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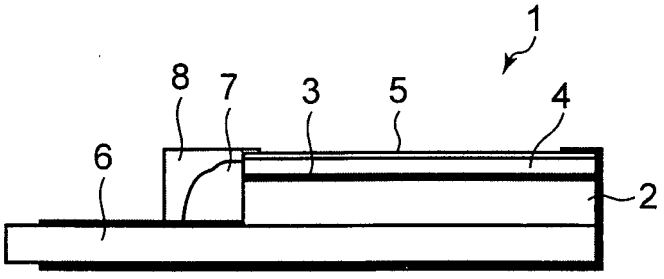
(54) **Electrode for electrolysis and electrolysis unit**

(57) There are disclosed an electrode for electrolysis capable of efficiently forming ozone by electrolysis of an electrolytic solution (e.g., water) at ordinary temperature with a low current density, and an electrolysis unit using the electrode. The electrode for electrolysis includes a substrate and a surface layer formed on the surface of the substrate, and the surface layer is made of an amorphous insulator, for example, a thin film of amorphous tantalum oxide, amorphous tungsten oxide or amorphous aluminum oxide.

FIG. 1



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Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to an electrode for electrolysis for use in an industrial or household electrolysis process.

[0002] In general, ozone is a substance having a very strong oxidizing power, and it is expected that water in which ozone is dissolved, so-called ozone water is applied to a broad range of cleaning sterilization treatment of water and sewage, food and the like, and a cleaning treatment of a semiconductor device manufacturing process. As methods for forming the ozone water, there are known a method for dissolving, in water, ozone formed by irradiation with an ultraviolet ray or electric discharge, a method for forming ozone in water by electrolysis of the water, and the like.

[0003] In Japanese Patent Application Laid-Open No. 11-77060 (Patent Document 1), an ozone water forming device is disclosed which includes ozone forming means for forming an ozone gas with an ultraviolet lamp and a tank to store water, whereby the formed ozone gas is supplied to the water in the tank to form the ozone water. Additionally, in Japanese Patent Application Laid-Open No. 11-333475 (Patent Document 2), an ozone water forming device is disclosed which mixes an ozone gas formed by a discharge type ozone gas forming device with water at a predetermined ratio by a mixing pump, in order to efficiently dissolve the ozone gas in the water.

[0004] However, in the above-mentioned ozone water forming method for generating the ozone gas by the ultraviolet lamp or the discharge system described above to dissolve this ozone gas in the water, the ozone gas forming device, an operation for dissolving the ozone gas in the water and the like are required, so that the device is liable to become complicated. The method is a method for dissolving the formed ozone gas in the water, and hence it has a problem that it is difficult to efficiently form the ozone water having a desired concentration.

[0005] In Japanese Patent Application Laid-Open No. 2002-80986 (Patent Document 3), as a method for solving the above-mentioned problem, a method for forming ozone in water by the electrolysis of the water is disclosed. In such a method, an electrode for forming ozone is used which is constituted of an electrode substrate material formed of a porous body or a mesh-like body, and an electrode catalyst including an oxide of a platinum group element or the like.

[0006] Moreover, in Japanese Patent Application Laid-Open No. 2007-016303 (Patent Document 4), it is disclosed that model tap water as an electrolytic solution is electrolytically treated with an electrode for electrolysis including a surface layer made of a dielectric material such as tantalum oxide, to form ozone.

[0007] However, in the method disclosed in Patent Document 3 described above, diamond is used as an electrode substance, and hence there is a problem that cost of the device itself soars.

[0008] Moreover, in the method for forming the ozone water by the electrolysis of water as disclosed in Patent Document 3, the platinum group element is a standard anode material, and has a characteristic that the element is hardly dissolved in an aqueous solution which does not include any organic substance. However, the element as the electrode for forming ozone has a low ozone forming efficiency, and it is difficult to efficiently form the ozone water by an electrolysis process. In such ozone water formation by the electrolysis process using the conventional electrode for forming ozone, the electrolysis for the ozone formation requires a high current density of 1 A/cm^2 or more, and an electrolyte needs to be set to a low temperature. This raises a problem that very high energy is consumed. Furthermore, platinum is expensive. When lead dioxide is used instead of platinum, there is a problem of toxicity.

[0009] Furthermore, even when the electrode for electrolysis disclosed in Patent Document 4 described above is used, ozone is formed, but further improvement of an ozone forming current efficiency has been demanded.

SUMMARY OF THE INVENTION

[0010] The present invention has been developed in order to solve a conventional technical problem, and an object thereof is to provide an electrode for electrolysis capable of efficiently forming ozone by electrolysis of water with a low current density.

[0011] An electrode for electrolysis according to the invention of a first aspect comprises a substrate and a surface layer formed on the surface of the substrate, characterized in that the surface layer is an amorphous insulator.

[0012] The electrode for electrolysis according to the invention of a second aspect is characterized in that in the above invention, the insulator is an oxide of a single metal or a composite metal oxide.

[0013] The electrode for electrolysis according to the invention of a third aspect is characterized in that in the above inventions, the insulator is tantalum oxide or tungsten oxide.

[0014] The electrode for electrolysis according to the invention of a fourth aspect is characterized in that in the inventions of the first and second aspects, the insulator is aluminum oxide.

[0015] The electrode for electrolysis according to the invention of a fifth aspect is characterized in that in the above inventions, a thickness of the surface layer is in a range of 20 nm or more to 2000 nm or less.

[0016] The electrode for electrolysis according to the invention of a sixth aspect is characterized in that in the above inventions, the substrate is provided with an intermediate layer positioned on an inner side of the surface layer and formed of a metal which is not easily oxidized on the surface of the substrate.

[0017] An electrolysis unit of the invention of a seventh

aspect is characterized in that an anode having water permeability is constituted of the electrode for electrolysis according to the above inventions, and the anode and a cathode having water permeability are arranged on both surfaces of a cation exchange film.

[0018] According to the invention of the first aspect, in the electrode for electrolysis including the substrate and the surface layer formed on the surface of the substrate, the surface layer is the amorphous insulator, so that ozone can efficiently be formed by the electrolysis of an electrolytic solution with a low current density by use of the electrode as the anode.

[0019] In particular, unlike the conventional technology, the temperature of the electrolytic solution does not have to be especially set to a low temperature, and the high current density is not required, so that power consumption required for the ozone formation can be reduced.

[0020] According to the invention of the second aspect, in the above invention, the insulator is the oxide of the single metal or the composite metal oxide. In particular, as in the invention of the third aspect, the insulator is tantalum oxide or tungsten oxide. In consequence, an empty level around a bottom of a conduction band at an energy level higher than Fermi level as much as about a half of a band gap receives electrons from an electrolyte, and owing to the electrons, an oxygen forming reaction is suppressed as compared with a case where the surface layer is made of a conductor, a crystallized metal oxide or the like. Instead, an ozone forming reaction is more efficiently caused.

[0021] Therefore, the electrons move with a higher energy level, whereby an ozone forming efficiency for causing the ozone forming reaction can be raised.

[0022] According to the invention of the fourth aspect, in the above inventions, the insulator is aluminum oxide, so that the electrode for electrolysis according to the above inventions can be made of a comparatively inexpensive material, and production cost can be reduced. Moreover, any toxic substance such as lead dioxide is not used, whereby an environmental load can be reduced.

[0023] According to the invention of the fifth aspect, in the above inventions, the thickness of the surface layer is in a range of 20 nm or more to 2000 nm or less, so that the surface layer can be made of a thin film, and the electrons can move in the electrode via impurities of the surface layer or Fowler-Nordheim tunneling. Therefore, owing to an electrode reaction in the anode, the empty level around the bottom of the conduction band at the energy level higher than Fermi level as much as about the half of the band gap can receive the electrons from the electrolyte, and the movement of the electrons is caused with the higher energy level, whereby the electrolysis can be performed with the low current density, and ozone can efficiently be formed.

[0024] According to the invention of the sixth aspect, in the above inventions, the substrate is provided with the intermediate layer positioned on the inner side of the surface layer and formed of the metal which is not easily oxidized on the surface of the substrate. Therefore, the electrode reaction can be caused with the high energy level in the surface of the surface layer. In consequence, ozone can efficiently be formed with a lower current density.

[0025] In particularly, according to such inventions, the intermediate layer is formed of the metal which is not easily oxidized on the surface of the substrate. Therefore, when the electrolysis is performed with the electrode, it is possible to avoid a disadvantage that the substrate surface is oxidized and non-conducted. In consequence, durability of the electrode can be improved. As compared with the whole substrate is made of the material constituting the intermediate layer, the production cost can be reduced. Even in such a case, ozone can similarly efficiently be formed.

