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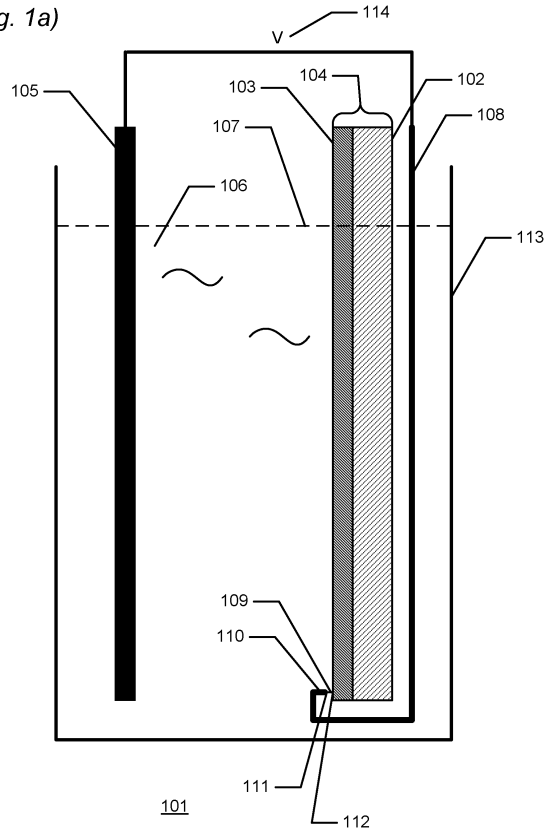
(54) Anodic growth of titanium dioxide nanostructures

(57) Disclosed is a method of producing nanostructures of titanium dioxide (TiO_2) by anodisation of titanium (Ti) in an electrochemical cell, comprising the steps of: immersing a non-conducting substrate coated with a layer of titanium, defined as the anode, in an electrolyte solution in the electrochemical cell; immersing a conducting substrate, defined as the cathode, in the electrolyte solution in the electrochemical cell; whereby the anode and the cathode are in electrical contact through the electrolyte solution; providing a voltage difference between the anode and the cathode; and providing an electrical contact to the layer of titanium on the anode, where the electrical contact is made in the electrolyte solution.

Fig. 1a)



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Description

Field of the invention

[0001] This invention generally relates to titanium dioxide nanostructures. More particularly, the invention relates to anodic growth of titanium dioxide nanostructures.

Background of the invention

[0002] Titanium dioxide (TiO_2, TiO2 or titania) is a nontoxic, highly photoactive, mechanically stabile, and cheap substance, which also has a favourable overlap with the UV portion of the solar spectrum. Titanium dioxide can be used for self-cleaning windows, photovoltaic cells, antibacterial agents, antifogging agents, hydrogen generation, for reducing pollution etc.

[0003] Titanium dioxide nanostructures can be used for sensors, dye sensitised solar cells, and photoelectrocatalysis which can be used for self-cleaning surfaces and hydrogen generation.

[0004] Titanium dioxide nanostructures can be prepared on a substrate, and the method for manufacturing titanium dioxide nanostructures may typically comprise anodization and a thermal process. A substrate is in the remainder of the application defined as a physical object, subject, component, surface, or material with a physical or spatial extent. The word substrate is not used in its chemical sense.

[0005] A method of growing titanium dioxide nanostructures on substrates can be by means of an electrochemical process as described in J.M. Macak et al. Current Opinion in Solid State and Materials Science 11 (2007) 3-18 and in C. A. Grimes, J. Mater. Chem., 2007, 17, 1451-1457. A substrate covered by a titanium (Ti) layer, i.e. a metal layer, is submerged in an electrolyte solution and works as the anode, i.e. the electrode where oxidation occurs. At the counter electrode, the cathode, reduction occurs. A voltage difference is applied to the circuit, and oxidation and anodizing of the titanium metal occurs and converts the titanium into titanium dioxide. However, the titanium metal layer in contact with the electrolyte in air may be rapidly etched away, whereby the electrical contact with the submerged portion of the titanium metal layer undergoing anodization is cut off, before all the titanium metal is converted into titanium dioxide nanostructures.

[0006] Transparent titanium dioxide nanotube arrays on non-conducting supports can be grown using a "bilayer technique" where two layers of titanium are used, a top layer and a bottom layer. The top layer of titanium is converted to a top layer of titanium dioxide nanotubes by anodizing, thus the top layer of titanium dioxide nanotubes is thereby grown on the bottom layer of titanium. The bottom layer of titanium is thus not converted, and this bottom layer of titanium must subsequently be oxidized thermally to give a transparent film. The bottom layer of titanium metal is necessary to obtain a complete conversion of the top layer.

[0007] WO2008/127508 discloses a method of preparing titania nanotubes involving anodization of titanium in the presence of chloride ions and at low pH (1-7) in the absence of fluoride. Inclusion of organic acids in the electrolyte solution leads to the incorporation into the nanotubes of up to 50 atom percent of carbon. In a two-stage method, a titanium anode is pre-patterned using a fluoride ion containing electrolyte and subsequently anodized in a chloride ion containing electrolyte to provide more evenly distributed nanotube arrays.

[0008] The article "On wafer TiO2 nanotube-layer formation by anodisation of Ti-films on Si" by J.M. Macak et al. from Chemical Physics Letters, Volume 428, Issues 4-6, 20 September 2006, Pages 421-425 discloses self-organized formation of anodic TiO2 nanotubular layers on flat and thin sputter-deposited layers of titanium on silicon. The TiO2 nanotubes were grown by anodisation of these substrates in HF/H2SO4 electrolytes at different potentials between 5 V and 20 V resulting in tubes with diameters ranging from 30 to 100 nm. The key to achieve an ordered layer from the thin film samples is to operate at low temperatures. This results in a conversion efficiency of Ti to TiO2 nanotubes close to 100% and prevents loss of large amounts of the tubes due to chemical dissolution.

[0009] The article "Fabrication of self-organized TiO2 nanotubes from columnar titanium thin films sputtered on semiconductor surfaces" by Yesudas Daniel Premchand et al. from Electrochemistry Communications, Volume 8, Issue 12, December 2006, Pages 1840-1844 discloses growing self-organized nanotube arrays of TiO2 from titanium (Ti) thin films deposited on p-type Si(1 0 0) substrates. Structural and morphological characterizations carried out by X-ray diffraction and scanning electron microscopy indicate that the sputtered crystalline Ti thin films used for subsequent anodisation are hexagonally closed packed (hcp-Ti) and show a columnar morphology. Electrochemical anodisation of the Ti films was carried out by potentiostatic experiments in 1 M H3PO4 + 1 M NaOH + 0.5 wt% HF electrolyte at room temperature. The TiO2 nanotubes on a semiconductor substrate have an average tube length of approximately 560 nm, diameter in the order of 80 nm and wall thickness approximately 20 nm.

[0010] The article "Preparation and characterisation of TiO2 nanotube arrays via anodisation of titanium films deposited on FTO conducting glass at room temperature" by Yuxin Tang et al. from Acta Physico-Chimica Sinica, Volume 24, Issue 12, December 2008, Pages 2191-2197 discloses preparing self-organized TiO2 nanotube arrays with micro-scale length on fluorine-doped tin oxide (FTO) conducting glass in NH4F/glycerol electrolyte by electrochemical anodisation of pure titanium films deposited by radio frequency magnetron sputtering (RFMS) at room temperature. The samples were characterized by means of field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and photoelectrochemistry methods.

[0011] Thus, growing titanium dioxide nanostructures on semi-conductor substrates, such as silicon, is well-known from the documents described above.

[0012] However, it remains a problem to provide an easier method for growing titanium dioxide nanostructures on non-conducting substrates.

Summary

[0013] Disclosed is a method of producing nanostructures of titanium dioxide (TiO2) by anodisation of titanium (Ti) in an electrochemical cell, comprising the steps of:

- immersing a non-conducting substrate coated with a layer of titanium, defined as the anode, in an electrolyte solution in the electrochemical cell;
- immersing a conducting substrate, defined as the cathode, in the electrolyte solution in the electrochemical cell; whereby the anode and the cathode are in electrical contact through the electrolyte solution;
- providing a voltage difference between the anode and the cathode; and
- providing an electrical contact to the layer of titanium on the anode, where the electrical contact is made in the electrolyte solution.

[0014] In some embodiments the method further comprises controlling the oxygen concentration in the electrolyte solution.

[0015] In some embodiments the electrical contact to the layer of titanium is provided at a point on the anode corresponding to a substantially lowest oxygen concentration in the electrolyte solution.

[0016] This may be the most optimal oxygen concentration for avoiding loss of electrical contact.

[0017] In some embodiments the anode is defined as having a distal end and a proximal end, and where the distal end is at the bottom of the electrochemical cell, and where the proximal end is at the air interface of the electrochemical cell, and wherein the electrical contact is made to the distal end of the anode.

[0018] In some embodiments the electrical contact to the layer of titanium is provided at a point on the anode which is at the largest possible distance from the surface of the electrolyte solution.

[0019] In some embodiments the electrical contact is provided by means of a cable immersed in the electrolyte solution, where the cable is defined as having a distal end and a proximal end, where the distal end contacts the titanium layer of the anode, and where the cable comprises a conducting core for providing the electrical contact to the titanium layer on anode.

[0020] It is understood that there may be one or more cables for providing the electrical contact.

[0021] Furthermore, the proximal end of the cable may be connected to the electrical circuit of the electrochemical cell, whereby the entire assembly of the non-conducting substrate and the conducting cable constitute the anode

[0022] In some embodiments the conducting core is made from a self-passivating material, which suppresses oxygen evolution.

[0023] In some embodiments the conducting core of the cable is covered by an electrical insulator material, where the electrical insulator material is removed at the distal end of the cable for exposing the conducting core for providing the electrical contact to the titanium layer on anode

[0024] In some embodiments the length of the insulator material removed at the distal end of the cable is in a range from about 0.5 mm to about 2 mm.

[0025] In some embodiments the non-conducting anode substrate is selected from the group consisting of:

- glass;
- polymer;
- ceramics.

[0026] In some embodiments the conducting cathode substrate is selected from the group consisting of:

- carbon (C);
- titanium (Ti);
- nickel (Ni);
- a steel alloy such as mild steel or stainless steel;
- platinum (Pt);
- iron (Fe);
- cobalt (Co);
- palladium (Pd);
- gold (Au).

[0027] Alternatively, the conducting cathode substrate can be made of any other conducting material.

[0028] In some embodiments the conducting cable core is made of a material selected from the group consisting of:

- titanium (Ti);
- aluminium (Al);
- tungsten (W);
- silicon (Si);
- zirconium (Zr);
- niobium (Nb);
- tantalum (Ta);
- hafnium (Hf).

[0029] Alternatively, the conducting cable core can be made of any other self-passivating material. Self-passivating materials work because they tend to suppress the oxygen evolution by forming a passivation layer. Consequently, oxygen evolving materials such as gold (Au) or platinum (Pt) can not be used as material for the cable core, since oxygen is developed and causes oxidation around the contact point.

[0030] In some embodiments the temperature in the electrolyte solution is in a range from about 5°C to about 60°C.

[0031] In some embodiments the voltage difference between the anode and cathode is in a range from about 5 V to about 40 V.

[0032] In some embodiments the produced titanium dioxide is amorphous assynthesized and in the anatase form after temperature treatment, where both are active forms.

