source of metal may include at least one dissolved zinc salt and at least one dissolved chloride. The at least one zinc salt may be nitrate, chloride, perchlorate or sulphate, for example. The organic solvent electrolyte solution may contain from 0.0001 Eq/L (gram equivalent/litre) to 0.1 Eq/L of zinc or from 0.0001 Eq/L of zinc to concentration of saturated solution and from 0.0001 Eq/L to 0.1 Eq/L of chloride or from 0.0001 Eq/L of chloride to concentration of saturated
solution to produce a chlorine-doped zinc oxide film having a thickness of about 10nm to about 500nm, for example.

Where a transparent conductive tin-doped indium oxide layer is to be formed, the ionic source of metal may include at least one dissolved indium salt and at least one dissolved tin salt. The dissolved indium salt may be nitrate, chloride, perchlorate or sulphate for example, and the at least one dissolved tin salt may be selected from nitrate, chloride, or sulphate, for example. The organic solvent electrolyte solution may contain gram equivalents of indium and tin in the ratio of between about 200:1 to 1:1 to produce a tin-doped indium oxide film having a thickness of about 10nm to about 500nm, for example.

Where a transparent conductive indium-doped cadmium oxide layer is to be formed, the ionic source of metal may include at least one dissolved cadmium salt and at least one dissolved indium salt. The dissolved cadmium salt may be nitrate, chloride, perchlorate or sulphate for example, and the at least one dissolved indium salt may be nitrate, chloride, perchlorate or sulphate for example. The organic solvent electrolyte solution may contain gram equivalents of cadmium and indium in the ratio of between about 1000:1 to 10:1 to produce an indium-doped cadmium oxide film having a thickness of about 10nm to about 500nm, for example.

The apparatus may be used as shown in Figure 2 with the substrate stationary but this will only produce a transparent metal oxide layer on the second conductive surface portion 30. To do this, the first and second electrolytes 14 and 16 are configured using a desired one of the options above to include chemicals that will produce the desired metal oxide layer and then the constant current power supply 108 is activated to apply a potential between the second and first electrodes 22 and 16 such that an electric current flows from the second electrode 22, through the second electrolyte 20 to the second conductive surface
portion 30, through the conductive surface 32 extending over the interior wall seal 172 to the first conductive surface portion 28 then through the first electrolyte 14 to the first electrode 16.

Referring to Figure 3 an equivalent circuit is shown generally at 201. The equivalent circuit includes the power supply 108 and wires 104 and 132 connected to the first and second electrodes 16 and 22. The second electrode (22) is represented by a first resistance 203. The second electrolyte 20 is represented by a second resistance 205, the second conductive surface portion (30) is represented by a third resistance 207, the first conductive surface portion (28) is represented by a fourth resistance 209, the first electrolyte 14 is represented by a fifth resistance 211 and the first electrode 16 is represented by a sixth resistance 213.

In effect, resistances 203, 205, 207, 209, 211 and 213 are connected in series across the positive and negative terminals of the power supply 108 such that the second electrode 22 is at a higher positive potential than the first electrode 16. This causes a voltage drop to occur across each of the resistances which sets the potential at an interface 215 between the second electrode 22 and the interface 217 between the second electrolyte and the second conductive surface portion 30 to be at a higher potential which facilitates a cathodic chemical reaction at the interface 217 that forms the transparent metal oxide layer. The second conductive surface portion 30 has a relatively low conductivity and therefore the negative cathodic potential is relatively uniform along the second conductive surface portion 30 and facilitates the formation of a corresponding uniform transparent metal oxide layer on the second conductive surface portion 30.

It will be appreciated that if an ion exchange path between the first electrolyte 14 and the second electrolyte 20 is present, a resistive current flow path as represented by resistance R7 in Figure 3, which shunts current between the first
and second conductive surface portions 28 and 30 which results in a decrease in plating efficiency at the second conductive surface. This decrease in plating efficiency results when the resistance due to the ion exchange path significantly reduces the combined voltage drop across the first and second conductive surface points 28 and 30 which reduces the current flow through the second conductive surface portion 30, which reduces the amount of electron exchange at the second conductive surface portion 30 and hence reduces the formation of the transparent metal oxide layer thereon.

Referring back to Figure 2, in the embodiment shown, the power supply 108 is provided with a current source 107 and provisions for counting coulombs of charges in the electric current that flows through the circuit 201 shown in Figure 3. Referring back to Figure 2 the power supply 108 further includes provisions, in communication with the provisions for counting coulombs, for ceasing the application of the electric potential when a coulomb charge count indicated by the provisions for counting coulombs meets a criteria associated with the desired thickness of the transparent metal oxide coated on the second conductive surface portion 30. The provisions for counting coulombs charges may include an ammeter with an integration function which can be implemented by a current shunt 109 and a processor circuit 111 for example, for monitoring voltage across the shunt to produce a signal indicative of current flow. The processor circuit 111 may include an integration program that integrates the current signal to produce a coulomb charge count value. The provisions for ceasing the application of the electric potential may include the processor circuit 111 and program code that causes the processor circuit 111 to compare the coulomb charge count with a predefined number associated with a desired thickness of the transparent metal oxide, and which activates an output of the processor circuit 111 operable to control a relay 113, for example, for interrupting the circuit to thereby cease the application of the electric potential to the first and second electrodes 16 and 20 and to cease the flow of electric current in the circuit. Alternatively, or in addition,
the processor circuit 111 may monitor an ion conductivity sensor (not shown) in the second electrolyte 20, to obtain a representation of conductivity of the second electrolyte, such conductivity being proportional to the number of metal ions in the second electrolyte. The processor circuit 109 may further include program code that causes it to activate output signals to automatically open valves (not shown) on drain conduits (not shown) connected to the drain openings 196 and 198 to drain the first and second electrolyte 14 and 20. The program code may also cause the processor circuit 109 to close the valves on the drain conduits and then open valves (not shown) on inlet conduits (not shown) connected to the electrolyte admittance openings 192 and 194 to allow new first and second electrolytes 14 and 20 to be admitted into the first and second open-faced containers 50 and 52. The program code may also direct the processor circuit 109 to cause the relay 113 to energize to cause the potential to be reapplied between the second and first electrodes 22 and 16 to thereby re-establish the flow of electric current after the first and second electrolytes 14 and 20 has been replaced.