[0026] In the electrolysis unit according to the invention of the seventh aspect, the anode having the water permeability is constituted of the electrode for electrolysis according to the above inventions, and the anode and the cathode having the water permeability are arranged on both the surfaces of the cation exchange film. Therefore, protons move in the cation exchange film, whereby even when the electrolytic solution is pure water, ozone can efficiently be formed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027]

FIG. 1 is a cross sectional view of an electrode for electrolysis according to the present invention (Examples 1, 3);

FIG. 2 is a flow chart of a manufacturing method of the electrode for electrolysis according to the present invention (Examples 1, 3);

FIG. 3 shows an X-ray diffraction pattern of the electrode for electrolysis according to the present invention (Example 1);

FIG. 4 is a schematically explanatory view of an electrolysis device according to the present invention;

FIG. 5 is a diagram showing an ozone forming current efficiency in a case where the electrode for electrolysis prepared on conditions is used (Example 1);

FIG. 6 is a flow chart of a manufacturing method of an electrode for electrolysis according to another example (Example 2);

FIG. 7 is a cross sectional view of the electrolysis according to the example (Example 2);

FIG. 8 is an X-ray diffraction pattern of the electrode for electrolysis according to the present invention (Example 2);

FIG. 9 is an X-ray diffraction pattern of the electrode for electrolysis according to the present invention (Example 2);

FIG. 10 is a diagram showing an ozone forming cur-

rent efficiency in a case where the electrode for electrolysis prepared on conditions is used (Example 2);
FIG. 11 is an X-ray diffraction pattern of the electrode for electrolysis according to the present invention (Example 3);
FIG. 12 is a diagram showing an ozone forming current efficiency in a case where the electrode for electrolysis prepared on conditions is used (Example 3); and
FIG. 13 is a schematic explanatory view of an electrolysis unit to which the electrode for electrolysis according to the present invention is applied.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0028] A preferable embodiment of an electrode for electrolysis according to the present invention will hereinafter be described with reference to the drawings. FIG. 1 is a cross sectional view of an electrode 1 for electrolysis of the present invention. As shown in FIG. 1, the electrode 1 for electrolysis is constituted of a substrate 2, a close contact layer 3 formed on the surface of the substrate 2, an intermediate layer 4 formed on the surface of the close contact layer 3, and a surface layer 5 formed on the surface of the intermediate layer 4. In the electrode 1 for electrolysis, the substrate 2 is provided with a titanium plate 6 as an electric conductor, and conduction can be realized between the titanium plate 6 and the intermediate layer 4 via a silver paste 7 as a conductive material. Furthermore, this silver paste 7 and the titanium plate 6 are coated with a seal material 8, and this does not contribute to electrolysis. It is to be noted that a way to realize the conduction is not limited to this example.

[0029] In the present invention, the substrate 2 is made of a conductive material of, for example, platinum (Pt), a valve metal such as titanium (Ti), tantalum (Ta), zirconium (Zr) or niobium (Nb), an alloy of two or more of these valve metals, silicon (Si) or the like. In particular, Si having the surface thereof treated so as to be flat is used in the substrate 2 for use in the present embodiment.

[0030] The close contact layer 3 is formed on the surface of the substrate 2 so as to improve a close contact property between the substrate 2 and the intermediate layer 4 formed of, for example, platinum on the surface of the close contact layer 3, and the close contact layer is made of titanium oxide, titanium nitride or the like. It is to be noted that in the present embodiment, titanium oxide is used.

[0031] The intermediate layer 4 is made of a metal which is not easily oxidized, for example, platinum or gold (Au), a conductive metal oxide such as iridium oxide, palladium oxide or ruthenium oxide, or an oxide superconductor. Alternatively, the intermediate layer is made of a metal which is oxidized but has conductivity, for example, ruthenium (Ru), rhodium (Rh), palladium (Pd), iridium (Ir) or silver (Ag) included in platinum group elements. It is to be noted that the metal oxide is not limited to the oxide beforehand constituting the intermediate layer 4, and may include a metal oxide obtained by electrolytic oxidization.

[0032] However, when the intermediate layer 4 is made of the metal oxide having the conductivity, for example, iridium oxide or the like, the conductor is adversely affected by oxygen atoms constituting the metal oxide. Therefore, it is preferable that the intermediate layer 4 is made of the metal which is not easily oxidized. In the present embodiment, the intermediate layer 4 is made of platinum.

[0033] It is to be noted that when the substrate 2 is made of platinum, needless to say, the surface of the substrate 2 is also made of platinum, so that the intermediate layer 4 does not have to be especially constituted. However, when the substrate 2 is made of platinum in this manner, steep rise of cost is incurred. Therefore, it is industrially preferable that the substrate 2 is made of an inexpensive material, and the intermediate layer 4 made of a noble metal or the like is formed on the surface of the substrate 2. There is not any special restriction on the above constitution, as long as the substrate 2 is made of a substance which does not have any conductivity, for example, a glass plate and at least a contact surface between the substrate 2 and the surface layer 5 described later is coated with a material having the conductivity. This can also suppress steep rise of cost required for the material for use in constituting the substrate 2.

[0034] Moreover, the surface layer 5 is an amorphous (an infinite form, non-crystalline) insulator provided together with the intermediate layer 4 so as to coat the intermediate layer 4. In the present embodiment, the insulator is made of tantalum oxide (TaOx), tungsten oxide (WOx) or aluminum oxide (AlOx) in the form of a layer on the surface of the substrate 2. This surface layer 5 is formed into a thin film having a predetermined thickness above 0 to 1 mm or less, preferably 20 nm or 2000 nm in the present embodiment.

[0035] It is to be noted that in the present embodiment, examples of the insulator include amorphous tantalum oxide, tungsten oxide and aluminum oxide, but the insulator is not limited to these examples, and an amorphous oxide of a single metal as an insulator may be used. Specific examples of the oxide include TiOx, NbOx, HfOx, NaOx, MgOx, KOx, CaOx, ScOx, VOx, CrOx, MnOx, FeOx, CoOx, NiOx, CuOx, ZnOx, GaOx, RbOx, SrOx, YOx, ZrOx, MoOx, InOx, SnOx, SbOx, CsOx, BaOx, LaOx, CeOx, PrOx, NdOx, PmOx, SmOx, EuOx, GdOx, TbOx, DyOx, HoOx, ErOx, TmOx, YbOx, LuOx, PbOx and BiOx. Alternatively, an amorphous composite metal oxide as an insulator, SiOx, GeOx or the like may be used.

(Example 1)

[0036] Next, a manufacturing method of an electrode 1 for electrolysis according to Example 1 of the present invention will be described with reference to a flow chart of FIG. 2. First, silicon (Si) constituting a substrate 2 is

pretreated in step S1. Here, it is preferable that phosphorous (P), boron (B) and the like are introduced as impurities into Si to improve the conductivity. Si having a very flat surface is used. It is to be noted that in the present example, Si is used as the substrate 2, but a conductive material may be used.

[0037] In the pretreatment, the substrate 2 of Si is treated with 5% of hydrofluoric acid to remove a native oxide film formed on the surface of the substrate 2. In consequence, the surface of the substrate 2 is further flattened. It is to be noted that the pretreatment does not have to be performed. Afterward, the surface of the substrate 2 is rinsed with pure water, and then in step S2, the substrate is introduced into a chamber of an existing sputtering system to form a film thereon.

[0038] In the step S2, a close contact layer 3 for improving a close contact property of an intermediate layer 4 as described above is formed on the surface of the substrate 2. The close contact layer 3 is formed on the substrate 2 by a reactive sputtering process. The close contact layer 3 is made of titanium oxide, so that the film is formed at room temperature for ten minutes on conditions that Ti is used as a first target, a supply power is 6.17 W/cm^2, an oxygen partial pressure is 52% (Ar:O_2 24:26) and a film forming pressure is 0.6 Pa. In consequence, the close contact layer 23 of titanium oxide having a thickness of about 50 nm is formed on the surface of the substrate 2. It is to be noted that in the present example, as a method for forming a film of the close contact layer 3, the reactive sputtering process is used, but the present invention is not limited to this example. For example, a sputtering process, a CVD process, an ion plating process, a plating process, or a combination of one of these processes and thermal oxidation may be used.

[0039] Subsequently, in step S3, the intermediate layer 4 is formed on the surface of the substrate 2 provided with the close contact layer 3. The intermediate layer 4 is formed on the surface of the substrate 2 by a sputtering process. In the present example, the intermediate layer 4 is made of platinum, so that the film is formed at room temperature for about one minute and eleven seconds on conditions that Pt (80 mmϕ) is used as a first target, a supply power is 4.63 W/cm^2, and an Ar gas pressure is 0.7 Pa. In consequence, the intermediate layer 4 having a thickness of about 200 nm is formed on the surface of the substrate 2 provided with the close contact layer 3. It is to be noted that in the present example, as a method for forming a film of the intermediate layer 4, the sputtering process is used, but the present invention is not limited to this example. For example, a CVD process, an evaporation process, an ion plating process, a plating process or the like may be used.

[0040] Subsequently, a surface layer 5 is formed on the surface of the substrate 2 provided with the intermediate layer 4. In the present example, the surface layer 5 is formed using a spin coat process, so that the surface of the substrate 2 provided with the intermediate layer 4 is coated with an organic aluminum compound solution as a surface layer constituting material. In the present example, the surface layer 5 is made of aluminum oxide, so that an organic aluminum compound is used in which a functional group such as a hydroxyl group, an aldehyde group, an alkyl group, a carboxyl group or an alkoxyl group is coordinated in aluminum having a coordination number of 3. Moreover, it is preferable that aluminum in this organic aluminum compound solution is in a range of about 0.4 wt% to 3 wt%. It is to be noted that in the present example, the organic aluminum compound solution is used as the surface layer constituting material, but the present invention is not limited to this example. An aluminum-containing compound from which a substance other than aluminum can be removed by calcinating, for example, aluminum chloride, aluminum bromide, aluminum iodide or the like may be used.