[0033] Consequently, it is an advantage that electrical contact by means of a contact point is made in the electrolyte solution, since the nanostructures grow towards this contact point, and hence electrical contact to the virgin titanium metal is maintained until all titanium metal is converted into titanium dioxide. This provides that a substantially complete conversion of titanium to titanium dioxide is obtained. In prior art approaches, the electrical contact is made above or near the interface between the electrolyte solution and the air, in which case the anodization proceeds fastest near the contact point causing loss of the electrical connection to the remaining titanium metal which is then left unconverted.

[0034] It is an advantage to grow the anodic film of titanium nanostructures on non-conducting substrates by controlling the oxygen concentration gradient, oxygen partial pressure or oxygen content over the growing nanostructures in such a way that the nanostructures anodizes faster further away from the contact point than closer to the contact point. This enables complete anodization of the entire surface without premature loss of contact. Thus the oxygen gradient controls the formation of nanostructures on the non-conducting substrate.

[0035] The electrical contact can be below the surface of the electrolyte solution near the part of the titanium film that is immersed deepest into the bath. Hereby, the electrical contact point can be located furthest from the highest oxygen concentration in the electrolyte solution.

[0036] Thus, a suitable oxygen (02) gradient may be achieved in practice by having a vertical geometry of the anode, and where the electrical contact is established at the bottom of the electrochemical cell, since the oxygen concentration will be lowest at the bottom of the electrochemical cell; and at the surface of the electrolyte solution the oxygen concentration will be highest.

[0037] It is an advantage that the oxygen concentration determines where the process proceeds fastest, so by controlling that the oxygen concentration is highest furthest away from the electrical contact, the process will start furthest away from the electrical contact, and thus the electrical connection is not cut-off before the entire titanium film is converted and oxidized to titanium dioxide.

[0038] It is an advantage that the oxygen concentration can be controlled for example by controlling the atmosphere of the electrolyte solution; or by providing an oxygen-free atmosphere in the electrolyte solution and then provide oxygen from an air tube or develop oxygen from an oxygen-developing auxiliary electrode, such as a gold wire, by means of electrolysis and placing the air tube or the oxygen-developing auxiliary electrode, e.g. a gold wire, furthest away from the electrical contact.

[0039] It is an advantage that the nanostructures can be grown in any direction, such as from the top to the bottom or from the bottom to the top in a vertical arrangement, or in a horizontal arrangement from one side to another or vice versa. The nanostructures can for example be grown from the bottom to the top, if the atmosphere around the arrangement is oxygen-free, and an oxygen-developing auxiliary electrode, such as a gold wire, for producing oxygen or an air tube is provided at the bottom of the anode and the electrical contact is provided at the top. An air tube or gas reservoir can provide an oxygen gradient, whereby the oxygen concentration is controlled. Thus, the oxygen supply in an oxygen-free atmosphere can be from a point source such as an auxiliary electrode, e.g. a gold wire, or an air tube, or it can be from a number of sources or from an entire surface.

[0040] It is an advantage that the growth direction of the nanostructures can be manipulated in any direction by controlling the oxygen gradient in such a manner that the anodization rate is enhanced by high oxygen concentration. In this manner, the anodization can be made to start in the distant point from the contact point avoiding loosing electrical contact during the anodization.

[0041] It is an advantage that titanium dioxide nanostructures such as nanotubes organise in vertically-oriented arrays, which provides an easy path for electron transport. The high surface area of titanium dioxide nanotubes facilitates faster hole transport for oxygen evolution. The internal reflections within the titanium dioxide nanotubes enhance light absorption, and titanium dioxide nanotubes can become super hydrophilic.

[0042] It is an advantage that the titanium dioxide film on the substrate is transparent, because then the film can be used for windows etc. without having to perform further process steps.

[0043] It is an advantage that the method is faster and with less complicated steps, e.g. no annealing may be necessary, compared to the prior art bilayer method where a thermal oxidation step is necessary.

[0044] It is an advantage that according to the present method, the titanium dioxide nanostructures is directly deposited on the substrate, whereas in the bilayer method, the titanium dioxide nanotube array is created on an other titanium layer of the bilayer and not directly on the substrate.

[0045] It is an advantage that the present method potentially can provide more homogenous titanium dioxide films, since there is a complete conversion of titanium into titanium dioxide directly on the substrate.

[0046] It is an advantage that if using a high voltage for the potential difference, no further thermal treatment for crystallisation of the titanium dioxide nanostructures may be provided.

[0047] It is an advantage that the present method is straightforward, cheap, and reproducible and suitable for large-scale production.

[0048] It is an advantage that titanium dioxide nanostructures can be grown to be directly deposited on non-conducting substrates instead of on conducting or semiconductor substrates, since thereby substrates such as polymers, plastics, glass, ceramics, paper etc. can be used as substrate.

[0049] It is an advantage that when using e.g. glass as the substrate for the titanium dioxide nanostructures, self-cleaning and anti-fogging windows can be produced. These windows can be used as windows in buildings and may thus require less maintenance or no maintenance, less or no cleaning, and this saves money, and time, and is an environment-friendly product.

[0050] Furthermore, it is an advantage that the titanium dioxide nanostructures can be grown on materials for making them anti-bacterial. This could be on glass, plastics, food, cosmetics, fibers, papers, packing, as coatings etc. for use in e.g. hospitals and on medical devices.

[0051] On an electrically conducting substrate electron transfer occurs, whereby electrical contact is created. However, when not using a conducting or semiconducting substrate, as in the present method, a contact point should be created for making an electrical circuit so that electron transfer can occur. The contact point may be necessary when using a non-conducting substrate even though there is a conducting layer of titanium metal present, because it may be necessary to maintain a constant electrical contact to the titanium layer. This contact point is achieved by means of the exposed and bare laid tip of the cable touching the non-conducting substrate.

[0052] A conductor is a material which contains movable electric charges. A flow of charges is electric current. Non-conducting materials or insulators lack mobile charges, and so resist the flow of electric current. Electrical resistance is a measure of the degree to which a material opposes an electric current through it. Since all conductors have some resistance, and all insulators will carry some current, there is no theoretical dividing line between conductors and insulators. However, there is a large gap between the conductance of materials that will carry a useful current at working voltages and those that will carry a negligible current for the purpose in hand, so the categories of insulator and conductor do have practical utility. Thus when the expressions conductor or conducting material are used in this application, what is meant is a material that will carry a useful current at working voltages, and when the expressions non-conductor, non-conducting material or insulator are used in this application, what is meant is a material that will only carry a negligible current at working voltages. Thus in practice a non-conducting material does not carry any current.

[0053] Electrical resistivity (also known as specific electrical resistance) is a measure of how strongly a material opposes the flow of electrical current. A low resistivity indicates a material that readily allows the movement of electrical charges. The SI unit of electrical resistivity is the ohm meter (Ω m). According to the present method, the cathode may comprise the conducting material carbon, and carbon has a resistivity of 3.5×10^{-5} Ω m at 20 °C. The anode may comprise the non-conducting material glass, and glass has a resistivity of 10^{10} to 10^{14} Ω m at 20 °C. As opposed to this, prior art discloses anodes comprising the material silicon, which has resistivity of 6.40×10^2 Ω m at 20 °C, and is defined as a semiconductor.

[0054] According to the present method, prior to the formation of the titanium dioxide nanostructures, the anode comprises the non-conducting substrate and the metallic layer of titanium. Titanium has fairly low electrical conductivity with an electrical resistivity of 0.420 $\mu\Omega\cdot$m at 20 °C. Thus the anode comprises a poorly conducting substance besides the non-conducting substrate. After the formation of the titanium dioxide nanostructures the anode comprises the non-conducting substrate and the layer of titanium dioxide nanostructures. Titanium dioxide has an electrical resistivity of 10^{12} $\Omega\cdot$m at 25°C.

[0055] According to the present method, e.g. the anode electrode and the cathode electrode are immersed in the electrolyte solution in the electrochemical cell, and by immersion is meant "at least partial immersion", i.e. "at least partly immersing". Thus, the electrodes may also be fully immersed.

[0056] According to the present method, the conducting core of the cable may be covered by an electrical insulator material, and by covering is meant "at least partial covering", i.e. "at least partially covered".

[0057] Nanostructures are defined as structures of the size of nanometers and thus with dimensions on nanometer-scale, and examples of nanostructures are arrays of nanotubes, films such as thin films, etc. Titanium dioxide nanostructures are defined as nanostructures comprising titanium dioxide. A nanotube is defined as a nanometer-scale tube-like structure. Nanostructures may be defined as having a size of 100 nanometers or smaller, however nanostructures may also be defined as having a size of more than 100 nanometers, such as for example less than 1000 nanometers.

[0058] The present invention relates to different aspects including the nanostructures of titanium dioxide described above and in the following, and corresponding methods, processes, products, apparatus, devices, uses and/or product means, each yielding one or more of the benefits and advantages described in connection with the first mentioned aspect, and each having one or more embodiments corresponding to the embodiments described in connection with the first mentioned aspect and/or disclosed in the appended claims.

[0059] In particular, disclosed herein is an apparatus for producing nanostructures of titanium dioxide (TiO2) by anodisation of titanium (Ti), comprising:

- an electrochemical cell comprising an electrolyte solution; an anode comprising a non-conducting substrate coated with a layer of titanium; and a cathode comprising a conducting substrate;

- means for providing a voltage difference between the anode and the cathode;
- means for providing an electrical contact to the layer of titanium on the anode made below the surface of the electrolyte solution.

[0060] In particular, disclosed herein is a kit for preparing nanostructures of titanium dioxide by anodisation of titanium comprising:

- an electrochemical cell;
- an electrolyte solution;
- an anode comprising a non-conducting substrate coated with a layer of titanium;
- a cathode comprising a conducting substrate;
- a cable comprising a conducting core for enabling an electrical contact to the titanium layer on the anode.

[0061] In particular, disclosed herein is a non-conducting substrate covered with nanostructures of titanium dioxide.

[0062] In particular, disclosed herein is a non-conducting substrate covered with nanostructures in the form of nanotube arrays of titanium dioxide, where a nanotube has a tube length of about 400 nm, an inner tube diameter of about 50 nm, and a thickness of the tube wall of about 10 nm.

[0063] Alternatively, the size and dimensions of the nanotubes can be varied.

[0064] In particular, disclosed herein is a use of a non-conducting substrate covered with nanostructures of titanium dioxide for photo-oxidation processes, such as self-cleaning surfaces.

Brief description of the drawings

[0065] The above and/or additional objects, features and advantages of the present invention, will be further elucidated by the following illustrative and nonlimiting detailed description of embodiments of the present invention, with reference to the appended drawings, wherein:

Fig. 1 shows an example of the experimental setup used for growing titanium dioxide nanostructures in the form of nanotube arrays.

Fig. 2 shows the region of the contact point before and after formation of nanostructures.

Fig. 3 shows the process of nanostructure formation.

Fig. 4 shows recorded images of titanium dioxide nanostructures in the form of nanotube arrays.

Fig. 5 shows a flowchart of an example of the process for producing the titanium dioxide nanostructures according to the present method.

Fig. 6 shows prior art.

Fig. 7 shows an example of an experimental set-up.

Fig. 8 shows an example of an experimental set-up.

Fig. 9 shows an example of an experimental set-up.

Fig. 10 shows an example of an experimental set-up.

Detailed description

[0066] In the following description, reference is made to the accompanying figures, which show by way of illustration how the invention may be practiced.