While the apparatus 10 shown in Figures 1 and 2 may be used to form a transparent metal oxide layer on the second conductive surface portion 30, it will be appreciated that this represents only a small portion of the overall conductive surface 32. In addition, it will be appreciated that due to the relatively low conductivity of the conductive surface 32 of the dielectric substrate 34, the negative cathodic potential on the second conductive surface 30 is lengthwise insufficiently uniform to facilitate the formation of a corresponding uniform transparent metal oxide layer on a practically useful length of the conductive surface 32 of the dielectric substrate 34. A larger area of the conductive surface of the dielectric substrate can receive a uniform transparent metal oxide layer if the substrate 34 is smoothly moved relative to the first and second electrolytes 14 and 20 to expose the entire length of the substrate 34 to the second electrolyte 20 and thereby gradually uniformly plate the conductive surface
thereof. The conductivity of the conductive surface 32 of the dielectric substrate 34, the lengths of the first and second open-faced containers 50 and 52 and the linear speed of the substrate 34 can be optimized to provide a high degree of uniformity in the thickness of the transparent metal oxide layer, optical transparency and conductivity on a given length of dielectric substrate.

Referring to Figure 4, the apparatus 10 may be employed to form a transparent metal oxide layer on a large portion of the conductive surface 32 of the dielectric substrate 34 by moving the dielectric substrate 34 relative to the first and second electrolytes 14 and 20 in a direction from the first electrolyte 14 to the second electrolyte 20 while the electric current is flowing to cause the transparent metal oxide layer to be formed in a lengthwise direction along the conductive surface 32 of the dielectric substrate 34.

To facilitate this relative movement of the substrate relative to the first and second electrolytes the apparatus 10 is provided with a first entrance capstan 220 and entrance pinch roller 222 and with an exit capstan 224 and exit pinch roller 226. The entrance and exit capstans 220 and 224 and the pinch rollers 222 and 226 have resiliently deformable outer surfaces that gently grip the dielectric substrate 34 and its conductive surface 32 to direct the dielectric substrate through the apparatus 10. The entrance capstan 220 is rotated in a clockwise direction and bears upon the conductive surface 32 of the dielectric substrate 34 while the entrance pinch roller 222 bears upon the uncoated surface of the dielectric substrate 34. The dielectric substrate 34 is thus pinched between the entrance capstan 220 and the entrance pinch roller 222 such that when the entrance capstan 220 rotates, the dielectric substrate 34 is pushed into the entrance opening 70 in a direction shown by arrow 228.

At the same time, the exit capstan 224 also rotates in a clockwise direction and bears upon the conductive surface 32 of the dielectric substrate 34 that has just
been coated due to exposure to the second electrolyte 20, while the exit pinch roller 226 bears upon the uncoated surface of the dielectric substrate 34 such that the substrate is pinched between the exit capstan 224 and the exit pinch roller 226, which further assists linear movement of the dielectric substrate 34 by drawing the substrate out of the exit opening 152. This allows a dielectric substrate having a conductive surface, of any length to be coated with a transparent metal oxide layer. The speed of rotation of the entrance and exit capstans 220 and 224 is such that the time that a given second surface portion 30 of the conductive surface 32 on the dielectric substrate 34 is exposed to the second electrolyte 20 is sufficient to cause a transparent metal oxide layer of a desired thickness to be formed thereon. As the concentration of metal ions in the second electrolyte 20 decreases the speed of rotation of the entrance and exit capstans 220 and 224 should be decreased accordingly, to maintain a uniform thickness in the layer being formed until the concentration of metal ions in the second electrolyte 20 reaches a predefined metal ion concentration at which point the sequence of ceasing the application of current, replacing the second electrolyte, and then reapplying the electric current, as described above, is initiated. A succession of sequences i.e. replenishments of the second electrolyte, may be required and the number of replenishments will depend upon the length of the dielectric substrate on which the transparent metal oxide layer is to be formed. In the embodiment shown, the entrance and exit capstans 220 and 224 may be rotated so as to produce a linear motion of the substrate 34 relative to the apparatus 10, on the order of between about 0.1 cm per minute and about 10 cm per minute, for example.

The lengths of the first or second open-faced containers and the speed of the dielectric substrate motion are independently optimised for high uniformity in conductive metal oxide thickness, optical transparency and conductivity on a large length of dielectric substrate.
Referring to Figure 5, the apparatus 10 shown in Figure 1 can be used in a system 250 according to a third embodiment of the invention to form a transparent metal oxide layer on a conductive surface 246 of a dielectric substrate 248 formed of a polymeric film such as, for example, Polyethylene Terephthalate (PET). In this case, a roll of PET film shown generally at 252 is provided on a spindle 254 and is operable to rotate in a counter clockwise direction 256 with a leading edge thereof being fed into the entrance opening 150 of the apparatus 10. The leading edge is routed through the entrance wall 54, over the first and second open-faced containers 50 and 52 and then through the exit opening 152 in the exit wall 62. The leading edge is then wrapped around a take up spindle 258 also operable to rotate in a counter clockwise direction. At least the take up spindle 258 is driven by a motor, for example (not shown) to draw the dielectric substrate 248 through the apparatus 10 over the first and second electrolytes 14 and 20, at a suitable speed to form the transparent metal oxide layer on the conductive surface 246 of the dielectric substrate 248. Thus, a transparent metal oxide layer can be formed on a PET film pre-formed with an initial transparent conductive surface and the PET film can be of any length. Replenishment of the second electrolyte as described above may be required, depending on the volume of the second electrolyte, the width of the film and the length of the film.