[0041] Then, in step S4, the surface constituting material is dripped on the surface of the substrate 2 provided with an intermediate layer 4 to form a thin film by a spin coat process. In the present example, conditions of the spin coat process are set to five seconds at 1000 rpm, 15 seconds at 3000 rpm. Afterward, the surface of the substrate is dried in an environment at room temperature and then 200°C for ten minutes (step S5). In consequence, a surface layer 5 is formed of the surface layer constituting material including the aluminum compound on the surface of the intermediate layer 4 of the substrate 2.

[0042] Afterward, in step S6, the substrate 2 provided with the intermediate layer 4 and the surface layer 5 is calcinated (annealed) at 400°C to 900°C in a muffle furnace, at 600°C in atmospheric air for ten minutes to obtain the electrode 1 for electrolysis. In consequence, the surface layer constituting material applied to the surface of the intermediate layer 4 is uniformly applied aluminum oxide. In the present example, the present film forming operation is performed once, whereby the calcinated and formed surface layer 5 of aluminum oxide has a thickness of about 25 nm. It is to be noted that the film forming operation may be repeated as much as a plurality of times to set the thickness of the surface layer 5 to about 20 nm to 2000 nm.

[0043] The surface layer 5 of the electrode 1 for electrolysis obtained as described above is all aluminum oxide. That is, the surface layer constituting material includes an aluminum-containing compound, for example, an organic aluminum compound in which a plurality of functional groups are coordinated in addition to aluminum. Alternatively, the material includes aluminum chloride, aluminum bromide, aluminum iodide or the like. The material is calcinated, whereby substances other than aluminum, that is, functional groups of organic substances, chloride, bromine and the like are removed. On the other hand, aluminum reacts with oxygen in the atmosphere to form aluminum oxide.

[0044] FIG. 3 shows an X-ray diffraction pattern of the surface layer 5 of the electrode 1 for electrolysis obtained

as described above. It is to be noted that in FIG. 3, the electrode 1 for electrolysis is constituted on conditions that a calcinating temperature in constituting the surface layer 5 are 700°C, 750°C, 800°C, 850°C and 900°C. In general, X-ray diffraction (XRD) is used in analysis of a crystal structure, whereby the crystal structure of aluminum oxide constituting the surface layer 5 can be analyzed. In the present example, the structure was observed using an X-ray diffraction apparatus (D8 Discover manufactured by Bruker AXS Co.).

[0045] According to the observation, diffraction peaks (2θ) shown in an X-ray diffraction pattern of the surface layer 5 of the electrode 1 for electrolysis obtained in the present example were about 36.1°, about 38° and about 39.6° regardless of the calcinating temperature at which the electrode 1 was constituted. In general, as the crystal structure of aluminum oxide, hexagonal system of α-alumina, β-alumina or the like is known, but diffraction peaks (2θ) of 35.15°, 57.50° and 43.36° inherent in aluminum oxide (Al_2O_3) were not present in any X-ray diffraction pattern of the surface layer 5 of the electrode 1 for electrolysis. Therefore, it is seen that aluminum oxide forming the surface layer 5 of the electrode 1 for electrolysis by the above method does not have any crystal structure, has an infinite form, and is, so-called amorphous. It is to be noted that in this case, the diffraction peak around 36.1° is a peak of titanium oxide (101) constituting a close contact layer 3, and the diffraction peak around 39.6° is a peak of platinum (111) constituting the intermediate layer 4.

[0046] It is to be noted that in the present example, the surface layer 5 is formed of amorphous aluminum oxide by coating the surface of the substrate (the surface of the intermediate layer 4 in the present example) with a surface layer constituting material including an aluminum compound by a spin coat process to calcinate the material at a predetermined temperature, but the method constituting the surface layer 5 with amorphous aluminum oxide is not limited to this example.

[0047] As another method, there is a method for forming the surface layer 5 by a thermal CVD process. In this thermal CVD process, the close contact layer 3 and the intermediate layer 4 are successively formed on the surface of the substrate 2 in the same manner as in the above example. Afterward, the organic aluminum compound as the surface layer constituting material is vaporized, and guided to a reaction tube by use of an appropriate carrier gas to perform a chemical reaction on the surface of the substrate 2 heated to a high temperature of, for example, 500°C to 900°C, preferably 600°C to 800°C.

[0048] In consequence, with regard to the substances excluding aluminum in the organic aluminum compound as the surface layer constituting material, for example, an organic substance is removed from the surface of the substrate 2 heated to the high temperature, and only aluminum reacts with oxygen in the atmosphere to form aluminum oxide on the surface of the substrate 2. Aluminum oxide formed on the surface of the substrate 2 (in actual, the surface of the intermediate layer 4) constitutes an amorphous thin film (an aluminum oxide film).

[0049] It is to be noted that in addition to this method, examples of the method for constituting the surface layer 5 of amorphous aluminum oxide include a dip process.

[0050] It is to be noted that in the present example, the close contact layer 3 made of titanium oxide is formed on the surface of the substrate 2 made of Si. Therefore, platinum constituting the intermediate layer 4 is directly diffused in the substrate 2 to form platinum silicide, and it can be prevented that the substrate surface is oxidized and non-conducted during electrolysis. The close contact layer 3 of titanium oxide can improve a close contact property between platinum constituting the intermediate layer 4 and the substrate 2. In consequence, durability of the electrode 1 can be improved.

(Electrolysis Method by use of Electrode for Electrolysis and Evaluation of Electrode)

[0051] Next, formation of ozone by electrolysis using the electrode 1 for electrolysis manufactured as described above will be described with reference to FIGS. 4 and 5. FIG. 4 is a schematically explanatory view of an electrolysis device 10 to which the electrode 1 for electrolysis is applied, and FIG. 5 is a diagram showing an ozone forming current efficiency in a case where the electrode for electrolysis prepared on conditions is used.

[0052] The electrolysis device 10 is constituted of a treatment tank 11, the electrode 1 for electrolysis as an anode, an electrode 12 as a cathode, and a power source 15 which applies a direct current to the electrodes 1, 12. Then, a cation exchange film (a diaphragm: Nafion (trade name) manufactured by Dupont) 14 is provided so as to be positioned between these electrodes 1 and 12, and divides the inside of the treatment tank 11 into one region where the electrode 1 is present and the other region where the electrode 12 is present. Moreover, a stirring device 16 is provided in a region in which the electrode 1 for electrolysis as the anode is immersed.

[0053] Furthermore, model tap water 13 as an electrolytic solution is received in this treatment tank 11. It is to be noted that in an experiment of the present example, the model tap water is used as the electrolytic solution, but the cation exchange film is provided, whereby even in a case where pure water is treated, a substantially similar effect is obtained. It is to be noted that the electrolytic solution for use in the experiment is an aqueous solution model tap water, and a component composition of this model tap water 13 includes 5.75 ppm of Na^+, 10.02 ppm of Ca^{2+}, 6.08 ppm of Mg^{2+}, 0.98 ppm of K^+, 17.75 ppm of Cl^-, 24.5 ppm of SO_4^{2-} and 16.5 ppm of CO_3^{2-}.

[0054] The electrode 1 for electrolysis is provided by the above-mentioned manufacturing method, a thickness of the surface layer 5 of the electrode 1 for electrolysis is about 25 nm, and a calcinating temperature in

forming the surface layer 5 is 600°C. For comparison, there are used an electrode for electrolysis (formed of AlOx by sputtering) in which the surface layer 5 is formed of aluminum oxide by a sputtering process instead of the spin coat process, an electrode for electrolysis (spin-coated with TaOx) in which the surface layer 5 is formed of tantalum oxide (TaOx) by the spin coat process, and an electrode for electrolysis (spin-coated with TiOx) in which the surface layer 5 is formed of titanium oxide (TiOx) by the spin coat process.

[0055] In the electrode for electrolysis formed of AlOx by the sputtering, the surface layer 5 is formed on the surface of the intermediate layer 4 formed in the same manner as in the above example, so that a target is the surface layer constituting material of Al, an rf power is set to 100 W, an Ar gas pressure is set to 0.9 Pa, and a distance between the substrate 2 and the target is set to 60 mm, to execute film formation at room temperature. Afterward, the substrate 2 provided with the surface layer 5 is obtained by executing thermal oxidation at 600°C in a muffle furnace in the atmospheric air for 30 minutes.

[0056] In the electrode for electrolysis spin-coated with TaOx, the surface layer 5 of tantalum oxide is formed on the surface of the intermediate layer 4 formed by a method similar to the present example, by the spin coat process on similar conditions. Then, the electrode is obtained by calcinating the surface layer at a temperature of 600°C in the atmospheric air for ten minutes. It is to be noted that a thickness of the surface layer 5 is about 25 nm.

[0057] In the electrode for electrolysis spin-coated with TiOx, the surface layer 5 of titanium oxide is similarly formed on the surface of the intermediate layer 4 by the spin coat process on the similar conditions. Then, the electrode is obtained by calcinating the surface layer at a temperature of 600°C in the atmospheric air for ten minutes. It is to be noted that a thickness of the surface layer 5 is about 50 nm. The surface layer 5 formed on the conditions is made of titanium oxide having an anatase type crystal structure.