[0067] Figure 1 shows an example of the experimental setup used for growing titanium dioxide nanostructures in the form of nanotube arrays. In fig. 1a) the nanotube arrays are grown in an electrochemical cell 101 comprising a non-conducting substrate 102 with a layer of titanium (Ti) 103. The non-conducting substrate and the titanium layer constitute the anode 104 of the electrochemical cell. The cathode 105 of the electrochemical cell comprises a conducting material. The anode 104 and the cathode 105 are immersed in and thereby in contact with an electrolyte solution 106 (indicated by waves in the solution). The interface 107 between the electrolyte solution 106 and the air is indicated by a dotted line. A cable 108 is also immersed in the electrolyte solution 106. The cable 108 comprises a self-passivating conducting core 109 covered by an electrical insulator material 110. The conducting core may be made of metal or other conducting, self-passivating materials. The electrical insulator material 110 is removed from the conducting core 109 at one end 111 of the cable 108, and this end 111 is in contact with the titanium layer 103. The length of the insulator material removed at the end of the cable may be in a range from about 0.5 mm to about 2 mm. The cable 108 is shown to be arranged between the anode 104 and the wall 113 of the electrochemical cell, the cable 108 then passes under the anode 104, and the cable 108 is then bended upwards and inwards towards the titanium layer 103 in order to make contact with the titanium layer 103. See details in fig. 2 and 3. The exposed conducting core 109 at the end 111 of the cable 108 touching the titanium layer 103 constitutes an electrical contact point 112.

[0068] A voltage (V) 114 is applied to the anode, oxidation at the anode 104 electrode occurs, and anodizing of the titanium metal 103 occurs and converts the titanium 103 into titanium dioxide. Anodizing is an electrolytic process, where the thickness of the natural oxide layer on the anode electrode in an electrical circuit is increased. Thus the metal layer of titanium 103 is gradually converted to titanium dioxide nanotube arrays. The arrays of nanotubes grow towards the contact point 112, and hence electrical contact to the virgin titanium metal 103 is maintained until all titanium metal 103 is converted into titanium dioxide. This provides that a substantially complete conversion of titanium 103 to titanium dioxide is obtained. In prior art approaches, the electrical contact is made above or near the interface between the electrolyte solution and the air, in which case the anodization proceeds fastest near the contact point causing loss of the electrical connection to the remaining titanium metal which is then left unconverted.

[0069] Thus, the growth of titanium nanostructures is controlled by the oxygen concentration, oxygen content, oxygen partial pressure or oxygen gradient in the electrolyte. So when the electrical contact is made on a part of the anode which is arranged at the bottom of the electrochemical cell, the oxidation proceeds on the anode from the surface of the electrolyte and downwards on the anode, because the oxygen content is highest at the surface of the electrolyte.

[0070] The growth of titanium nanostructures may start and proceed fastest at the point on the anode, where the oxygen content in the electrolyte solution is highest, so if an air bobble, which contains 21 % oxygen is placed for instance halfway down the anode, then the formation of nanostructures happens at that point on the anode first.

[0071] For example, a cable having a core of gold for making the electrical contact would not work in the experimental setup shown in fig. 1, because gold will develop oxygen at the high pressure potential at the bottom of the electrochemical cell, and the nanostructures will then form around the contact point due to the produced oxygen from gold, and when nanostructures are formed at the contact point by converting the metallic titanium layer, the electrical contact is cut off, because the metallic titanium disappear.

[0072] The non-conducting substrate of the anode may comprise glass, polymer, plastics, ceramics etc.

[0073] The conducting cathode substrate may comprise carbon (C) or other conducting materials, such as for example platinum (Pt), gold (Au), iron (Fe), cobalt (Co), palladium (Pd), titanium (Ti), nickel (Ni), steel alloys such as mild steel, stainless steel etc.

[0074] It may be an advantage to have some amount of platinum coated on the cathode substrate to facilitate continuous removal of oxygen (02) via reaction with the hydrogen (H2), which is formed due to the anodization at the anode, and hereby the chemical reaction 02 + H2 -> H2O can take place.

[0075] The electrolyte solution may comprise Ammonium flouride (NH4F or NH_4F), water (H2O or H_2O), and Ethylene glycol (CH_2OHCH_2OH). Alternatively, the electrolyte solution may comprise other substances. However, fluoride (F) may be an essential substance in the electrolyte solution.

[0076] The temperature of the electrolyte solution may be in a range from about 5°C to about 60°C.

[0077] The voltage difference between the anode and cathode may be in a range from about 5 V to about 40 V. The magnitude of the voltage difference may determine the size of the formed titanium dioxide nanotubes.

[0078] The distance between the anode and the cathode in the electrochemical cell may be 35 mm. Alternatively, the distance the may be shorter or larger than this.

[0079] The produced titanium dioxide may be in the amorphous, rutile or anatase form.

[0080] The conducting core 109 of the cable 108 may be made of the metal titanium (Ti). Alternatively and/or additionally, other self-passivating, conducting materials, such as metals, may be used for the core material, e.g. aluminium (Al), tungsten (W), silicon (Si), zirconium (Zr), niobium (Nb), tantalum (Ta) and Hafnium (Hf) etc.

[0081] The electrical insulating material 110 of the cable 108 may be Teflon (brand name). The name Teflon is a collective terms used for the chemical names poly (tetrafluoroethylene) or poly(tetrafluoroethene) (PTFE), as well as PFA (perfluoroalkoxy resin) and FEP (fluorinated ethylene-propylene). Alternatively and/or additionally, other insulating materials may be used for the coating of the conducting core, e.g. rubber-like polymers, composite polymers, plastics, silicon rubber, glass, porcelain etc.

[0082] The arrangement of the cable in relation to the anode can be different from what is shown in fig. 1. Alternatively, the cable can be arranged to contact the titanium layer from below instead of from the side as shown in fig. 1. The cable can also be arranged between the anode and cathode, and the cable can then be bended inwards towards the titanium layer. Other arrangements for the internal positions of the different parts relative to each other are possible.

[0083] The titanium layer 103 of the anode 103 is deposited on the non-conducting substrate prior to the method of growing titanium dioxide nanotube arrays from metallic titanium. The titanium may be deposited on the non-conducting substrate by means of physical vapor deposition, such as sputtering or evaporation or chemical methods such as chemical vapor deposition, etc..

[0084] After the titanium dioxide nanotube arrays are formed, they can be annealed for increasing the activity.

[0085] Fig. 1b) shows an example of the experimental setup used for growing titanium dioxide nanostructures in the form of nanotube arrays. All the reference numbers refer to the same as in fig. 1a). However, in fig. 1b) the anode 104 and the cathode 105 are completely immersed in the electrolyte solution 106 (indicated by waves in the solution). The interface 107 between the electrolyte solution 106 and the air is indicated by a dotted line.

[0086] Fig. 2 shows the region of the contact point before and after formation of nanostructures in the form of nanotube arrays. Fig. 2a) shows the region of the contact point before the formation of nanotube arrays. The contact point 212 is between the titanium layer 203 on the non-conducting substrate 202 and the exposed conducting core 209 of the cable 208. Thus, the cable core is covered by an electrical insulating material 210, which is removed at the end 211.

[0087] Fig. 2b) shows the region of the contact point after the formation of nanotube arrays. The contact point 212 is between the titanium remaining metal layer 203 (see fig. 2a) on the non-conducting substrate 202 and the exposed conducting core 209 of the cable 208. The titanium diode nanotube arrays 215 have formed above the contact point 212. Below the contact point 212 titanium nanotube arrays 215 have also formed.

[0088] If using the setup as described above, and examining the substrate afterwards, there is titanium dioxide on the substrate and no titanium left on the substrate, except for the small spot where the contact point was made. At the spot of the contact point, no conversion from titanium to titanium dioxide has occurred, and consequently the spot is dark and not transparent as the rest of the substrate.

[0089] When using the substrate covered with titanium dioxide nanostructures in the form of nanotube arrays for e.g. a window glass, the region of the substrate, where the dark spot from the contact point is present, may be cut away, so that the entire window glass mounted in a window frame is transparent.

[0090] If a window glass, e.g. having a size suitable for being mounted in a typical building, is produced, then there may be provided more than one contact point when producing the substrate with the titanium dioxide nanostructures in the form of nanotube arrays, for ensuring that the entire substrate can be covered with titanium dioxide nanotube arrays. As mentioned above, the region of the substrate, where the dark, non-transparent spots from the contact points are present, can be cut off, so that the entire substrate is transparent, when mounted as e.g. a window glass in a building façade.

[0091] Fig. 2c) shows the region of the contact point before the formation of nanotube arrays, when the cable core is not covered by an electrical insulating material. The contact point 212 is between the titanium layer 203 on the non-conducting substrate 202 and the conducting core 209 of the cable 208. Thus in this figure, the cable core 209 is exposed along its entire length, and it is thus not covered by an electrical insulating material, being removed at the end.

[0092] Fig. 3 shows the process of formation of nanostructures in the form of nanotube array. Fig. 3a) shows the direction of the titanium dioxide nanotube array formation is from the top and down (TiO_2 NT forming in the figure). The conducting core 309 of the cable 308 is connected to the titanium layer 303 on the non-conducting substrate 302 by means of the contact point 312. The titanium dioxide nanotube arrays 315 are initially formed at the top end, the nanotube arrays 315 then gradually form downwards and finally all titanium is converted to titanium dioxide nanotube arrays, see fig. 3b). The arrow with Δt indicates that the titanium dioxide nanotube arrays are formed over a period of time.

[0093] By examining the anode with the growing titanium dioxide nanotube arrays during the formation, it was verified that the direction of growth is as described above, since the top part of the anode had titanium dioxide nanotube arrays while the bottom part of the anode had not. The examination was by means of visual inspection and scanning electron microscopy (SEM).

[0094] The growth of the nanostructures is regulated by the oxygen concentration gradient. However, the direction of growth of the nanostructures can alternatively and/or additionally be due to electrical field effects, chemical transport phenomena, and/or other physical or chemical effects.

[0095] Fig. 4 shows recorded images of titanium dioxide nanotubes arrays.

[0096] The images are made by means of scanning electron microscopy (SEM). Fig. 4a) shows titanium dioxide nanotubes arrays seen in a top-view. From above the nanotubes are round and hollow. Fig. 4b) shows the titanium dioxide nanotube arrays seen from a side-view. From the side the nanotubes are thin and elongated.

[0097] A nanotube may have a tube length of about 400 nm, an inner tube diameter of about 50 nm, and a thickness of the tube wall of about 10 nm. However, other dimensions of a nanotube are also possible.

[0098] Fig. 5 shows a flowchart of an example of the process for producing the titanium dioxide nanostructures in the form of nanotube arrays according to the present method.

[0099] In step 501, a layer of metallic titanium is deposited on a non-conducting substrate. The titanium may be deposited by means of physical vapor deposition, such as sputtering or evaporation or chemical methods such as chemical vapor deposition.

[0100] In step 502, the non-conducting substrate with the titanium layer is immersed in an electrolyte solution. The non-conducting substrate with the titanium layer may be attached at its top end to a stand by means of a clamp. The non-conducting substrate with the titanium layer works as the anode in the electrochemical cell.

[0101] In step 503, a cable with a self-passivating conducting core and e.g. an insulating cover is also attached at its top end to a stand by means of a clamp. If the core is covered by insulating material, the insulating material at the bottom end of the cable which is immersed in the electrolyte, is removed to expose the conducting core for providing an electrical contact point to the titanium layer on the non-conducting substrate.

[0102] In step 504, a conducting substrate is also immersed in the electrolyte solution. The conducting substrate may be attached at its top end to a stand by means of a clamp. The conducting electrode works as the cathode in the electrochemical cell.

[0103] In step 505, a voltage difference is applied between the anode and the cathode, and oxidation and anodizing of the anode begins, whereby the titanium on the non-conducting substrate begins to convert to titanium dioxide nanotube arrays.