Referring to Figure 6, an apparatus according to a fourth embodiment of the invention is shown generally at 300. The apparatus 300 includes a deep tray container 302 having first and second end walls 304 and 306, first and second side walls 308 and 310 and a bottom wall 312. Elongated openings 314 are provided in the bottom wall 312 to accommodate heating elements, as described above. The deep tray container 302 is made of a chemically stable and thermally conductive material such as, for example, Teflon® refloowed aluminium suitable for inertly holding a volume of an initial electrolyte 316. A substrate 318 having a conductive surface 320 to be coated is placed in the deep tray container 302
such that the conductive surface 320 is face up, in contact with the initial electrolyte 316. Referring to Figure 7, the deep tray container 302 has a fill opening 303 in on the first end wall 304 and has a drain opening 307 in an opposite end wall 306, for side filling and draining of electrolyte respectively.

Referring back to Figure 6, in this embodiment, an apparatus similar to that shown at 10 in Figure 2, in an inverted position is shown generally at 350. The apparatus 350 is similar to that shown in Figure 2, in that it has a generally rectangular shape and it has entrance, exit and interior walls 352, 354 and 356 and side walls, only one of which is shown at 358, and has a bottom wall portion 360. The bottom wall portion 360 faces upward and is the uppermost part of the apparatus because the apparatus is used in an inverted orientation as shown. The apparatus 350 however, differs from that shown in Figure 2 in that the entrance and exit walls 352 and 354 have no entrance and exit openings and the interior wall 356 is not shorter than the entrance and exit walls 352 and 354. Rather, the entrance, exit and interior walls 352, 354 and 356 have coplanar distal end surfaces 362, 364, 366 on which are provided respective elastomeric seals 368, 370 and 372. Similar seals are provided on coplanar distal end surfaces of the end walls 358. A first open-faced container 380 therefore is formed between the entrance wall 352, the interior wall 356, and the end walls 358 and the bottom portion 360. Similarly, a second open-faced container 382 is formed between the exit wall 354, the interior wall 356, the end wall 358 and the bottom wall portion 360. The apparatus 350 of this embodiment also differs from the apparatus shown in Figure 2 in that first and second electrodes 390 and 392 respectively, the same as those shown at 16 and 22 in Figure 2, are shown extending though respective elongated openings 393 and 394 in the bottom wall portion 360 to extend into the first and second open faced containers 380 and 382 respectively. The openings 393 and 394 are sealed by elastomeric seals 396 and 398 respectively of the type described above in connection with seals 76 and 78, to prevent any electrolyte in the first and second open-faced containers
380 and 382 from leaking though the bottom portion 360. In addition, the bottom
portion 360 has at least one opening, in this case first and second pluralities of
openings shown generally at 400 and 402 associated with the first and second
open-faced containers 380 and 382 respectively for releasing air as the
apparatus 350 is lowered into the deep tray container 302 as will be explained
below. The apparatus 350 is connected to provisions 420 for positioning the first
and second open-faced containers 380 and 382 face down on the conductive
surface 320 of the dielectric substrate 318 such that the substrate extends under
the entrance wall 352, the exit wall 354 and the interior wall 356 and the first and
second pairs of end walls 358 such that first and second conductive surface
portions 422 and 424 of the dielectric substrate 318 face the first and second
open-faced containers 380 and 382 as shown in broken outline in Figure 7. In
the embodiment shown, the provisions for effecting this positioning of the
apparatus 350 is provided by a telescopic robotic arm having a horizontally
extendable and retractable arm 430 and a vertical retractable and extendable
stand 432.

As seen by the depiction of the apparatus 350 in broken outline, the apparatus is
lowered into the deep tray 302 by the vertical retractable and extendable stand
432. The deep tray 302 and the apparatus 350 are dimensioned such that the
first and second pairs of end walls 358, 359 abut inside surfaces of the side walls
308 and 310.

Referring to Figure 7, the apparatus 350 is lowered into the deep tray container
302 until the seals 368, 370 and 372 and the end wall seals are in contact with
the conductive surface 320 of the substrate 318 so as to close the open-faced
containers 380 and 382 with first and second conductive surface portions 422
and 424 of the substrate 318 respectively to thereby create first and second
electrolyte-isolated electrochemical cells within the first and second open-faced
containers 380 and 382. The first and second open-faced containers 380 and
382 are nearly submerged in the initial electrolyte 316 capturing a first volume 381 of the initial electrolyte 316 in the first open-faced container 380 and capturing a second volume 383 of the initial electrolyte 316 in the second open-faced container 382, while leaving an air gap between the surface of the first volume and the bottom wall portion 360 and an air gap between the surface of the second volume and the bottom wall portion 360. The seals, 368, 370 and 372 and end wall seals thus act to seal the entrance wall 352, exit wall, 354 interior wall 356 and the first and second end walls 358 against the conductive surface 320 of the substrate 318 to contain a first volume 381 of the initial electrolyte 316 in the first open-faced container 380 and to contain a second volume 383 of the initial electrolyte 316 in the second container 382.

The air gaps enable electrolyte adjustment chemicals to be added to the first and/or second volumes through the openings 400 and 402. For example, it may be desirable to add acid or alkali to the first volume to adjust the pH of the first volume of electrolyte to a desired value to protect the first electrode from metal oxide formation on its surface.