[0058] It is to be noted that the film thicknesses of the surface layers of the above electrodes for electrolysis are obtained by conversion substrated on carried amounts of A1, Ta and Ti acquired by evaluation with a X-ray fluorescence analysis device (JSX-3220ZS Element Analyzer manufactured by JEOL Ltd.).

[0059] On the other hand, platinum is used in the electrode 12 as the cathode. Alternatively, the electrode may be constituted of an insoluble electrode in which platinum is calcinated on the surface of a titanium substrate, a platinum-iridium-substrated electrode for electrolysis, a carbon electrode or the like.

[0060] According to the above constitution, 150 ml of model tap water 13 is received in each region of the treatment tank 11, and the electrode 1 for electrolysis and the electrode 12 are immersed in the model tap water, respectively. It is to be noted that a distance between the electrodes is 10 mm. Then, the power source 15 applies a constant current with a current density of about 25 mA/cm^2 to the electrode 1 for electrolysis and the electrode 12. Moreover, a temperature of the model tap water 13 is +15°C.

[0061] In the present example, to evaluate an amount of ozone to be formed by each electrode for electrolysis, an amount of ozone formed in the model tap water 13 after the electrolysis for five minutes on the above conditions is measured by an indigo process (DR4000 manufactured by HACH Co.), and a ratio of a charge which has contributed to the ozone formation with respect to the total amount of the supplied charge, that is, an ozone forming current efficiency is calculated.

[0062] As shown in FIG. 5, in the experiment, in a case where the electrode 1 for electrolysis prepared in the present example (the surface layer 5 was made of AlOx by the spin coat process) was used, the ozone forming current efficiency was about 5.64%. On the other hand, when the surface layer 5 of AlOx was constituted by the sputtering process, the ozone forming current efficiency was about 4.0%. In consequence, it has been seen that the ozone forming current efficiency is high in a case where the surface layer 5 is constituted by the spin coat process as compared with a case where the surface layer 5 is constituted by the sputtering process.

[0063] Moreover, when the surface layer 5 was made of another material such as TaOx by the spin coat process (in the experiment, the surface layer of the electrode for electrolysis was made of crystallized tantalum oxide), the ozone forming current efficiency was about 1.5%. When the layer was made of TiOx (in the experiment, the surface layer of the electrode for electrolysis was made of titanium oxide having the anatase type crystal structure), the ozone forming current efficiency was about 0.3%. It has been seen that even in a case where the surface layer 5, is formed into a substantially equal film thickness by a similar method, when the surface layer 5 is made of AlOx, the ozone forming current efficiency is remarkably high as compared with a case where the surface layer is made of TaOx (crystallized tantalum oxide in the experiment) or TiOx (crystallized titanium oxide in the experiment).

[0064] It is seen from the above experiment result that ozone can be formed in the electrolytic solution even by the electrolysis of the electrolytic solution by use of each electrode for electrolysis as the anode. However, in a case where the electrode 1 for electrolysis having the surface layer 5 of AlOx formed by the spin coat process of the present example is used, the ozone forming current efficiency is remarkably high as compared with a case where the surface layer 5 is formed of another material by another process. This is supposedly because the thin-film surface layer 5 of amorphous aluminum oxide is formed on the surface of the substrate 2 (actually the intermediate layer 4) by the spin coat process on the conditions.

[0065] In particular, a thin film of amorphous aluminum oxide is formed into a thickness of 20 nm to 2000 um, so that electrons move to the intermediate layer 4 made of

a conductive material via an impurity level in the surface layer 5 or Fowler-Nordheim tunneling.

[0066] Usually, when a metal electrode is used as the electrode for electrolysis, an empty level right above Fermi level receives the electrons from an electrolyte, whereby an electrode reaction in the anode preferentially causes an oxygen forming reaction. When the surface layer 5 is made of the crystallized metal oxide, a metal segregates in a grain boundary between crystals, and a current flows. Even in this case, the empty level right above the Fermi level receives the electrons from the electrolyte, whereby the oxygen forming reaction is preferentially caused by the electrode reaction in the anode.

[0067] On the other hand, in a case where the electrode 1 for electrolysis provided with the surface layer 5 is used as in the example, the surface layer 5 is made of amorphous aluminum oxide, so that an empty level around a bottom of a conduction band having an energy level higher as much as an about half of a band gap than the Fermi level receives the electrons from the electrolyte. Owing to the electrons, the oxygen forming reaction is suppressed unlike the above case, and instead an ozone forming reaction is more efficiently caused.

[0068] Therefore, in a case where the electrode 1 for electrolysis according to the present invention is used, it is supposed that the electrons move at a higher energy level to cause the ozone forming reaction, and an ozone forming efficiency rises as compared with a case where the electrode for electrolysis of platinum or the like, or the electrode for electrolysis provided with the surface layer of crystallized tantalum oxide or titanium oxide is used.

[0069] In consequence, a current having a predetermined low current density of 0.1 mA/cm^2 to 2000 mA/cm^2, preferably 1 mA/cm^2 to 1000 mA/cm^2 is applied to the electrode 1 for electrolysis, whereby ozone can efficiently be formed. Even when the temperature of the electrolytic solution is not especially set to a low temperature and is set to ordinary temperature of +15°C as in the present example, ozone can efficiently be formed. Therefore, power consumption required for the ozone formation can be reduced.

[0070] Moreover, the surface layer 5 of the electrode 1 capable of realizing the efficient ozone formation can be formed by the spin coat process as described above, so that productivity can be improved as compared with a case where the layer is formed by a conventional sputtering process. Moreover, the electrode for electrolysis can be manufactured with low manufacturing cost, and an inexpensive equipment can be realized. The surface layer 5 is formed by the thermal CVD process as described above, whereby satisfactory stability and high production efficiency can be realized. Furthermore, any toxic substance such as lead dioxide is not used, whereby an environmental load can be reduced.

(Example 2)

[0071] Next, a manufacturing method of an electrode 21 for electrolysis according to Example 2 of the present invention will be described with reference to a flow chart of FIG. 6. It is to be noted that FIG. 7 is a schematic constitution diagram of the electrode 21 for electrolysis obtained by the example. First, in step S11, Si constituting a substrate 22is pretreated in the same manner as in the above example. A material of the substrate 22 is similar to that of the above example, so that description thereof is omitted. Subsequently, in step S12, the substrate is introduced into a chamber of an existing sputtering device to form a film.

[0072] In the step S12, a close contact layer 23 for improving a close contact property of an intermediate layer 24 is formed on the surface of the substrate 22 as described above. The close contact layer 23 is formed on the substrate 22 by a reactive sputtering process in the same manner as in the above example. The close contact layer 23 is made of titanium oxide, so that the film is formed at room temperature for ten minutes on conditions that Ti is used as a first target, a supply power is 6.17 W/cm^2, an oxygen partial pressure is 52% (Ar:O_2 24:26) and a film forming pressure is 0.6 Pa. In consequence, the close contact layer 23 made of titanium oxide having a thickness of about 50 nm is formed on the surface of the substrate 22.

[0073] Subsequently, in step S13, the intermediate layer 24 is formed on the surface of the substrate 22 provided with the close contact layer 23 in the same manner as in the above example. The intermediate layer 24 is formed on the substrate 22 by a sputtering process. In the present example, the intermediate layer 24 is made of platinum, so that the film is formed at room temperature for about one minute and eleven seconds on conditions that Pt (80 mmϕ) is used as a first target, a supply power is 4.63 W/cm^2, and an Ar gas pressure is 0.7 Pa. In consequence, the intermediate layer 24 having a thickness of about 200 nm is formed on the surface of the substrate 22 provided with the close contact layer 23.

[0074] Subsequently, a surface layer 25 is formed on the surface of the substrate 22 provided with the intermediate layer 24. In the present example, the surface layer 25 is formed by a sputtering process. In a case where the surface layer is made of tantalum oxide, the film is formed at room temperature for five to 180 minutes on conditions that the target is changed to Ta as a surface layer constituting material, an rf power is 100 W, an Ar gas pressure is 0.9 Pa and a distance between the substrate 22 and the target is 60 mm (step S14). In consequence, the surface layer 25 having a thickness of about 7 nm to 1000 nm is formed on the surface of the intermediate layer 24 of the substrate 22. It is to be noted that the film thicknesses of the intermediate layer 24 and the surface layer 25 are obtained by conversion substrated on carried amounts of Pt and Ta acquired by evaluation with a X-ray fluorescence.

[0075] Afterward, in step S15, the substrate 22 provided with the surface layer 25 is thermally oxidized at temperatures of 300°C, 400°C, 500°C and 600°C in a muffle furnace in the atmospheric air for 30 minutes, to obtain the electrode 21 for electrolysis. In consequence, a tantalum metal constituting the surface layer 25 formed on the surface of the intermediate layer 24 is uniformly oxidized. It is to be noted that the tantalum metal is thermally oxidized to constitute tantalum oxide, so that a thickness of the surface layer 25 is about 14 nm to 2000 nm.

[0076] It is to be noted that here, Ta is an example of the material constituting the surface layer 25. However, this material may be changed to W, whereby a tungsten metal constituting the surface layer 25 is thermally oxidized to constitute tungsten oxide.