[0104] In step 506, a time period passes, while the anodizing of the titanium to titanium dioxide nanotube arrays is in progress, and eventually, the conversion from titanium to titanium dioxide nanotube arrays is complete, and the non-conducting substrate is covered with the to titanium dioxide nanotube arrays.

[0105] Fig. 6 shows an example of prior art.

[0106] Fig. 6 shows that in the prior art process using a non-conducting support, the electrical contact point to the titanium is made at the top of the anode, that is above or near the interface between the electrolyte solution and the air, and in this case the anodization proceeds fastest near the contact point causing loss of the electrical connection to the remaining titanium metal which is then left unconverted.

[0107] In a different prior art process (not shown), transparent titanium dioxide nanotube arrays can be grown on non-conducting supports using a "bilayer-technique" where two layers of titanium are used, a top layer and a bottom layer. The top-layer of titanium is converted to a top-layer of titanium dioxide nanotubes by anodizing, thus the top layer of titanium dioxide nanotubes is thereby grown on the bottom layer of titanium. The bottom layer of titanium is thus not converted, and this bottom layer of titanium must subsequently be oxidized thermally to give a transparent film.

Experimental examples

[0108] In the following, some experimental examples according to the present invention are given. The invention is not restricted to them, but may also be embodied in other ways within the scope of the subject matter.

Example A

[0109] The electrolyte solution comprises: Ammonium fluoride (NH4F, 0.3%) water (H2O, 2%), and Ethylene glycol (CH2OHCH2OH, 97.7%). The temperature of the electrolyte solution is: 298 K, and the voltage difference between the anode and the cathode is: 10 V.

[0110] The conducting cable core for providing the electrical contact point is made of titanium.

[0111] See also fig. 1-3.

Example B

[0112] The electrolyte solution comprises: Ammonium fluoride (NH4F, 0.3%) water (H2O, 2%), and Ethylene glycol (CH2OHCH2OH, 97.7%). The temperature of the electrolyte solution is: 298 K, and the voltage difference between the anode and the cathode is: 10 V.

[0113] The conducting cable core for providing the electrical contact point is made of aluminium.

[0114] Regarding the conducting cable core, it should be made of a self-passivating material, which titanium (Ti) and aluminium (Al) as used above are, but materials such as tungsten (W), silicon (Si), zirconium (Zr), niobium (Nb), tantalum (Ta) and hafnium (Hf) can also be used since these are also self-passivating. These materials work because they tend to suppress the oxygen evolution by forming a passivation layer.

[0115] Consequently, oxygen evolving materials such as gold (Au) or platinum (Pt) can not be used as material for the cable core, since oxygen bobbles up and causes oxidation around the contact point.

Example C

[0116] The electrolyte solution comprises: 0.2 M Ammonium fluoride (NH4F, 0.3%) and 0.1 M H_3PO_4 aqueous electrolyte. The temperature of the electrolyte solution is: 298 K, and the voltage difference between the anode and the cathode is: 10 V.

Example D

[0117] See fig. 7.

[0118] The electrolyte solution comprises: Ammonium fluoride (NH4F, 0.3%) water (H2O, 2%), and Ethylene glycol (CH2OHCH2OH, 97.7%). The temperature of the electrolyte solution is: 298 K, and the voltage difference between the anode and the cathode is: 10 V.

[0119] Oxygen in the electrolyte solution is removed by sonication and N_2 (or Ar) purging for a couple of hours for providing an oxygen-free atmosphere in the electrolyte solution.

[0120] A gold (Au) wire 701 is placed near the bottom of the anode 702. A voltage V1 of 5 V is applied to the Au wire 701 until oxygen covers the Au wire 701. The wire for voltage bias V2 is connected at the top of the anode 702. The growth direction is controlled by the oxygen release from the gold wire, and the nanostructures grow from below where the oxygen release occurs and up while having the wire connected at the top.

[0121] Thus the growth of nanostructures is controlled by providing an oxygen-free atmosphere of the electrolyte solution, and then developing oxygen from a gold wire by means of electrolysis and placing the oxygen-developing gold wire furthest away from the electrical contact.

Example E

[0122] See fig. 8.

[0123] The electrolyte solution comprises: Ammonium fluoride (NH4F, 0.3%) water (H2O, 2%), and Ethylene glycol (CH2OHCH2OH, 97.7%). The temperature of the electrolyte solution is: 298 K, and the voltage difference between the anode and the cathode is: 10 V.

[0124] Oxygen in the electrolyte solution is removed by sonication and N_2 (or Ar) purging for a couple of hours for providing an oxygen-free atmosphere in the electrolyte solution.

[0125] A small air tube 801 for providing oxygen is placed under the anode 802. The wire for voltage bias V2 is connected at the top of the anode 802. By using the N2 atmosphere and the tube with air at the bottom of the anode, the nanostructures grow from below and up while having the wire connected at the top.

[0126] Thus the growth of nanostructures is controlled by providing an oxygen-free atmosphere of the electrolyte solution, and then providing oxygen from an air tube and placing the air tube furthest away from the electrical contact.

Example F

[0127] See fig. 9.

[0128] The electrolyte solution comprises: Ammonium fluoride (NH4F, 0.3%) water (H2O, 2%), and Ethylene glycol (CH2OHCH2OH, 97.7%). The temperature of the electrolyte solution is: 298 K, and the voltage difference between the anode and the cathode is: 10 V.

[0129] Oxygen in the electrolyte solution is removed by sonication and N_2 (or Ar) purging for a couple of hours for providing an oxygen-free atmosphere in the electrolyte solution.

[0130] The anode 902 is placed horizontally in the bottom of the container with electrolyte solution, and a Ti wire 903 for voltage bias V1 is connected at the end of the anode 902. A gold (Au) wire 901 is placed at the other end of the anode 902. A voltage V2 of 5 V is applied to the Au wire 901 until oxygen covers the Au wire 901. The growth direction of the nanostructures is controlled by the oxygen release from the gold wire, and the nanostructures grow from the end of the anode where the oxygen release occurs and to the other end of the anode where the wire is connected.

[0131] Thus the growth of nanostructures is controlled by providing an oxygen-free atmosphere of the electrolyte solution, and then developing oxygen from a gold wire by means of electrolysis and placing the oxygen-developing gold wire furthest away from the electrical contact.

Example G

[0132] See fig. 10.

[0133] The electrolyte solution comprises: Ammonium fluoride (NH4F, 0.3%) water (H2O, 2%), and Ethylene glycol (CH2OHCH2OH, 97.7%). The temperature of the electrolyte solution is: 298 K, and the voltage difference between the anode and the cathode is: 10 V.

[0134] Oxygen in the electrolyte solution is removed by sonication and N_2 (or Ar) purging for a couple of hours for providing an oxygen-free atmosphere in the electrolyte solution.

[0135] The anode 1002 is placed horizontally in the bottom of the container with the electrolyte solution and a Ti wire 1003 for voltage bias V is connected at the end of the anode 1002. A small air tube 1001 for providing oxygen is placed at the other end of the anode 1002. By using the N2 atmosphere and the tube with air at one end of the anode, the nanostructures grow from this end of the anode and to the other end of the anode where the wire is connected. Thus the growth of nanostructures is controlled by providing an oxygen-free atmosphere of the electrolyte solution, and then providing oxygen from an air tube and placing the air tube furthest away from the electrical contact.

[0136] Many variations of the electrolyte solution, temperature and voltage difference are known to work.

[0137] Although some embodiments have been described and shown in detail, the invention is not restricted to them, but may also be embodied in other ways within the scope of the subject matter defined in the following claims. In particular, it is to be understood that other embodiments may be utilised and structural and functional modifications may be made without departing from the scope of the present invention.

[0138] In device claims enumerating several means, several of these means can be embodied by one and the same item of hardware. The mere fact that certain measures are recited in mutually different dependent claims or described in different embodiments does not indicate that a combination of these measures cannot be used to advantage.

[0139] It should be emphasized that the term "comprises/comprising" when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

Claims

1. A method of producing nanostructures of titanium dioxide (TiO_2) by anodisation of titanium (Ti) in an electrochemical cell, comprising the steps of:

   - immersing a non-conducting substrate coated with a layer of titanium, defined as the anode, in an electrolyte solution in the electrochemical cell;
   - immersing a conducting substrate, defined as the cathode, in the electrolyte solution in the electrochemical cell; whereby the anode and the cathode are in electrical contact through the electrolyte solution;
   - providing a voltage difference between the anode and the cathode; and
   - providing an electrical contact to the layer of titanium on the anode, where the electrical contact is made in the electrolyte solution.

2. A method according to claim 1, wherein the method further comprises controlling the oxygen concentration in the electrolyte solution.

3. A method according to any of claims 1-2, wherein the electrical contact to the layer of titanium is provided at a point on the anode corresponding to a

substantially lowest oxygen concentration in the electrolyte solution.

4. A method according to any of claims 1-3, wherein the electrical contact to the layer of titanium is provided at a point on the anode which is at the largest possible distance from the surface of the electrolyte solution.

5. A method according to any of claims 1-4, wherein the electrical contact is provided by means of a cable immersed in the electrolyte solution, where the cable is defined as having a distal end and a proximal end, where the distal end contacts the titanium layer of the anode, and where the cable comprises a conducting core for providing the electrical contact to the titanium layer on anode.

6. A method according to claim 5, wherein the conducting core is made from a self-passivating material, which suppresses oxygen evolution.

7. A method according to any of claims 5-6, wherein the conducting core of the cable is covered by an electrical insulator material, where the electrical insulator material is removed at the distal end of the cable for exposing the conducting core for providing the electrical contact to the titanium layer on anode.

8. A method according to any of claims 1-7, wherein the non-conducting anode substrate is made of a material selected from the group consisting of:

- glass;
- polymer;
- ceramics.

9. A method according to any of claims 1-8, wherein the conducting cathode substrate is made of a material selected from the group consisting of:

- carbon;
- titanium;
- nickel;
- a steel alloy;
- platinum;
- gold;
- iron;
- cobalt;
- palladium;
- titanium.

10. A method according to any of claims 1-9, wherein the conducting cable core is made of a material selected from the group consisting of:

- titanium;
- aluminium;
- tungsten;
- silicon;
- zirconium;
- niobium;
- tantalum;
- hafnium.

11. An apparatus for producing nanostructures of titanium dioxide (TiO2) by anodisation of titanium (Ti), comprising:

- an electrochemical cell comprising an electrolyte solution; an anode comprising a non-conducting substrate coated with a layer of titanium; and a cathode comprising a conducting substrate;
- means for providing a voltage difference between the anode and the cathode;
- means for providing an electrical contact to the layer of titanium on the anode made below the surface of the electrolyte solution.

12. A kit for preparing nanostructures of titanium dioxide by anodisation of titanium comprising:

- an electrochemical cell;
- an electrolyte solution;
- an anode comprising a non-conducting substrate coated with a layer of titanium;
- a cathode comprising a conducting substrate;
- a cable comprising a conducting core for enabling an electrical contact to the titanium layer on the anode.

13. A non-conducting substrate covered with nanostructures of titanium dioxide obtainable by the method according to any of claims 1-10.

14. A non-conducting substrate covered with nanostructures in the form of nanotube arrays of titanium dioxide according to claim 13, where a nanotube has a tube length of about 400 nm, an inner tube diameter of about 50 nm, and a thickness of the tube wall of about 10 nm.

15. A use of a non-conducting substrate covered with anodized nanostructures of titanium dioxide for photo-oxidation processes.