Still referring to Figure 7, the power supply 108 described in connection with Figure 2 is connected to the first and second electrodes 390 and 392 respectively such that the second electrode 392 is more positive than the first electrode 390 to thereby cause a current to flow from the second electrode 392 into the second volume 383 of electrolyte in the second open faced container 382, through the second conductive surface portion 424 through the conductive surface 320 (not shown on Fig 7) under the interior wall 356 into the first conductive surface portion 422 and then into the first volume 381 of electrolyte in the first open-faced container 380 and then into the first electrode 390. This causes the second conductive surface portion 424 to be more negative than the second electrode 392 thereby causing the transparent metal oxide layer to form on the second conductive surface portion 424.
If the apparatus 350 is kept stationary in the tray 302, only the second conductive surface portion 424 in contact with the electrolyte in the second open faced container 382 will be coated. To coat a larger surface area however, the horizontally extendable and retractable arm 430 may be moved, in a direction shown by arrow 433 while holding the tray 302 and the dielectric substrate 318 stationary, to move the apparatus 350 into the position shown in broken outline in Figure 7. The horizontally extendable and retractable arm 430 may be moved in the direction of arrow 433 at a linear speed of about 0.1 cm per minute to about 10 cm per minute, for example, as in the first embodiment, to cause the first and second open faced containers 380 and 382 to be scanned over the conductive surface 320 of the substrate 318 to continuously coat substantially all of the conductive surface 320, from the second conductive surface portion 424 shown in solid outline to a final second conductive surface portion 440 finally in contact with the electrolyte in the second open-faced container 382 in the final position of the apparatus 350 shown in broken outline in Figure 7. It will be appreciated that a transparent metal oxide conductive surface is not formed on a final first surface portion 442 because this portion is not exposed to the second volume 383 of electrolyte in the second open-faced container 382, where the final second conductive surface portion 440 is at a potential more negative than the second electrode 392. Thus, a small portion (final first surface portion 442) of the conductive surface 320 on the substrate 318 will not be coated with the transparent metal oxide, in this embodiment.

Referring to Figure 8, an apparatus according to a fifth embodiment of the invention is shown generally at 500. The apparatus 500 includes an electrochemical cell assembly shown generally at 502 and a pressing assembly shown generally at 504.
Referring to Figure 9, the electrochemical cell assembly 502 is shown in an exploded view and includes a first electrode 503 comprising a rectangular dielectric substrate 507 having a conductive surface 506 on which is to be formed a transparent metal oxide layer. The substrate 507 has first and second end edges 508 and 510 to which are connected clamps 512 and 514 respectively. The clamps 512 and 514 are as described in connection with clamp 92 in Figure 2. Clamps 512 and 514 are electrically connected together by wires 513 and 515 that are at the same electrical potential and are connected to the negative terminal 106 of the power supply 108, described in connection with Figure 2. A space-defining frame gasket 516 is positioned on the conductive surface 506 of the dielectric substrate 507. The space-defining frame gasket may be made from a soft elastic rubber material such as, Viton™ produced by Dupont, for example. The gasket 516 has a rectangular form matching a corresponding uncovered area of the first conductive layer 506, between the first and second clamps 512 and 514 and between side edges, only one of which is shown at 518 in Figure 9. The gasket 516 is formed to have a rectangular opening 520 defined by an inner wall 522 of the gasket 516. The inner wall 522 defines a space 524 bounded by the inner wall 522 and a portion 526 of the conductive surface 506 of the dielectric substrate 504. The gasket 516 has a frame portion 528 having first and second openings 530 and 532 extending therethrough and in communication with the space 524. These openings 530 and 532 receive and hold first and second conduits 534 and 536 respectively for receiving and draining electrolyte respectively from the space 524 as will be described below.

The electrochemical cell assembly 502 further includes a second electrode 505 comprising a second substrate 550 having a second conductive surface 552 and third and fourth clamps 554 and 556 disposed along first and second edges 558 and 560 respectively of the second substrate 550 and in contact with the second conductive surface 552. The clamps 554 and 556 are the same as the clamps
shown at 512 and 514 and hence the same as the clamp shown at 92 in Figure 2. These clamps 554 and 556 are electrically connected to each other by wires 555 and 557 connected to the positive terminal 134 of the power supply 108 described in connection with Figure 2.

Referring back to Figure 9, the second electrode 505 is placed against a planar face 517 of the gasket 516 such that the planar face 517 of the gasket 516 contacts the portion of the conductive surface 552 between the clamps 554 and 556.