[0077] FIG. 8 shows an X-ray diffraction pattern of the electrode 21 for electrolysis (the surface layer 25 is made of tantalum oxide) obtained as described above, and FIG. 9 shows an X-ray diffraction pattern of the electrode 21 for electrolysis (the surface layer 25 is made of tungsten oxide) obtained as described above. X-ray diffraction is used in the same manner as in the above example, whereby a crystal structure of tantalum oxide (tungsten oxide) constituting the surface layer 25 can be analyzed. Even in such an example, the structure was observed using an X-ray diffraction apparatus (D8 Discover manufactured by Bruker AXS Co.).

[0078] FIG. 8 shows the X-ray diffraction patterns of the electrode 21 oxidized at 600°C, 500°C, 400°C and 300°C in order from the upside. It is to be noted that for comparison, an X-ray diffraction pattern of an electrode (having the surface only of Pt) which is not provided with the surface layer 25 is shown in the bottom. In consequence, in the electrode 21 oxidized at a temperature of 600°C, a diffraction peak (a peak shown by a solid circle in FIG. 8) inherent in tantalum oxide (Ta_2O_5) and a diffraction peak (a peak shown by * in FIG. 8) inherent in platinum constituting the intermediate layer 24 are recognized. Therefore, it is seen that the surface layer 25 of crystalline tantalum oxide (Ta_2O_5) is formed on the conditions.

[0079] On the other hand, in the electrode 21 oxidized at a temperature of 400°C, a diffraction peak (a peak shown by a open circle in FIG. 8) inherent in tantalum oxide (TaO) and a diffraction peak inherent in platinum are recognized. Therefore, it is seen that the surface layer 25 of crystalline tantalum oxide (TaO) is formed on the conditions.

[0080] Moreover, in the electrode 21 oxidized at a temperature of 300°C, a diffraction peak (a peak shown by a black triangle in FIG. 8) inherent in tantalum (Ta) and a diffraction peak inherent in platinum are recognized. Therefore, it is seen that a part of the surface layer 25 remains as tantalum on the conditions.

[0081] On the other hand, in the electrode 21 oxidized at a temperature of 500°C, any diffraction peak inherent in tantalum oxide or tantalum described above is not recognized, and the diffraction peak inherent in platinum and a halo indicating an amorphous state (a non-crystalline state) are recognized. Therefore, it is seen that the surface layer 25 of amorphous tantalum oxide is formed on the conditions. It is to be noted that even in comparison with the X-ray diffraction pattern of the platinum electrode shown for comparison, it is easily seen that the amorphous state is present in the electrode on the conditions.

[0082] FIG. 9 shows the X-ray diffraction patterns of the electrode 21 oxidized at 600°C, 500°C, 400°C and 300°C in order from the upside. It is to be noted that for comparison, an X-ray diffraction pattern of an electrode (having the surface only of Pt) which is not provided with the surface layer 25 is shown in the bottom in the same manner as described above. According to the patterns, in the electrode 21 oxidized at a temperature of 600°C, 500°C or 400°C, a diffraction peak (a peak shown by a open circle in FIG. 9) inherent in tungsten oxide (WO_3) and a diffraction peak (a peak shown by * in FIG. 9) inherent in platinum constituting the intermediate layer 24 are recognized. Therefore, it is seen that the surface layer 25 of crystalline tungsten oxide (WO_3) is formed on the conditions.

[0083] On the other hand, in the electrode 21 oxidized at a temperature of 300°C, the above-mentioned diffraction peak inherent in tungsten oxide (WO_3) is not recognized, and the diffraction peak inherent in platinum only is recognized. Therefore, it is seen that the surface layer 25 of amorphous tungsten oxide is formed on the conditions.

(Electrolysis Method by use of Electrode for Electrolysis and Evaluation of Electrode)

[0084] Next, formation of ozone by electrolysis using the electrode 21 for electrolysis manufactured as described above will be described with reference to FIG. 10. FIG. 10 is a diagram showing an ozone forming current efficiency in a case where the electrode for electrolysis prepared on the conditions is used. In the drawing, a solid circle shows an ozone forming current efficiency in a case where the surface layer 25 is made of tantalum oxide, and a open circle shows an ozone forming current efficiency in a case where the surface layer 25 is made of tungsten oxide. It is to be noted that experiment results are obtained using an electrolysis device 10 of the above example, and a constitution of the device and experiment conditions are similar to those described above, so that description thereof is omitted.

[0085] According to this experiment, in a case where the surface layer 25 of tantalum oxide was constituted, when the oxidizing temperature was 300°C, the ozone forming current efficiency was about 3.6%. The ozone forming current efficiencies were about 6.6% at an oxidizing temperature of 400°C, about 7.2% at an oxidizing temperature of 500°C, and about 2.4% at an oxidizing temperature of 600°C. Here, at the oxidizing temperature of 300°C, 400°C or 600°C, the surface layer has a crystal structure of tantalum oxide or tantalum. On the other

hand, at the oxidizing temperature of 500°C, amorphous tantalum oxide which does not have any crystal structure is formed as the surface layer 25.

[0086] According to such a result, it is seen that in a case where the surface layer 25 of tantalum oxide is formed and the surface layer of amorphous tantalum oxide which does not have any crystal structure is formed, the ozone forming current efficiency is highest.

[0087] Moreover, in a case where the surface layer 25 of tungsten oxide was constituted, when the oxidizing temperature was 300°C, the ozone forming current efficiency was about 6.1%. The ozone forming current efficiencies were about 2.4% at an oxidizing temperature of 400°C, about 3.6% at an oxidizing temperature of 500°C, and about 4.2% at an oxidizing temperature of 600°C. Here, at the oxidizing temperature of 400°C, 500°C or 600°C, the surface layer has a crystal structure of tungsten oxide. On the other hand, at the oxidizing temperature of 300°C, amorphous tungsten oxide which does not have any crystal structure is formed as the surface layer 25.

[0088] According to such a result, it is seen that in a case where the surface layer 25 of tungsten oxide is formed and the surface layer of amorphous tungsten oxide which does not have any crystal structure is formed, the ozone forming current efficiency is highest.

(Example 3)

[0089] Next, an electrode for electrolysis according to Example 3 of the present invention will be described. It is to be noted that a manufacturing method of an electrode 31 for electrolysis obtained according to such an example is similar to that shown in the flow chart of FIG. 2 in Example 1, and a schematic constitution diagram is substantially similar to FIG. 1, so that detailed description of the manufacturing method is omitted.

[0090] That is, in the electrode for electrolysis according to the example, a close contact layer 3 of titanium oxide is formed on the surface of Si constituting a substrate by a sputtering process as described above, and an intermediate layer 4 of platinum is formed on the surface of the close contact layer 3 by the sputtering process.

[0091] Subsequently, a surface layer 5 is formed on the surface of a substrate 2 provided with the intermediate layer 4. In such an example, the surface layer 5 is formed by a spin coat process, so that the surface of the substrate 2 provided with the intermediate layer 4 is coated with an organic tantalum compound solution as a surface layer constituting material. In the present embodiment, the surface layer 5 of tantalum oxide is formed using a $Ta(OEt)_5$ solution in the present example. It is to be noted that in the present example, ethyl acetate is used as a solvent of the $Ta(OEt)_5$ solution. It is to be noted that in the present example, the $Ta(OEt)_5$ solution is used as the surface layer constituting material, but the present invention is not limited to this example. There is not any special restriction on the material, as long as the material is a tantalum-containing compound which can be calcinated to remove a substance other than tantalum therefrom, thereby forming a film of tantalum oxide. In the present example, ethyl acetate is used as the solvent, but the present invention is not limited to this example, and another solvent such as an alcohol-substrated solvent may be used.

[0092] Then, the surface layer constituting material is dripped on the surface of the substrate 2 provided with the intermediate layer 4 to form a thin film by the spin coat process. Conditions in the spin coat process according to such an example are five seconds with 1000 rpm and 15 seconds at 3000 rpm in the same manner as in Example 1. Afterward, the film is dried in an environment at room temperature for ten minutes and then at 200°C for ten minutes.

[0093] Afterward, the substrate 2 provided with the intermediate layer 4 and the surface layer 5 is calcinated (annealed) at 400°C to 700°C in a muffle furnace in the atmospheric air for ten minutes, to obtain the electrode for electrolysis. In consequence, the surface of the intermediate layer 4 is uniformly coated with tantalum oxide as the surface layer constituting material.

[0094] The surface layer 5 of the electrode 1 for electrolysis obtained as described above is all tantalum oxide. That is, the surface layer constituting material is a tantalum-containing compound which is calcinated as described above to remove therefrom substances other than tantalum, that is, functional groups of organic substances and the like. On the other hand, tantalum reacts with oxygen in the atmosphere to constitute tantalum oxide.

[0095] FIG. 11 shows an X-ray diffraction pattern of the electrode 1 for electrolysis (the surface layer 5 is made of tantalum oxide) obtained as described above. X-ray diffraction is used in the same manner as in the above examples, whereby a crystal structure of tantalum oxide constituting the surface layer 5 can be analyzed. Even in such an example, the structure was observed using an X-ray diffraction apparatus (D8 Discover manufactured by Bruker AXS Co.).

[0096] FIG. 11 shows the X-ray diffraction patterns of the electrode 1 calcinated at 700°C, 600°C, 500°C and 400°C in order from the upside. According to the patterns, in the electrode 1 calcinated at a temperature of 700°C or 600°C, a diffraction peak (a peak shown by a solid circle in FIG. 11) inherent in tantalum oxide (Ta_2O_5) is recognized. Therefore, it is seen that the surface layer 5 of crystalline tantalum oxide (Ta_2O_5) is formed on the conditions.