Fig. 1a)

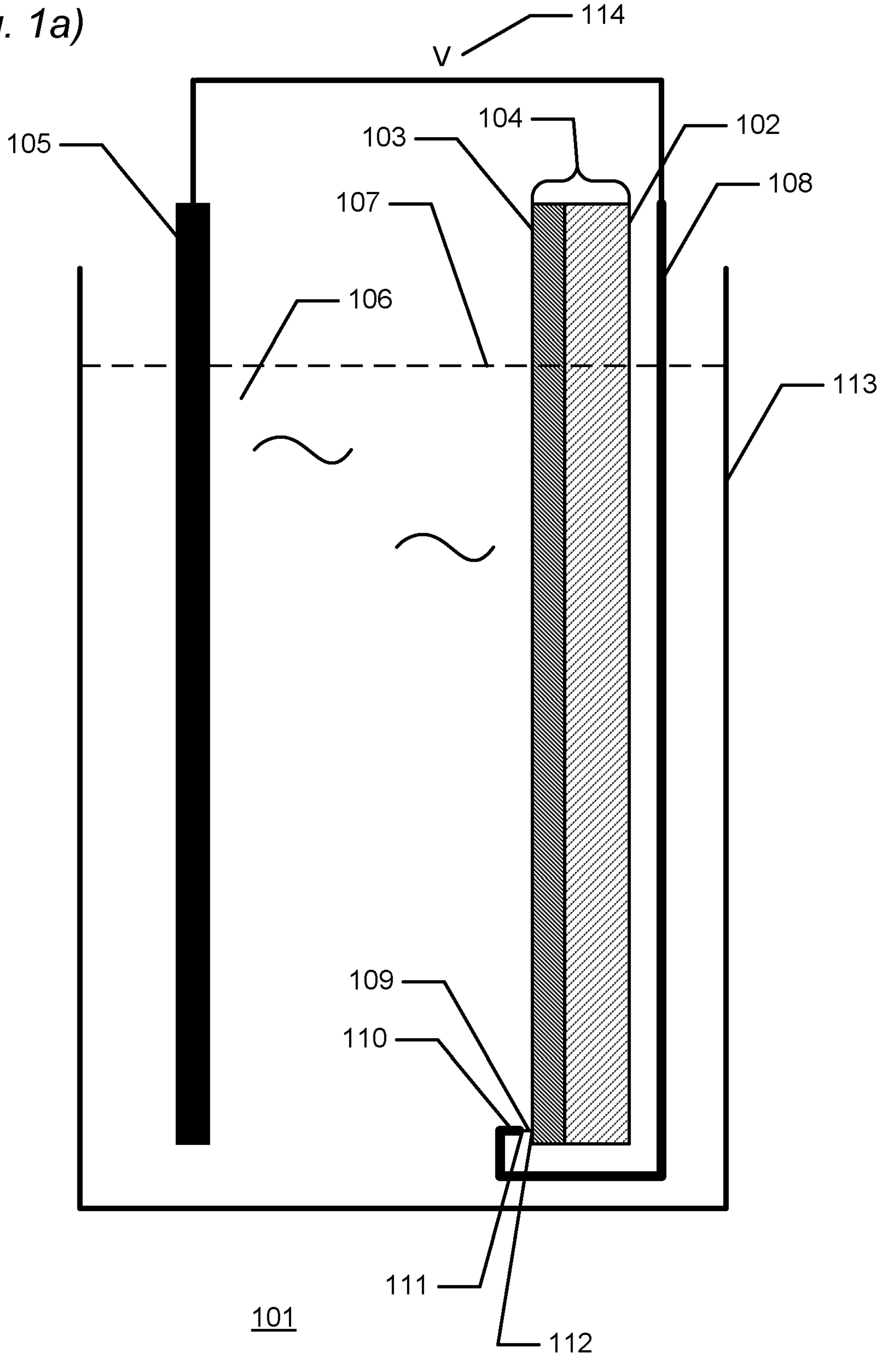


Fig. 1b)

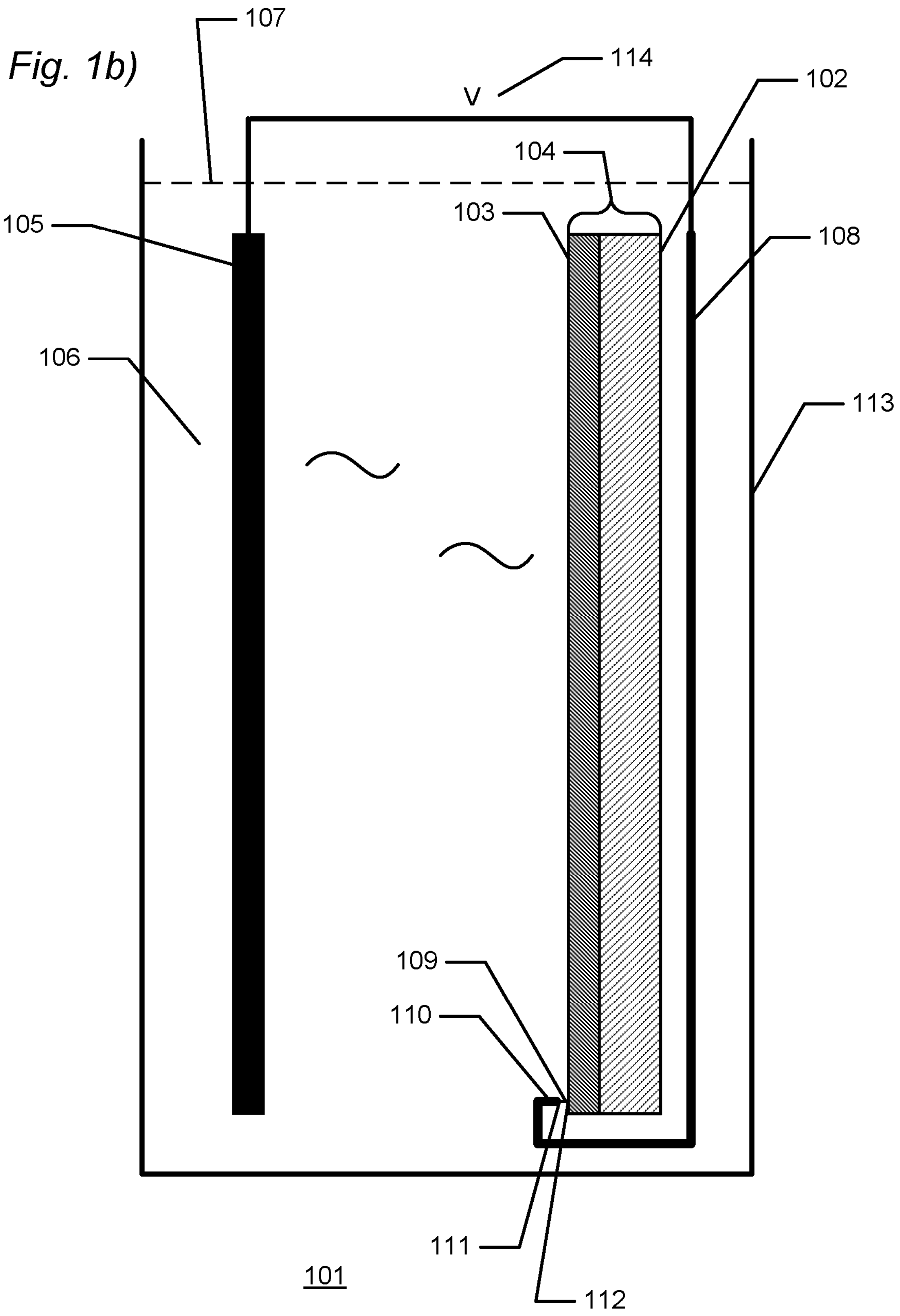


Fig. 2a)

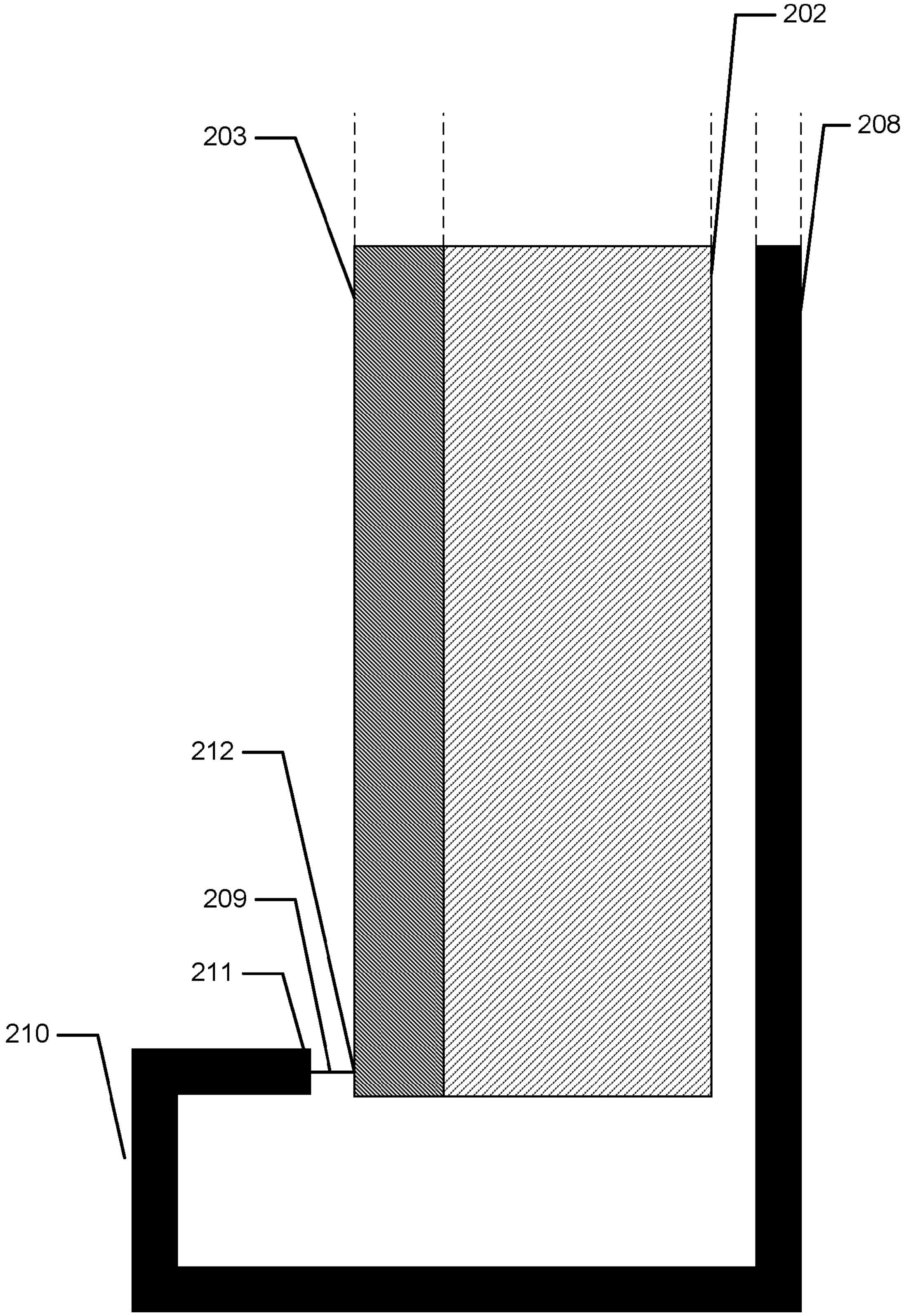


Fig. 2b)