Referring back to Figure 8, the pressing assembly 504 includes first and second steel plates 600 and 602 shaped to have respective surface portions that contact areas of the first and second substrates 504 and 505 respectively that are unoccupied by the clamps 512, 514, 555, and 556 and are further shaped to have first and second outwardly extending side portions, only the first outwardly extending side portion 604 of the first plate 600 being shown in Figure 8 and both the first and second outwardly extending side portions 606 and 608 of the second plate 602 being shown in Figure 8. The first outwardly extending side portions 604 and 606 include first openings 610 and 612. Opening 610 in the first plate 600 is threaded and opening 612 in the second plate 602 is smooth to receive a bolt 614, therethrough. Similar openings are provided on the second outwardly extending portions, of which only the outwardly extending portion 608 is shown with a bolt 616 received therein. The bolts 614 and 616 are the same and each has a threaded portion 618, a smooth portion 620 and a head portion 622. Bolt 614 is received through the opening 612 to allow the threads 618 to engage with mating threads in the threaded opening 610. Bolt 616 is similarly engaged with corresponding openings on the second outwardly extending side portions of the first and second plates 600 and 602. The bolts 614 and 616 are then tightened to draw the first and second plates 600 and 602 together to thereby press the first and second conductive surfaces 506 and 552 against opposite face sides of
the gasket 516 thereby sealing the space 524 (see Figure 9). An electrolyte having a composition as explained in connection with the second electrolyte described above in connection with the first embodiment is then pumped into the space (524) through the first conduit 534 and air is allowed to escape through the second conduit 536 until the space (524) is completely filled with electrolyte. Then, the power supply 108 is activated to apply an electric potential between the conductive surface 506 of the dielectric substrate 507 to be coated with the transparent metal oxide and the first conductive surface 552 of the substrate 550, such that the first conductive surface 552 of the second substrate 550 has a positive polarity relative to the conductive surface 506 of the dielectric substrate 507 to cause an electric current to flow between the first conductive surface 552 and the conductive surface 506 of the dielectric substrate 507 through the electrolyte in the space (524) to cause an electrochemical reaction to occur at the conductive surface 506 of the dielectric substrate 507 to form the transparent metal oxide layer on the conductive surface 506 of the dielectric substrate 507. As described above in connection with the first embodiment, the power supply 108 has provisions for counting coulombs of charges in the electric current and may have provisions for ceasing the application of the electric potential when a coulomb count criterion associated with a desired thickness of the transparent metal oxide. In addition, the power supply may have provisions for interrupting the current when a concentration of metal ions in the second electrolyte meets a metal ion concentration criterion. The apparatus may further include provisions for removing ion-depleted electrolyte from the space 524 by blowing air into the first conduit 534 thereby forcing the electrolyte out through the second conduit 536, for example. Alternatively, or in addition, the electrolyte may be flushed out with a flushing fluid such as a solvent with no metal ions, for example. Once the electrolyte has been flushed, a new volume of electrolyte may be admitted into the space 524 by pumping it through the first conduit 534 as described above.
Then, the power supply 108 may be automatically or manually re-activated to re-establish the electric current after the electrolyte has been replaced.

In each of the embodiments described above, there is provided a process and apparatus for electrochemically forming a transparent metal oxide on a conductive surface of a dielectric substrate such as glass, polymer or ceramic material. The above described apparatus and processes they perform provide a metal oxide layer having a high uniformity of thickness and a high degree of uniformity of electrical conductivity and optical transparency. This high degree of uniformity can be achieved over a relatively large conductive surface of the dielectric substrate by using above-described the methods of moving the substrate while holding the electrolytes stationary as described in connection with the first, second, third and fourth embodiments above or by moving the electrolytes while holding the substrate stationary as in the fourth embodiment.

In the case of the first, second, third and fourth embodiments, the conductive layer on the substrate is coated with the transparent metal oxide layer with little or no degradation of the counter electrodes used in the respective first and second electrochemical cells employed.

While specific embodiments of the invention have been described and illustrated, such embodiments should be considered illustrative of the invention only and not as limiting the invention as construed in accordance with the accompanying claims.
THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method of forming a transparent metal oxide layer on a conductive surface of a dielectric substrate, the method comprising:

   exposing first and second conductive surface portions of the conductive surface of the dielectric substrate to first and second electrolytes respectively;

   forming a first electrochemical cell comprised of the first conductive surface portion in contact with said first electrolyte and a first electrode in contact with said first electrolyte and spaced apart from the first conductive surface portion;

   forming a second electrochemical cell comprised of the second conductive surface portion in contact with said second electrolyte and a second electrode in contact with said second electrolyte and spaced apart from the second conductive surface portion;

   wherein said first and second electrochemical cells are electrically connected together in series by the conductive surface; and

   wherein said first electrolyte has first chemicals that facilitate conduction of electric current through said first electrolyte without facilitating significant electrochemical reaction at said first electrode or at the first conductive surface portion; and

   wherein said second electrolyte has second chemicals that facilitate conduction of electric current through said second electrolyte, said
second chemicals including a non-aqueous solvent, metal ions in a metal ion concentration at least sufficient to facilitate formation of the transparent metal oxide layer to a desired thickness and a source of oxygen suitable to facilitate formation of the transparent metal-oxide layer on the second conductive surface portion;

applying an electric potential between said first and second electrodes such that said second electrode has a positive polarity relative to said first electrode to cause an electric current to flow between said second electrode and said first electrode in series through said second electrolyte, the second conductive surface portion, the first conductive surface portion and said first electrolyte;

such that said second electrode is at a sufficiently more positive potential than the second conductive surface portion to cause an electrochemical reaction to occur at the second conductive surface portion to form said transparent metal oxide layer on the second conductive surface portion.

2. The method of claim 1 wherein said non-aqueous solvent is protic or aprotic.

3. The method of claim 1 or 2 further comprising releasing metal ions capable of forming the transparent metal oxide layer to be optically transparent in the visible region of the electromagnetic spectrum, from salts soluble in said non-aqueous solvent.

4. The method of any one of claims 1 - 3 further comprising causing said second electrolyte to include a dopant electrochemically embeddable into
the transparent metal oxide layer to produce a conductive transparent metal oxide layer.

5. The method of claim 4 further comprising admitting a chemical supplement into at least one of said first and second electrolytes.

6. The method of any one of claims 1 - 5 further comprising counting coulombs of charges in said electric current and ceasing the application of said electric potential when a coulomb charge count meets a charge count criterion associated with a desired thickness of said transparent metal oxide layer.

7. The method of any one of claims 1 - 6 further comprising interrupting said current when said metal ion concentration in said second electrolyte meets a metal ion concentration criterion, replacing said second electrolyte, and re-establishing said electric current.

8. The method of any one of claims 1 - 7 further comprising moving said substrate relative to said first and second electrolytes in a direction from said first electrolyte to said second electrolyte while said electric current is flowing, to cause said transparent metal oxide layer to be formed in a lengthwise direction along the conductive surface of the substrate.