[0097] On the other hand, in the electrode 1 calcinated at a temperature of 500°C or 400°C, a diffraction peak inherent in tantalum oxide (Ta_2O_5) described above is not recognized, and a halo indicating an amorphous state (a noncrystalline state) is recognized. Therefore, it is seen that the surface layer 5 of amorphous tantalum oxide is formed on the conditions.

(Electrolysis Method by use of Electrode for Electrolysis and Evaluation of Electrode)

[0098] Next, formation of ozone by electrolysis using the electrode 1 for electrolysis manufactured as described above will be described with reference to FIG. 12. FIG. 12 is a diagram showing an ozone forming current efficiency in a case where the electrode for electrolysis prepared on the conditions is used. It is to be noted that experiment results are obtained using an electrolysis device 10 of the above example, and a constitution of the device and experiment conditions are similar to those described above, so that description thereof is omitted.

[0099] According to this experiment, when the calcinating temperature was 400°C, the ozone forming current efficiency was about 7.0%. The ozone forming current efficiencies were about 12.0% at a calcinating temperature of 500°C, about 6.1% at a calcinating temperature of 600°C, and about 4.6% at a calcinating temperature of 700°C. Here, at the calcinating temperature of 600°C or 700°C, the surface layer has a crystal structure of tantalum oxide. On the other hand, at the calcinating temperature of 500°C or 400°C, amorphous tantalum oxide which does not have any crystal structure is formed as the surface layer 5.

[0100] According to such a result, it is seen that in a case where the surface layer of tantalum oxide is formed and the surface layer of amorphous tantalum oxide which does not have any crystal structure is formed, the ozone forming current efficiency is high as compared with a case where the surface layer 5 of tantalum oxide having a crystal structure is formed.

[0101] It is seen from the experiment results of Examples 2 and 3 that an electrolytic solution may be electrolyzed using either electrode for electrolysis as an anode to form ozone in the electrolytic solution. However, in a case where the surface layer 5 (25) of amorphous tantalum oxide or amorphous tungsten oxide is formed, an ozone forming efficiency is high as compared with a case where the surface layer of crystalline tantalum oxide or tungsten oxide is formed.

[0102] This is supposedly because a thin film of amorphous tantalum oxide or tungsten oxide is formed, so that electrons move to an intermediate layer made of a conductive material via impurities in the surface layer or Fowler-Nordheim tunneling.

[0103] Moreover, usually, when a metal electrode is used as the electrode for electrolysis, an empty level right above Fermi level receives the electrons from an electrolyte, whereby an electrode reaction in the anode preferentially causes an oxygen forming reaction. When the surface layer is made of the crystallized metal oxide, a metal segregates in a grain boundary between crystals, and a current flows. Even in this case, the empty level right above the Fermi level receives the electrons from the electrolyte, whereby the oxygen forming reaction is preferentially caused by the electrode reaction in the anode.

[0104] On the other hand, in a case where the electrode for electrolysis provided with the surface layer as in the above examples is used, the surface layer is made of an amorphous metal oxide such as amorphous tantalum oxide or tungsten oxide, so that an empty level around a bottom of a conduction band having an energy level higher as much as an about half of a band gap than the Fermi level receives the electrons from the electrolyte. Owing to the electrons, the oxygen forming reaction is suppressed unlike the above case, and instead an ozone forming reaction is more efficiently caused.

[0105] Therefore, in a case where the electrode for electrolysis according to the above examples is used as the anode, it is supposed that the electrons move at a higher energy level to cause the ozone forming reaction, and an ozone forming efficiency rises as compared with a case where the electrode for electrolysis of platinum or the like, or the electrode for electrolysis provided with the surface layer of crystallized tantalum oxide (the crystallized metal oxide) is used.

[0106] In consequence, a current having a predetermined low current density of 0.1 mA/cm^2 to 2000 mA/cm^2, preferably 1 mA/cm^2 to 1000 mA/cm^2 is applied to the electrode 1 for electrolysis, whereby ozone can efficiently be formed. Even when the temperature of the electrolytic solution is not especially set to a low temperature and is set to ordinary temperature of +15°C as in the present example, ozone can efficiently be formed. Therefore, power consumption required for the ozone formation can be reduced.

[0107] Moreover, the surface layer 5 of the electrode 1 capable of realizing the efficient ozone formation can be formed by not only the sputtering process but also the spin coat process as described above, so that productivity can be improved. Moreover, the electrode for electrolysis can be manufactured with low manufacturing cost, and an inexpensive equipment can be realized.

[0108] Furthermore, as in the above examples, the substrate 2 of Si is provided with the intermediate layer 4 including at least a metal which is not easily oxidized, a metal oxide having conductivity or a metal having conductivity even when oxidized, and the surface layer 5 is further formed on the surface of the intermediate layer 4 as described above, so that the electrons can effectively move in the surface layer 5. Therefore, the electrode reaction can be caused with a high energy level in the surface of the surface layer 5, and ozone can efficiently be formed with a lower current density.

[0109] It is to be noted that in a case where the substrate 2 is made of a material similar to that of the intermediate layer 4, that is, a material including at least a metal which is not easily oxidized, a metal oxide having conductivity or a metal having conductivity even when oxidized, it is possible to constitute an electrode capable of similarly efficiently forming ozone without being especially provided with the intermediate layer 4. However, the substrate 2 is coated with the intermediate layer 4 made of the above material as in the present invention,

whereby it is possible to realize with low production cost the electrode 1 capable of similarly efficiently forming ozone.

[0110] Moreover, the electrode for electrolysis according to the examples of the present invention is not limited to the electrode shown in the electrolysis device 10, and may be used as, for example, an anode for an electrolysis unit 26 shown in FIG. 13.

[0111] That is, the electrolysis unit 26 shown in FIG. 13 is constituted of the electrode 1 or 21 for electrolysis constituting the anode according to the above examples, an electrode 28 constituting the cathode, and a cation exchange film 29.

[0112] The electrode 1 (or 21 as the anode) and the electrode 28 (the cathode) are provided with a plurality of water permeable holes 27A and 28A for securing water permeability, respectively. Then, the electrodes 1 and 28 are arranged on both surfaces of the cation exchange film (Nafion (trade name) manufactured by Dupont Co. was used in the present example) 29, to constitute the electrolysis unit 26,

[0113] According to such a constitution, the electrolysis unit 26 is immersed in a treatment tank in which an electrolytic solution is received, and a constant current with a predetermined current density is applied between both the electrodes 1, 28. In consequence, an appropriate zero gap is maintained between the electrode 1 and the cation exchange film 29 and electrode 28, and protons move in the cation exchange film 29, whereby ozone can efficiently be formed even when the electrolytic solution is pure water. The water permeable holes 27A and 28A allow a formed gas to flow therethrough, whereby stable ozone formation can be realized.

Claims

1. An electrode for electrolysis comprising a substrate and a surface layer formed on the surface of the substrate,
   wherein the surface layer is an amorphous insulator.

2. The electrode for electrolysis according to claim 1, wherein the insulator is an oxide of a single metal or a composite metal oxide.

3. The electrode for electrolysis according to claim 1 or 2, wherein the insulator is tantalum oxide or tungsten oxide.

4. The electrode for electrolysis according to claim 1 or 2, wherein the insulator is aluminum oxide.

5. The electrode for electrolysis according to claim 1, 2, 3 or 4, wherein a thickness of the surface layer is in a range of 20 nm or more to 2000 nm or less.

6. The electrode for electrolysis according to claim 1, 2, 3, 4 or 5, wherein the substrate is provided with an intermediate layer positioned on an inner side of the surface layer and made of a metal which is not easily oxidized on the surface of the substrate.

7. An electrolysis unit in which an anode having water permeability is constituted of the electrode for electrolysis according to claim 1, 2, 3, 4, 5 or 6 and in which the anode and a cathode having water permeability are arranged on both surfaces of a cation exchange film.