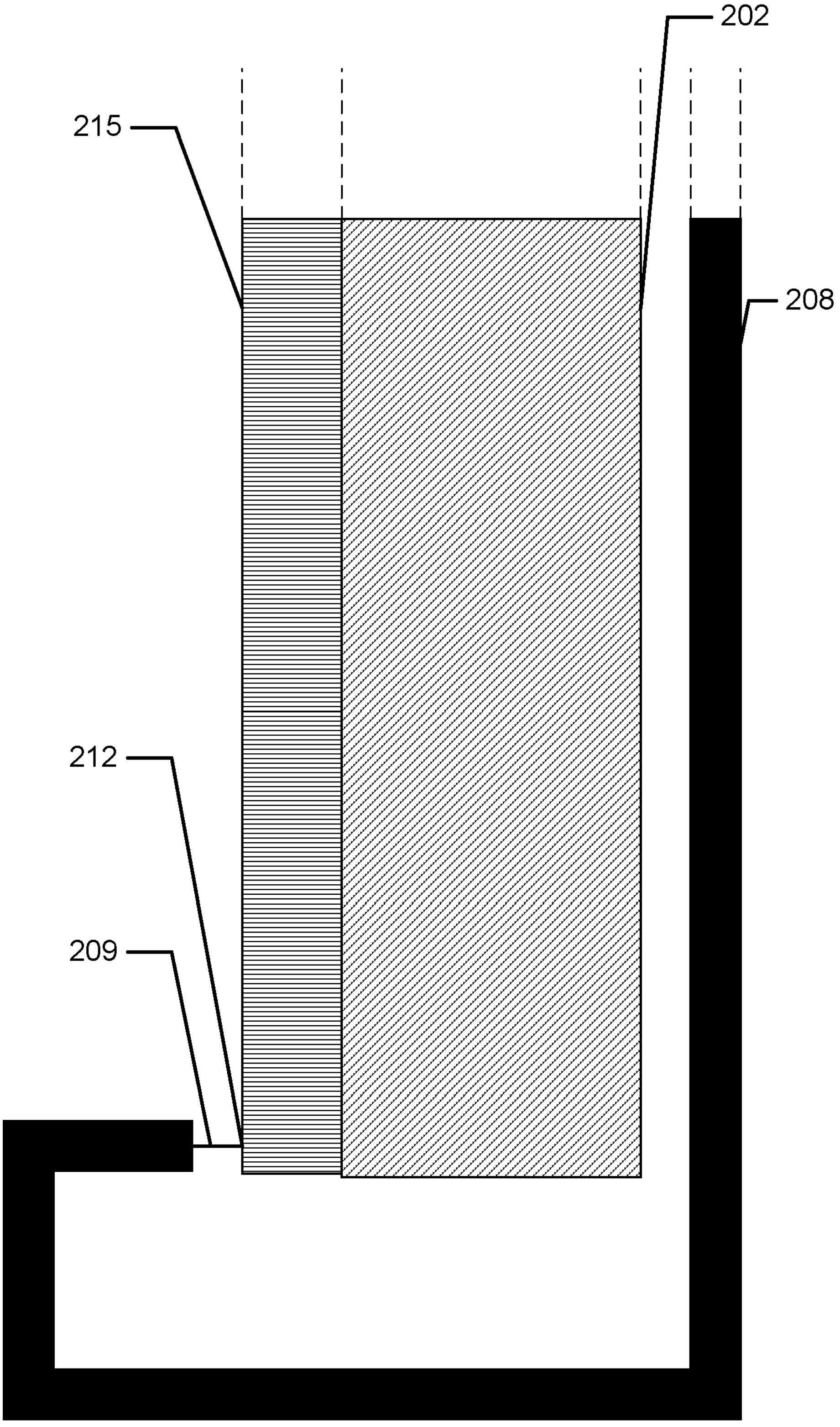


Fig. 2c)

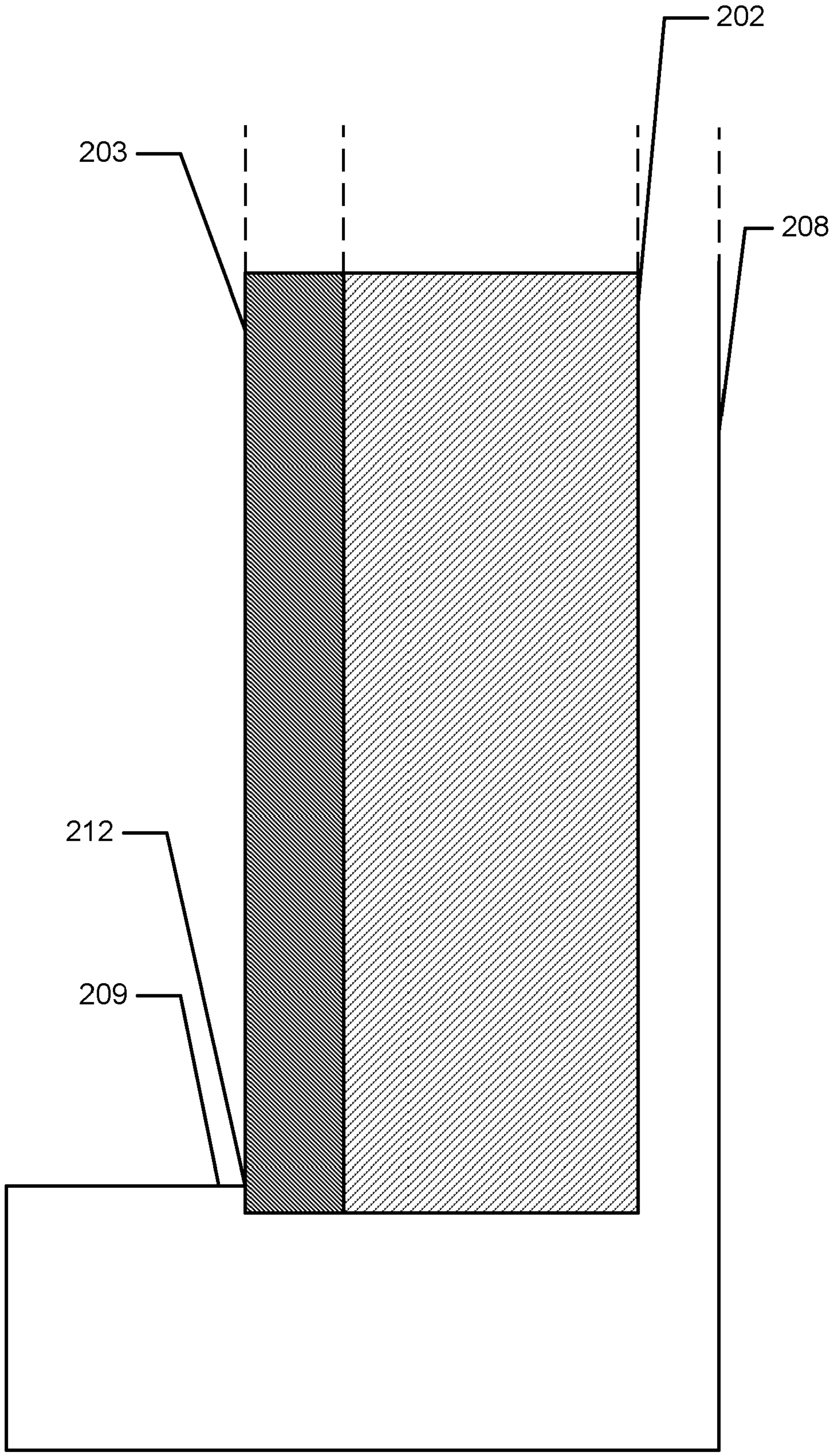


Fig. 3

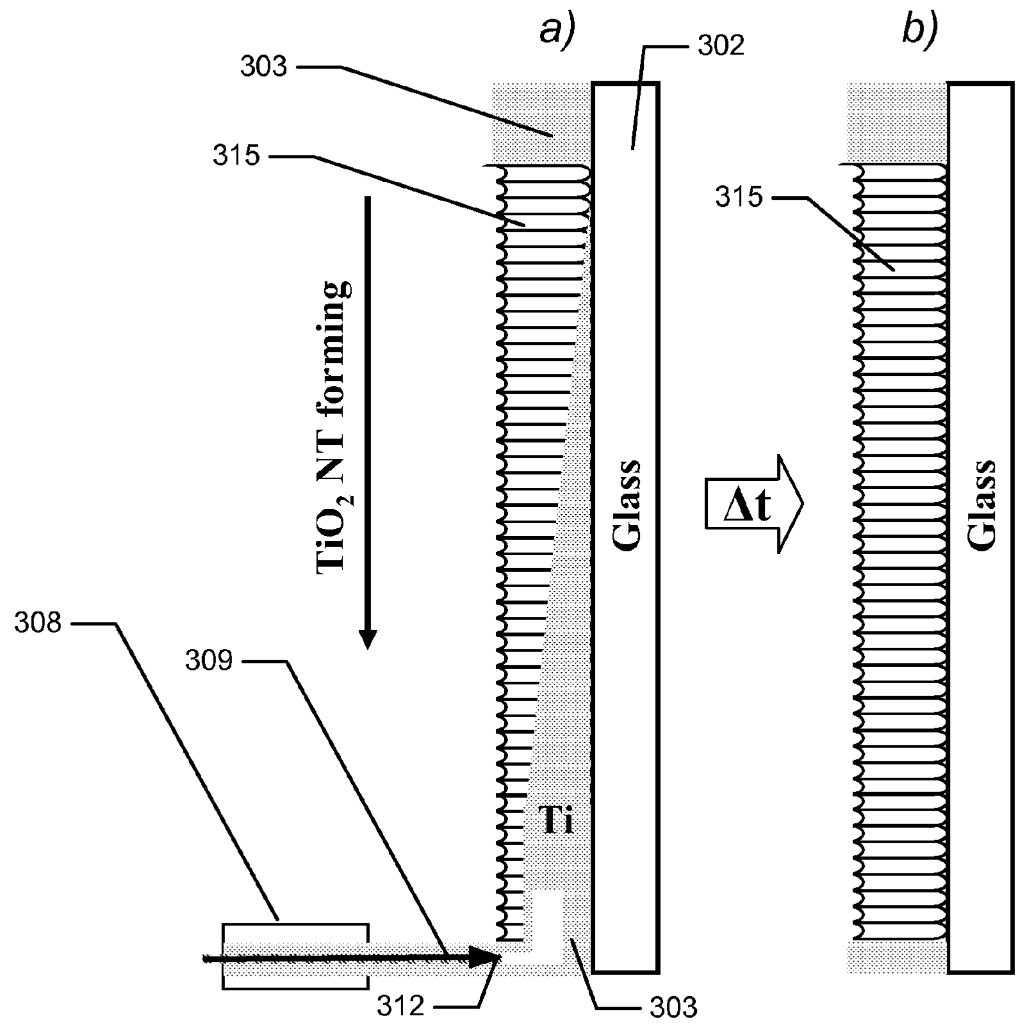
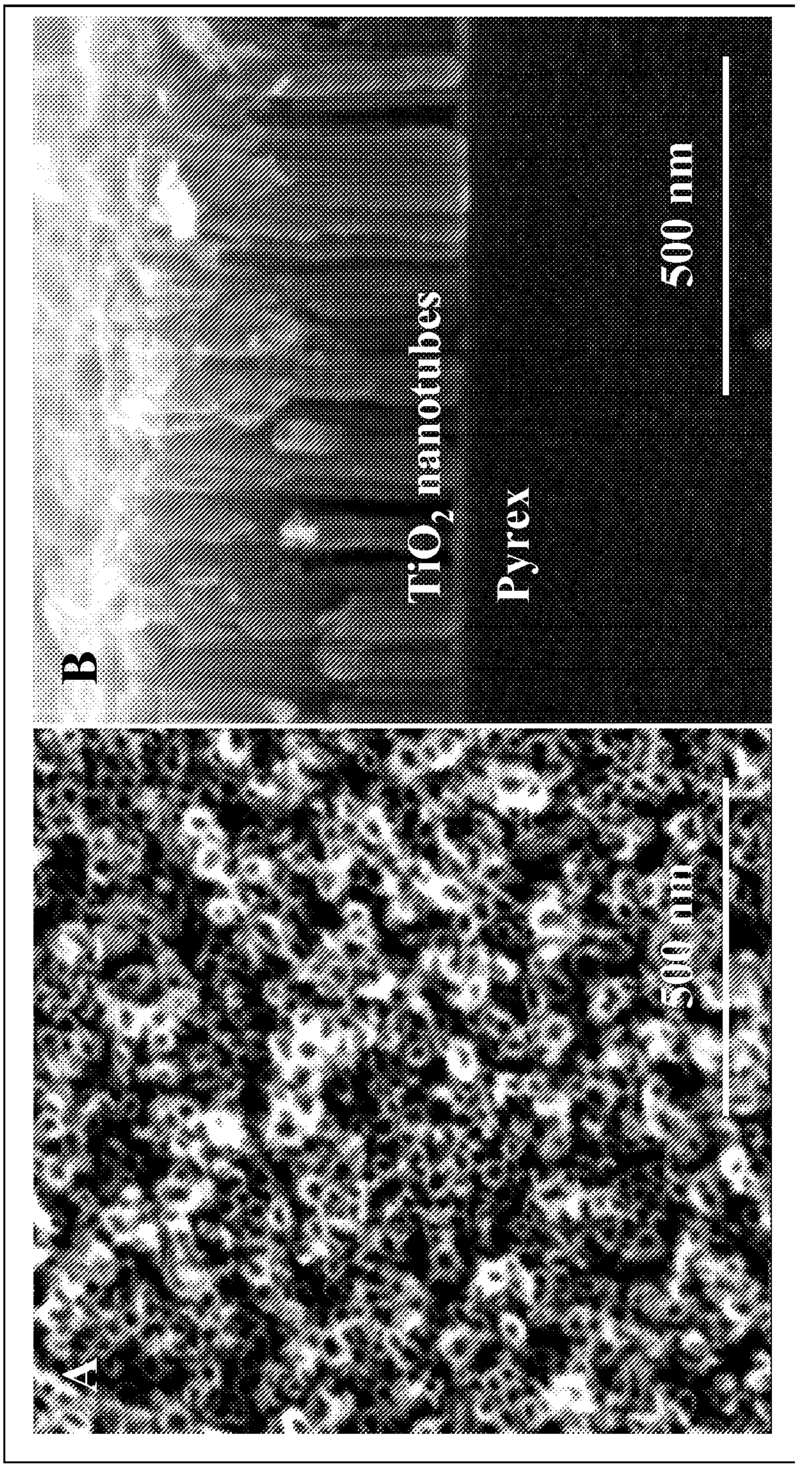