9. The method of any one of claims 1 - 7 wherein forming said first and second electrochemical cells comprises holding said first electrolyte in a first open-faced container and holding said second electrolyte in a second open-faced container.

10. The method of claim 9 further comprising defining said first and second open-faced containers by an entrance wall, an interior wall, an exit wall,
first end wall portions and a first bottom wall portion, such that said first open-faced container is defined between said entrance wall, said interior wall, said first end wall portions and said first bottom wall portion and such that said second open-faced container is defined between said interior wall, said exit wall, second end wall portions and a second bottom wall portion.

11. The method of claim 10 further comprising causing said first electrode to extend through said entrance wall, a first end wall portion or said first bottom wall portion, at a first position in parallel spaced apart relation to said substrate and causing said second electrode to extend through said exit wall, a second end wall portion or said second bottom wall portion, at a second position in parallel spaced apart relation to said substrate.

12. The method of any one of claims 9 - 11 further comprising admitting the dielectric substrate having the conductive surface through an entrance opening in said entrance wall and causing said substrate to extend over said first and second open-faced containers such that said conductive surface faces said first and second open-faced containers, wherein said first conductive surface portion is a portion of the conductive surface that extends over said first container and wherein said second conductive surface portion is a portion of said conductive surface that extends over said second open-faced container and wherein the method further comprises causing a portion of said substrate to extend through an exit opening in an exit wall of said second open-faced container.

13. The method of claim 12 further comprising causing said entrance opening, and said exit opening to be sealed against the conductive layer on said dielectric substrate to prevent leakage of said first and second electrolytes respectively from said entrance and exit openings respectively.
14. The method of claim 13 further comprising causing said interior wall to be sealed against the conductive surface on said dielectric substrate to prevent exchange of said first and second electrolytes at said interior wall.

15. The method of any one of claims 9 - 14 further comprising moving said substrate relative to said first and second electrolytes in a direction from said first electrolyte to said second electrolyte while said electric current is flowing, to cause said transparent metal oxide layer to be formed in a lengthwise direction along the conductive surface of the substrate.

16. The method of claim 15 wherein moving comprises moving said substrate while holding said first and second open-faced containers stationary.

17. The method of any one of claims 9 - 11 further comprising causing the first and second open-faced containers to be placed open-face down on the conductive surface of the dielectric substrate such that the substrate extends under said entrance wall, said interior wall, said exit wall, and said first and second end wall portions such that the first and second conductive surfaces of the dielectric substrate face said first and second open-faced containers, wherein said first conductive surface portion is a portion of the conductive surface that extends under said first open-faced container and wherein the second conductive surface portion is a portion of said conductive surface that extends under said second open-faced container and wherein the method further comprises causing a portion of said conductive surface of the dielectric substrate to extend under said exit wall of said second open-faced container.

18. The method of claim 17 further comprising holding said dielectric substrate with the conductive surface face-up in a container holding an initial
electrolyte and wherein causing the first and second open-faced containers to be placed open-face down on the conductive surface of the dielectric substrate comprises causing the first and second open-faced containers to be substantially submerged in said initial electrolyte and causing said entrance wall, said exit wall, and said first and second end wall portions to be sealed against said substrate to contain a first volume of said initial electrolyte in said first open-faced container and to contain a second volume of said initial electrolyte in said second open-faced container.

19. The method of claim 18 further comprising causing said interior wall to be sealed against the conductive surface of said dielectric substrate to prevent leakage of said first and second electrolytes respectively under said interior wall.

20. The method of any one of claims 9 - 12 and 17 - 19 further comprising moving said substrate relative to said first and second electrolytes in a direction from said first electrolyte to said second electrolyte while said electric current is flowing, to cause said transparent metal oxide layer to be formed in a lengthwise direction along the conductive surface of the substrate.

21. The method of claim 20 wherein moving comprises moving said first and second open-faced containers while holding said substrate stationary.

22. A method of forming a transparent metal oxide layer on a first conductive surface of a first dielectric substrate, the method comprising:

   pressing a first conductive surface of the first dielectric substrate against a space-defining frame gasket on a second conductive
surface of a second dielectric substrate such that the frame defines a sealed space between the first conductive surface and the second conductive surface;

admitting an electrolyte having chemicals that facilitate conduction of electric current through said electrolyte into the sealed space through an opening in said frame gasket, said chemicals including a non-aqueous solvent, metal ions in a metal ion concentration at least sufficient to facilitate formation of the transparent metal oxide layer to a desired thickness and a source of oxygen suitable to facilitate formation of the transparent metal-oxide layer on the first conductive surface; and

applying an electric potential between said first and second conductive surfaces such that said first conductive surface has a negative polarity relative to said second conductive surface to cause an electric current to flow between said second conductive surface and said first conductive surface through said electrolyte to cause an electrochemical reaction to occur at the first conductive surface to form said transparent metal oxide layer on the first conductive surface.

23. The method of claim 22 wherein said non-aqueous solvent is protic or aprotic.

24. The method of claim 22 or 23 further comprising releasing metal ions capable of forming the transparent metal oxide layer to be optically transparent in the visible region of the electromagnetic spectrum, from salts soluble in said non-aqueous solvent.
25. The method of any one of claims 22 - 24 further comprising causing said second electrolyte to include a dopant electrochemically embeddable into the transparent metal oxide layer to produce a conductive transparent metal oxide layer.

26. The method of claim 25 further comprising admitting a chemical supplement into said electrolyte.

27. The method of any one of claims 22 - 26 further comprising counting coulombs of charges in said electric current and ceasing the application of said electric potential when a coulomb charge count meets a coulomb charge count criterion associated with a desired thickness of said transparent metal oxide layer.