FIG. 1

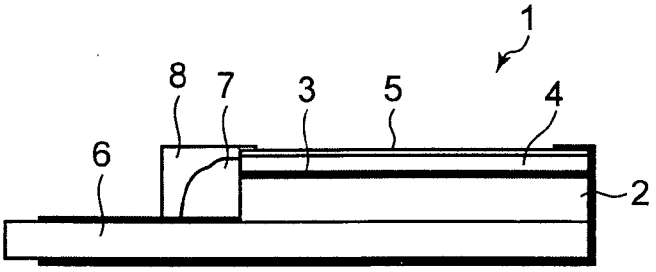


FIG. 2

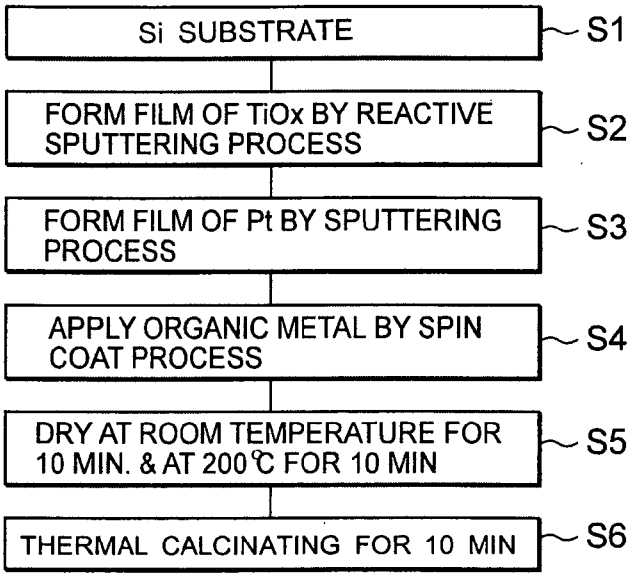


FIG. 3

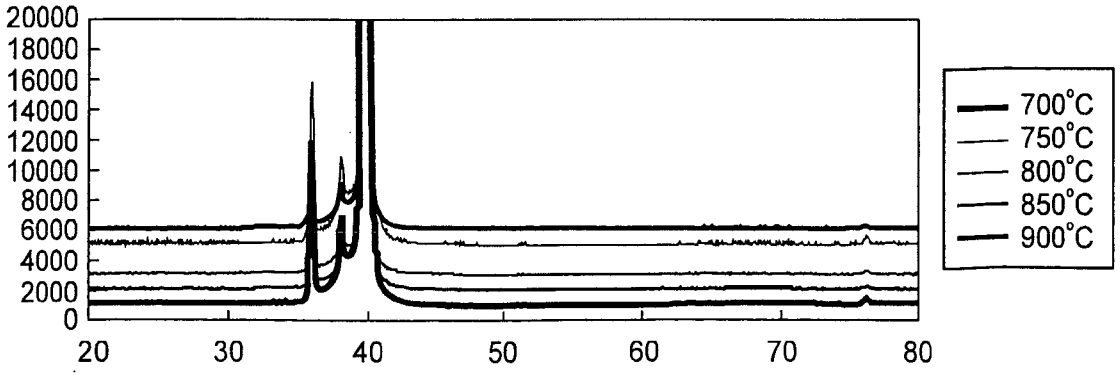


FIG. 4

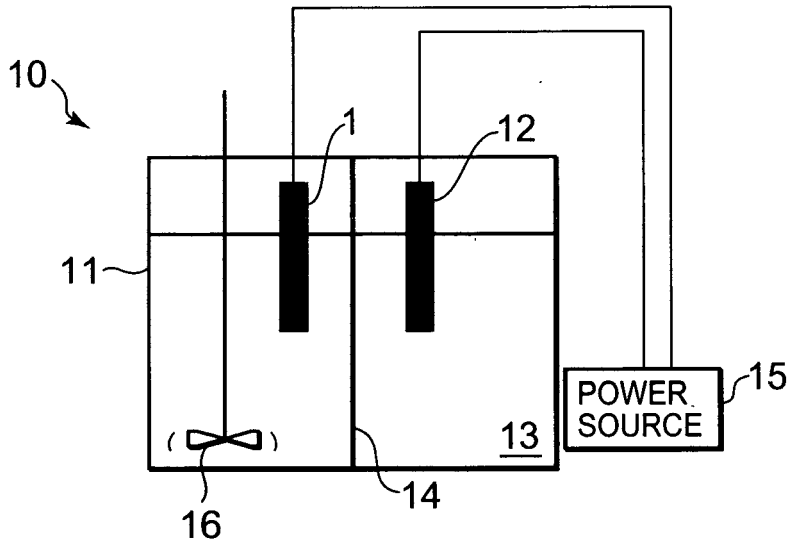

10
1
12
11
POWER SOURCE
15
13
14
16

FIG. 5

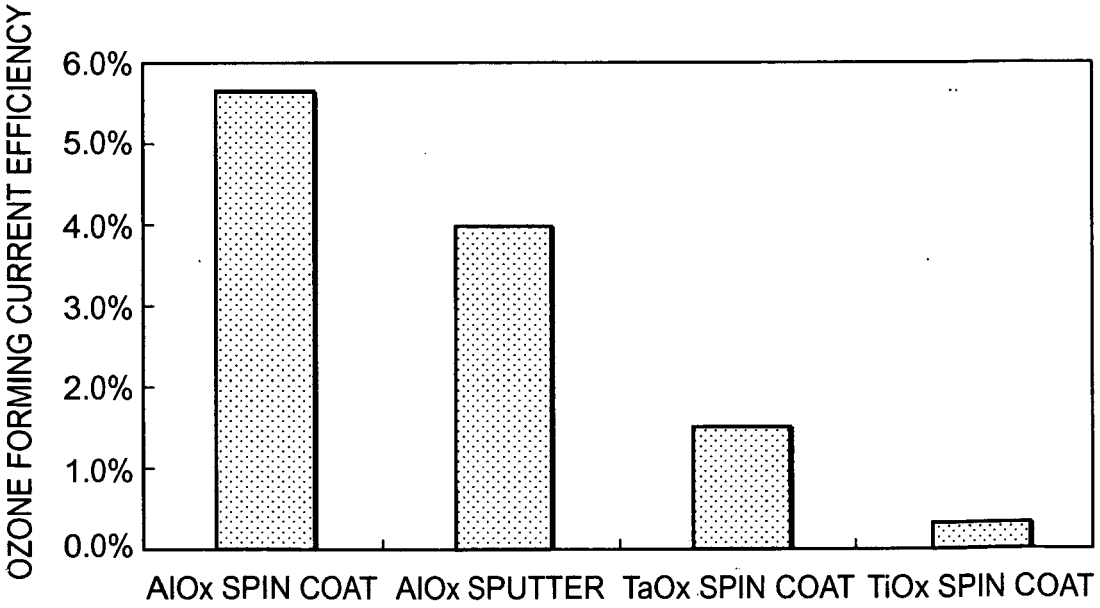

OZONE FORMING CURRENT EFFICIENCY
6.0%
5.0%
4.0%
3.0%
2.0%
1.0%
0.0%
AlOx SPIN COAT
AlOx SPUTTER
TaOx SPIN COAT
TiOx SPIN COAT

FIG. 6

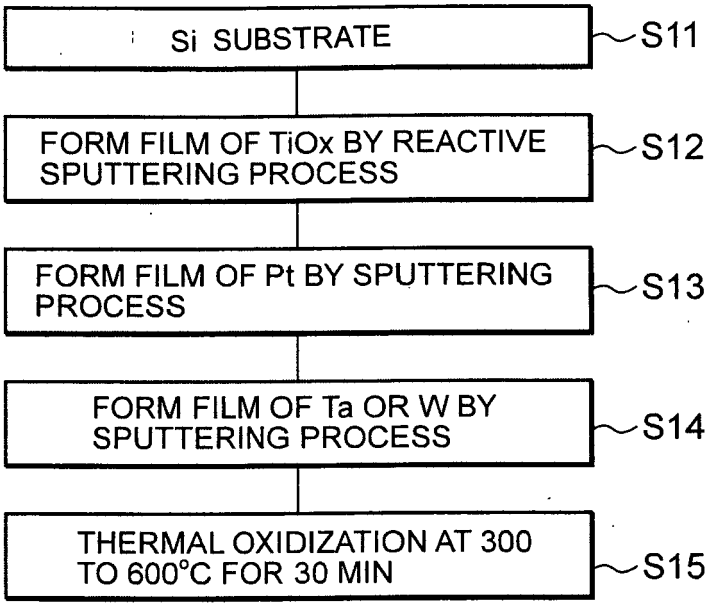

Si SUBSTRATE
S11
FORM FILM OF TiOx BY REACTIVE SPUTTERING PROCESS
S12
FORM FILM OF Pt BY SPUTTERING PROCESS
S13
FORM FILM OF Ta OR W BY SPUTTERING PROCESS
S14
THERMAL OXIDIZATION AT 300 TO 600°C FOR 30 MIN
S15

FIG. 7

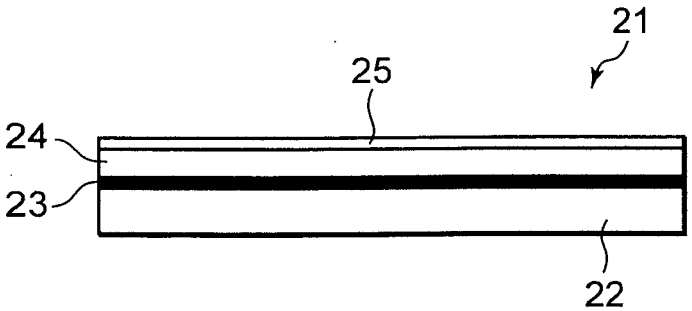

21
25
24
23
22

FIG. 8

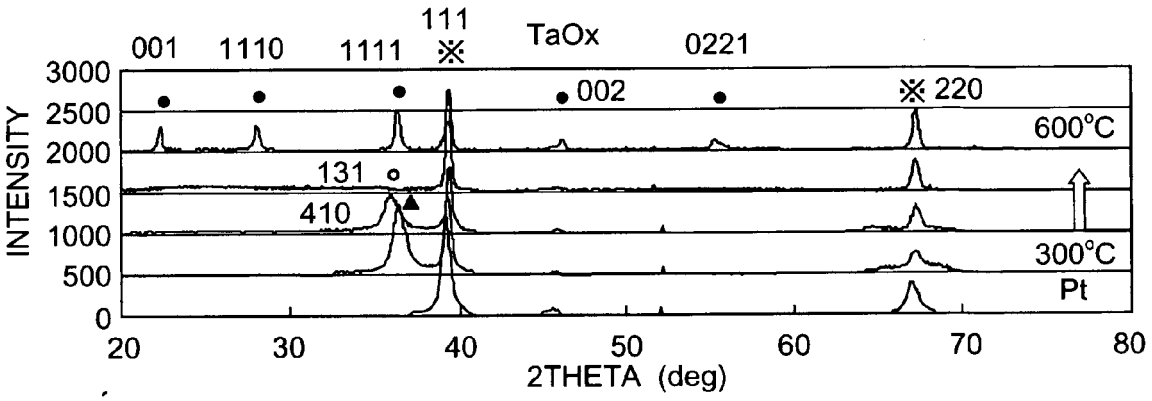

001
1110
1111
111
※
TaOx
0221
002
※ 220
600°C
131
410
300°C
Pt
INTENSITY
3000
2500
2000
1500
1000
500
0
20
30
40
50
60
70
80
2THETA (deg)