a)
b)
303
302
315
TiO₂ NT forming
Glass
Δt
315
Glass
Ti
308
309
312
303

Fig. 4



a)

b)

Fig. 5

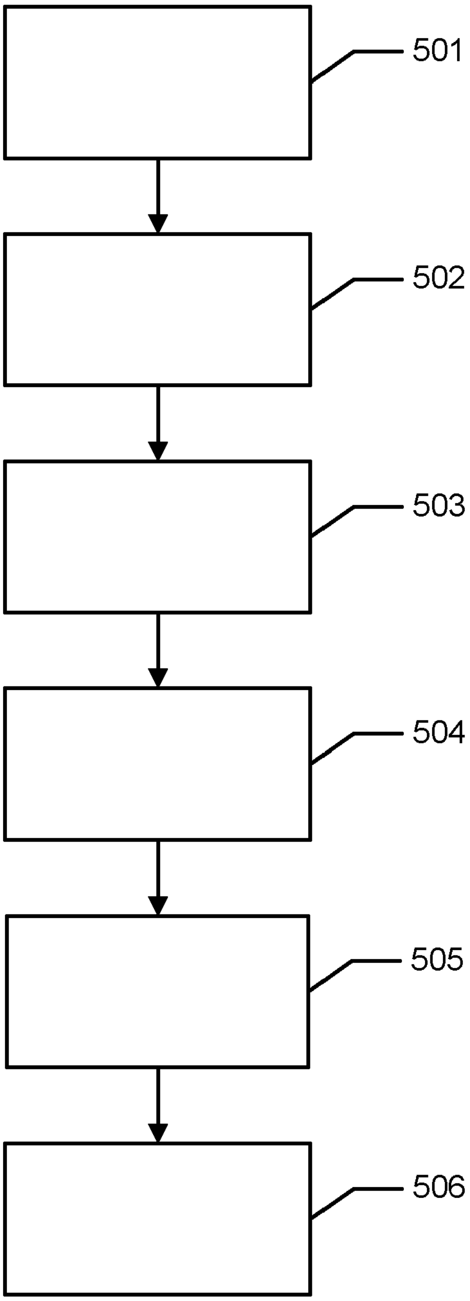


Fig. 6

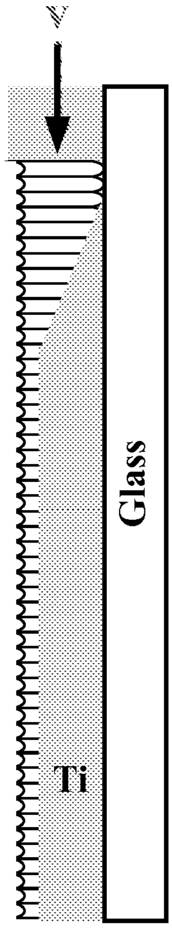


Fig. 7

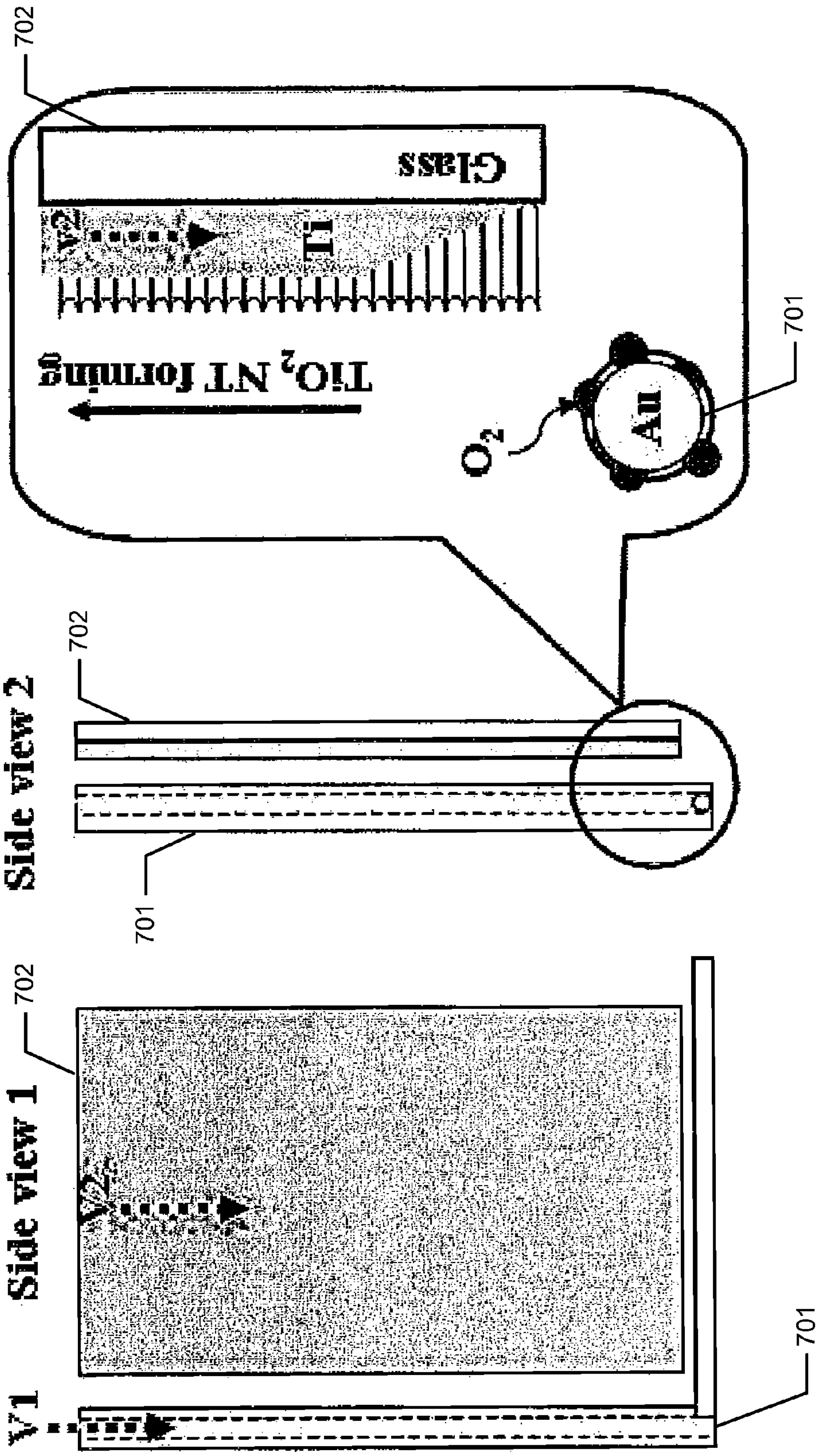

Side view 1
Side view 2
V1
V2
702
701
TiO$_2$ NT forming
Glass
Ti
Au
O$_2$

Fig. 8

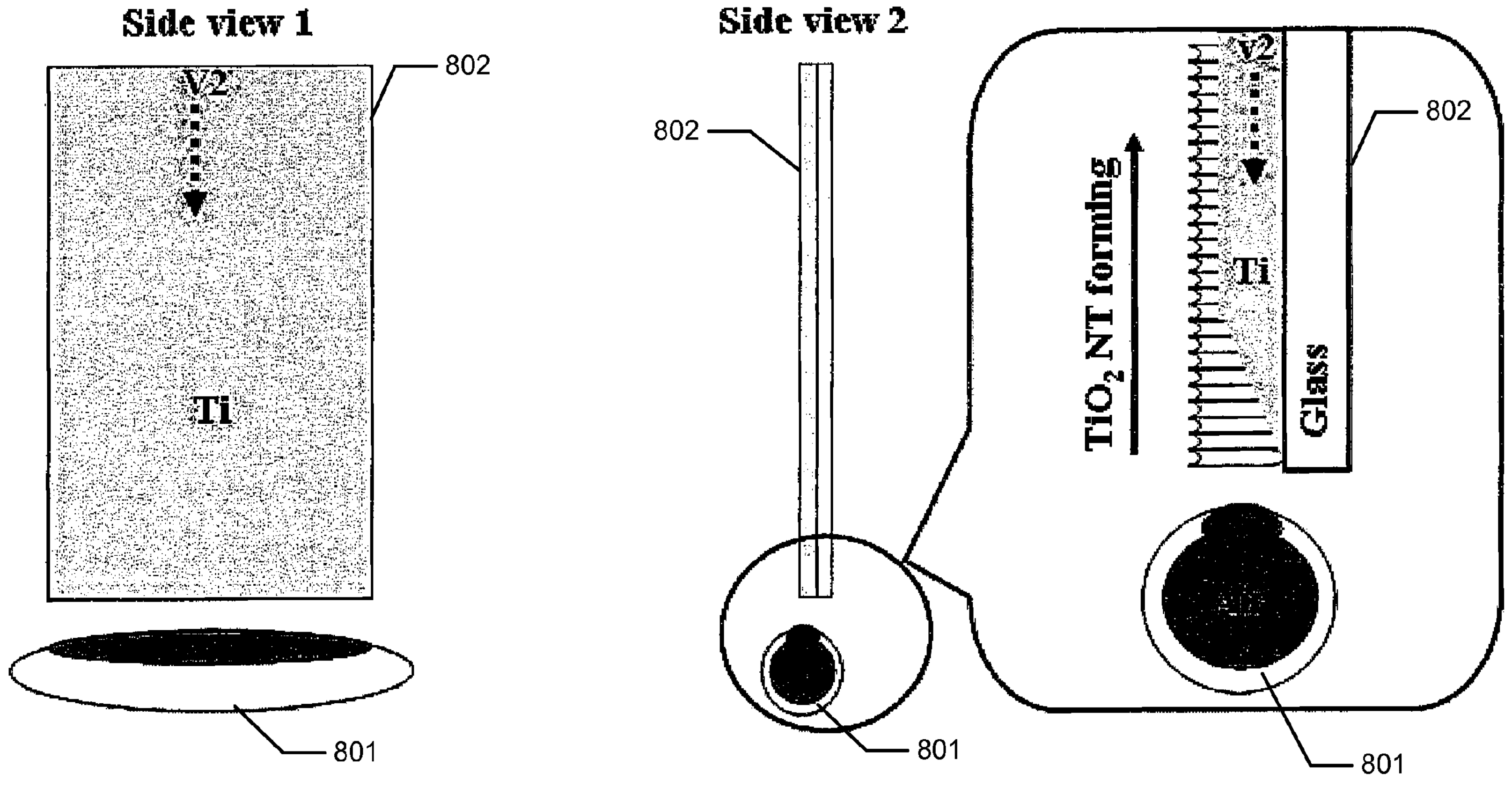

Side view 1
V2
Ti
802
801
Side view 2
802
801
TiO_2 NT forming
V2
Ti
Glass
802
801

Fig. 9

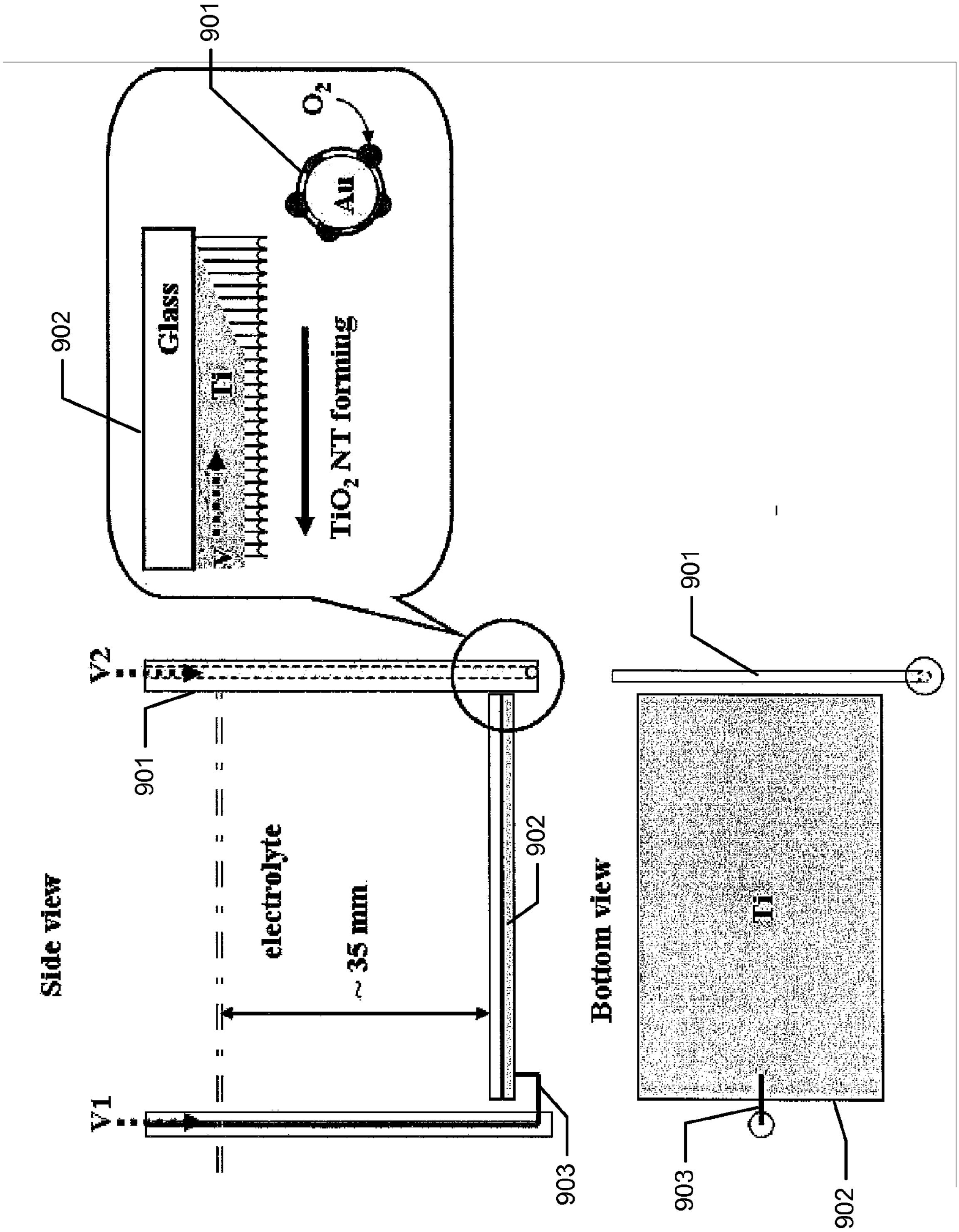
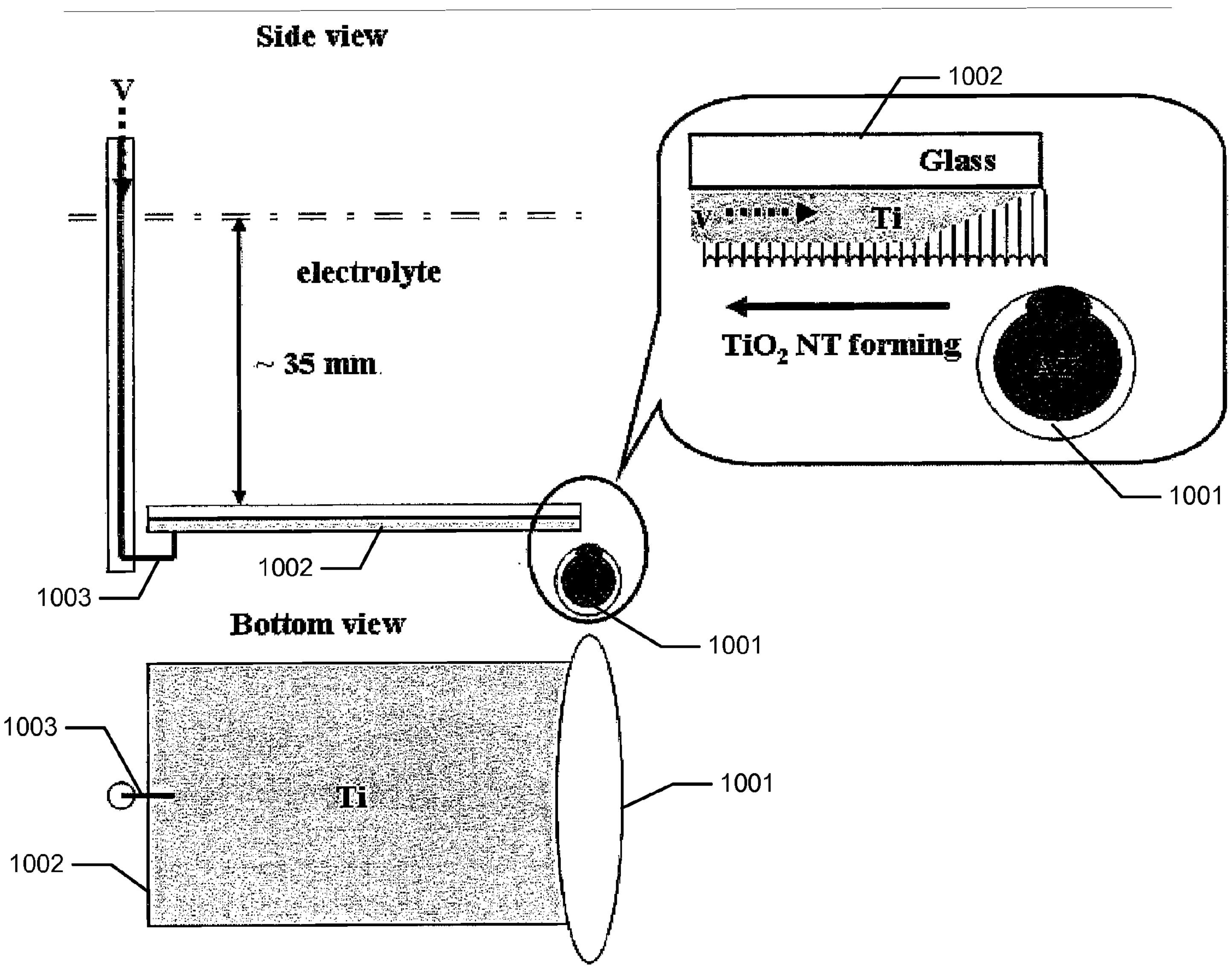

Side view
V1
V2
901
902
903
electrolyte
~ 35 mm
Glass
Ti
V
TiO_2 NT forming
Au
O_2
Bottom view
Ti
901
903
902

Fig. 10


Side view
V
electrolyte
~ 35 mm
1003
1002
1001
1002
Glass
V
Ti
TiO₂ NT forming
1001
Bottom view
1003
Ti
1002
1001

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EUROPEAN SEARCH REPORT

Application Number
EP 09 15 5996

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2005/003078 A1 (LU FU-HSING [TW] ET AL) 6 January 2005 (2005-01-06) * claims 1,2 * * figure 1 * * paragraphs [0007], [0018], [0021], [0026] * -----	1-15	INV. C25D11/26
X	GB 2 063 920 A (ATOMIC ENERGY AUTHORITY UK) 10 June 1981 (1981-06-10) * claims 1,5-8 * * page 1, line 40 - line 52 * * page 2, line 19 - line 25 * -----	1-15	
X	US 3 180 807 A (QUINN ROSS A) 27 April 1965 (1965-04-27) * claims 1-4 * * figures 5,6 * * column 2, line 59 - line 72 * * column 3, line 1 - line 7 * * column 3, line 27 - line 41 * * column 4, line 30 - line 35 * -----	1-15	TECHNICAL FIELDS SEARCHED (IPC)
X	US 2005/103639 A1 (LU FU-HSING [TW] ET AL) 19 May 2005 (2005-05-19) * claims 1-3,16-20 * * figure 2 * * paragraphs [0008], [0016], [0019], [0025] * -----	1-15	C25D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	19 August 2009	Perednis, Dainius

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 09 15 5996

19-08-2009

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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