28. The method of any one of claim 22 - 26 further comprising interrupting said current when a metal ion concentration in said electrolyte meets a metal ion concentration criterion, replacing said electrolyte, and re-establishing said electric current.

29. The method of any one of claims 22 - 28 wherein said pressing comprises pressing sufficiently to compress said space-defining frame gasket to sufficiently seal said sealed space to prevent leakage of said electrolyte from said sealed space.

30. The method of any one of claims 22 - 29 wherein said applying an electric potential comprises fastening first and second conductive clamps on first and second opposite edges respectively of said first substrate to make electrical contact with said first conductive surface at opposite edges of said first substrate and fastening third and fourth of conductive clamps on third and fourth edges of said dielectric substrate to make electrical contact.
contact with said second conductive surface on said dielectric substrate and connecting said first and second clamps to a positive terminal of a current source and connecting said third and fourth clamps to a negative terminal of the current source.

31. An apparatus for forming a transparent metal oxide layer on a conductive surface of a dielectric substrate, the apparatus comprising:

- means for holding a first electrolyte and a first electrode in contact with said first electrolyte;

- means for holding a second electrolyte and a second electrode in contact with said second electrolyte;

- means for simultaneously exposing first and second conductive surface portions of the conductive surface of the dielectric substrate to said first and second electrolytes respectively, such that the first and second conductive surface portions are spaced apart from the first and second electrodes respectively to form first and second electrochemical cells respectively and whereby said first and second electrochemical cells are electrically connected together in series by the conductive surface of the dielectric substrate;

wherein said first electrolyte has first chemicals that facilitate conduction of electric current through said first electrolyte without facilitating significant electrochemical reaction at said first electrode or at the first conductive surface portion; and

wherein said second electrolyte has second chemicals that facilitate conduction of electric current through said second electrolyte, said
second chemicals including a non-aqueous solvent, metal ions in a metal ion concentration at least sufficient to facilitate formation of the transparent metal oxide layer to a desired thickness and a source of oxygen suitable to facilitate formation of the transparent metal-oxide layer on the second conductive surface portion;

means for applying an electric potential between said first and second electrodes such that said second electrode has a positive polarity relative to said first electrode to cause an electric current to flow between said second electrode and said first electrode in series through said second electrolyte, the second conductive surface portion, the first conductive surface portion and said first electrolyte;

such that said second electrode is at a sufficiently more positive potential than the second conductive surface portion to cause an electrochemical reaction to occur at the second conductive surface portion to form said transparent metal oxide layer on the second conductive surface portion.

32. The apparatus of claim 31 wherein said non-aqueous solvent is protic or aprotic solvent.

33. The apparatus of claim 31 or 32 further comprising releasing metal ions capable of forming the transparent metal oxide layer to be optically transparent in the visible region of the electromagnetic spectrum, from salts soluble said in non-aqueous solvent.

34. The apparatus of any one of claims 31 - 33 further comprising causing said second electrolyte to include a dopant electrochemically embeddable
into the transparent metal oxide layer to produce a conductive transparent metal oxide layer.

35. The apparatus of any one of claims 31 - 34 further comprising means for counting coulombs of charges in said electric current and means, in communication with said means for counting coulombs, for ceasing the application of said electric potential when a coulomb charge count indicated by said means for counting coulombs meets a coulombs count criterion associated with a desired thickness of said transparent metal oxide layer.

36. The apparatus of any one of claim 31 - 35 further comprising means for interrupting said current when a metal ion concentration in said second electrolyte meets a metal ion concentration criterion, means for replacing said second electrolyte, and means for re-establishing said electric current after second electrolyte has been replaced.

37. The apparatus of any one of claims 31 - 36 further comprising means for moving said substrate relative to said first and second electrolytes in a direction from said first electrolyte to said second electrolyte while said electric current is flowing, to cause said transparent metal oxide layer to be formed in a lengthwise direction along the conductive surface of the substrate.

38. The apparatus of any one of claims 31 - 36 wherein said means for holding said first electrolyte and said first electrode comprises a first open-faced container and wherein said means for holding said second electrolyte and said second electrode comprises a second open-faced container.
39. The apparatus of claim 38 wherein said first open-faced container comprises an entrance wall and an interior wall, a pair of first end walls and a first bottom wall portion and wherein said second open-faced container comprises said interior wall and an exit wall and a pair of second end walls and a second bottom wall portion wherein said first and second open-faced containers have first and second end wall portions.

40. The apparatus of claim 39 wherein said first electrode extends through said entrance wall, at least one of said first end wall portions or said first bottom wall portion, at a first position in parallel spaced apart relation to said substrate and wherein said second electrode extends through said exit wall, at least one of said second end wall portions or said second bottom wall portion, at a second position in parallel spaced apart relation to said conductive surface of the dielectric substrate.

41. The apparatus of any one of claims 39 or 40 wherein said means for simultaneously exposing the first and second surface portions of the conductive surface of the substrate comprises an entrance opening in said entrance wall and an exit opening in said exit wall, for receiving and positioning said dielectric substrate to cause said dielectric substrate to extend over said first and second open-faced containers such that said first conductive surface portion faces said first open-faced container and such that said second conductive surface portion faces said second open-faced container.

42. The apparatus of claim 41 further comprising entrance and exit seals operably configured to seal said entrance opening and said exit opening against the conductive surface of said dielectric substrate to prevent leakage of said first and second electrolytes respectively from said entrance and exit openings respectively.
43. The apparatus of claim 42 further comprising an interior wall seal operably configured to seal said interior wall against the conductive surface of said dielectric substrate to prevent exchange of said first and second electrolytes at said interior wall.

44. The apparatus of any one of claims 38 - 43 further comprising means for moving said substrate relative to said first and second electrolytes in a direction from said first electrolyte to said second electrolyte while said electric current is flowing, to cause said transparent metal oxide layer to be formed in a lengthwise direction along the conductive surface of the substrate.