FIG. 9

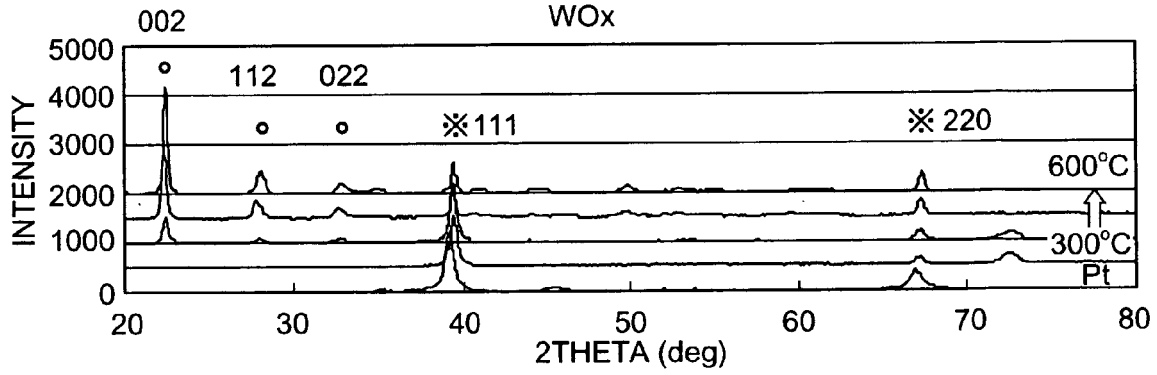

002
WOx
112
022
※111
※ 220
600°C
300°C
Pt
INTENSITY
5000
4000
3000
2000
1000
0
20
30
40
50
60
70
80
2THETA (deg)

FIG. 10

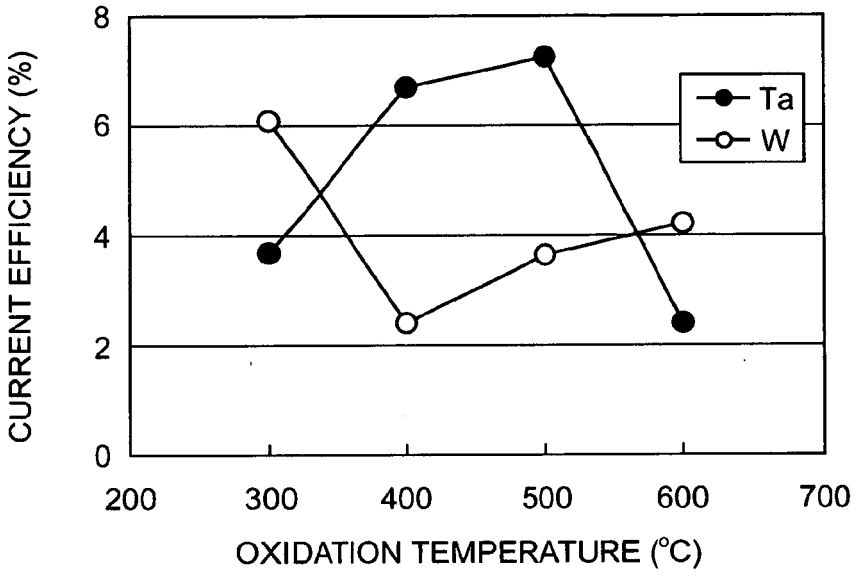

CURRENT EFFICIENCY (%)
8
6
4
2
0
200
300
400
500
600
700
OXIDATION TEMPERATURE (°C)
Ta
W

FIG. 11

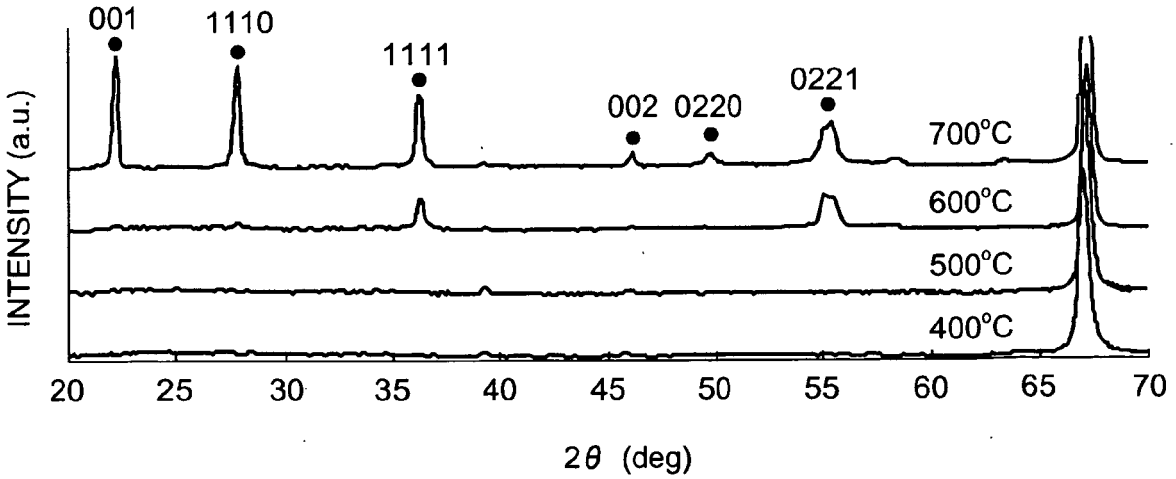

INTENSITY (a.u.)
001
1110
1111
002
0220
0221
700°C
600°C
500°C
400°C
20
25
30
35
40
45
50
55
60
65
70
2θ (deg)

FIG. 12

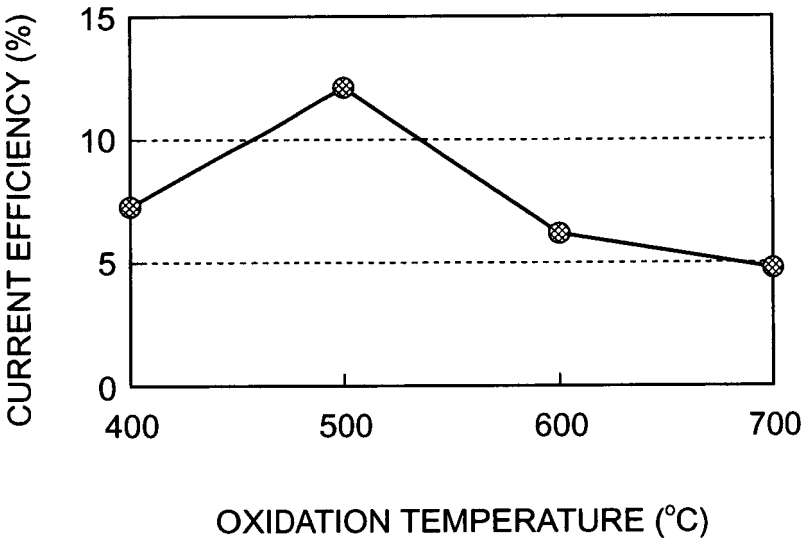
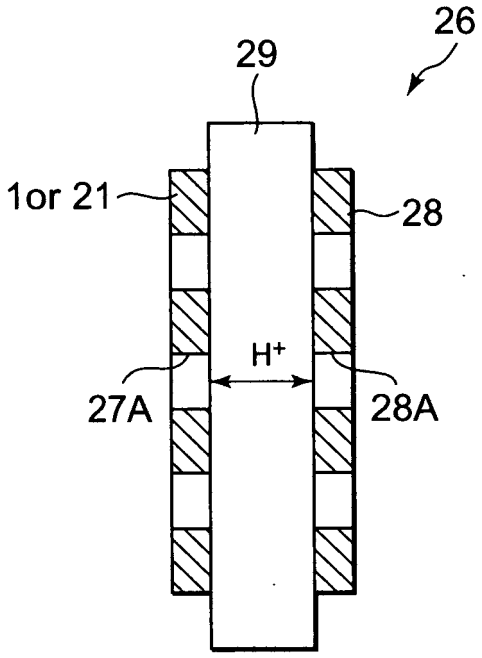

CURRENT EFFICIENCY (%)
15
10
5
0
400
500
600
700
OXIDATION TEMPERATURE (°C)

FIG. 13


26
29
1or 21
28
H+
27A
28A

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 11077060 A **[0003]**
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- JP 2002080986 A **[0005]**
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