45. The apparatus of claim 44 wherein said means for moving comprises means for moving said substrate and means for holding said first and second open-faced containers stationary while said substrate is being moved.

46. The apparatus of any one of claims 39 - 40 further comprising means for positioning said first and second open-faced containers face down on the conductive surface of the dielectric substrate such that the substrate extends under said entrance wall, said interior wall, said exit wall, and said first and second pairs of end walls such that the first and second conductive surfaces of the dielectric substrate face said first and second open-faced containers.

47. The apparatus of claim 46 further comprising:

   means for holding a volume of an initial electrolyte;
means for holding said dielectric substrate with the conductive surface face-up in said initial electrolyte; and

wherein said means for positioning said first and second open-faced containers face down on the conductive surface of the dielectric substrate comprises means for causing the first and second open-faced containers to be substantially submerged in said initial electrolyte; and

means for sealing said entrance wall, said exit wall, and said first and second end wall portions against said substrate to contain a first volume of said initial electrolyte in said first open-faced container and to contain a second volume of said initial electrolyte in said second open-faced container.

48. The apparatus of claim 47 further comprising means for sealing said interior wall against the conductive surface of said dielectric substrate to prevent leakage of said first and second electrolytes respectively at said interior wall.

49. The apparatus of any one of claims 45 - 47 further comprising means for moving said substrate relative to said first and second electrolytes in a direction from said first electrolyte to said second electrolyte while said electric current is flowing, to cause said transparent metal oxide layer to be formed in a lengthwise direction along the conductive surface of the substrate.

50. The apparatus of claim 49 wherein said means for moving comprises means for moving said first and second open-faced containers and means
for holding said substrate stationary while said first and second open-faced containers are being moved.

51. An apparatus for forming a transparent metal oxide layer on a first conductive surface of a first dielectric substrate, the apparatus comprising:

a space-defining frame gasket positioned on the first conductive surface of the first dielectric substrate, the gasket having an inner wall defining a space bounded by said inner wall and a portion of the first conductive surface of the first dielectric substrate;

a second substrate having a second conductive surface;

means for pressing the first conductive surface of the first substrate against the space-defining frame gasket to cause said space to be a sealed space;

an opening in said frame gasket for admitting into the sealed space an electrolyte having chemicals that facilitate conduction of electric current through said electrolyte, said chemicals including non-aqueous solvent, metal ions and a source of oxygen suitable to facilitate formation of the transparent metal-oxide layer on the first conductive surface; and

means for applying an electric potential between said second conductive surface of said second dielectric substrate and said first conductive surface of said first substrate such that said first conductive surface of said first substrate has a negative polarity relative to said second conductive surface of said second dielectric substrate to cause an electric current to flow between said second
conductive surface and said first conductive surface, through said electrolyte to cause an electrochemical reaction to occur at the first conductive surface to form said transparent metal oxide layer on the first conductive surface.

52. The apparatus of claim 51 wherein said non-aqueous solvent is protic or aprotic solvent.

53. The apparatus of claim 51 or 52 further comprising releasing metal ions capable of forming the transparent metal oxide layer to be optically transparent in the visible region of the electromagnetic spectrum, from salts soluble in said non-aqueous solvent.

54. The apparatus of any one of claims 51 - 53 further comprising causing said second electrolyte to include a dopant electrochemically embeddable into the transparent metal oxide layer to produce a conductive transparent metal oxide layer.

55. The apparatus of claim 53 or 54 further comprising means for counting coulombs of charges in said electric current and means in communication with said means for counting coulombs for ceasing the application of said electric potential when a coulomb charge count indicated by said means for counting coulombs meets a coulomb count criterion associated with a desired thickness of said transparent metal oxide layer.

56. The apparatus of any one of claim 52 - 55 further comprising means for interrupting said current when a metal ion concentration in said electrolyte meets a metal ion concentration criterion, means for replacing said electrolyte, and means for re-establishing said electric current after said electrolyte has been replaced.
57. The apparatus of any one of claims 52 - 56 wherein said means for pressing is operably configured to compress said space-defining frame gasket to sufficiently seal said sealed space to prevent leakage of said electrolyte from said sealed space.

58. The apparatus of any one of claims 51 - 57 wherein said means for applying an electric potential comprises first and second conductive clamps on first and second opposite edges respectively of said first substrate in electrical contact with said first conductive coating at opposite side edges of said first substrate and third and fourth conductive clamps on third and fourth opposite edges of said dielectric substrate in electrical contact with said second conductive surface of opposite side edges of said dielectric substrate, wherein said first and second clamps are operably configured to be connected to a negative terminal of a current source and wherein said third and fourth clamps are operably configured to be connected to a positive terminal of the current source.
A. CLASSIFICATION OF SUBJECT MATTER

IPC: C25D 11/02 (2006.01) . B82Y 30/00 (2011.01) . H05K 3/22 (2006.01) . G02F 1.1333 (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)

IPC: C25D 11/02 (2006.01) . B82Y30/00 (2011.01) . H05K 3/22 (2006.01) . G02F 1.1333 (2006.01)

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

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

Databases: Total patent, P.A.T, ACS Publications

Keywords: Transparent Conductive Oxide, layer, coat, dielectric, indium, substrate, electrohle.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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[X] See patent family annex.

[ ] Further documents are listed in the continuation of Box C.

[ ] 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

[ ] 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

[ ] document member of the same patent family

Date of the actual completion of the international search: 22 August 2013 (22-08-2013)

Date of mailing of the international search report: 30 September 2013 (30-09-2013)

Authorized officer: Patrick Mamputu

Tel.: 1-819-994-9537
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