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(54) ELECTROLYZING ELECTRODE AND PRODUCTION METHOD OF PERSULFURIC ACID-DISSOLVING LIQUID BY USE OF THE ELECTRODE

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(57) **ABSTRACT**

An object is to provide an electrolyzing electrode capable of electrolyzing water with a low current density to thereby produce ozone water with a high efficiency. An ozone producing electrode comprises: a substrate; and a surface layer formed on the surface of the substrate and including a dielectric material, and the surface layer is formed to have a thickness which is larger than 0 and is 2000 nm or less. Especially, the substrate is constituted of a conductive material, the dielectric material constituting the surface layer is made of a tantalum oxide or an aluminum oxide, and an electrolytic solution is electrolyzed with the low current density to thereby produce ozone with the high efficiency.

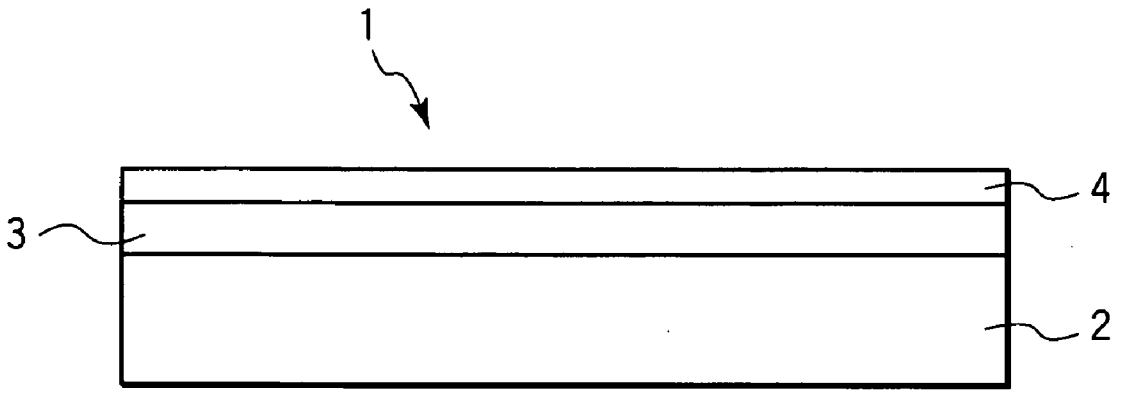


FIG. 1

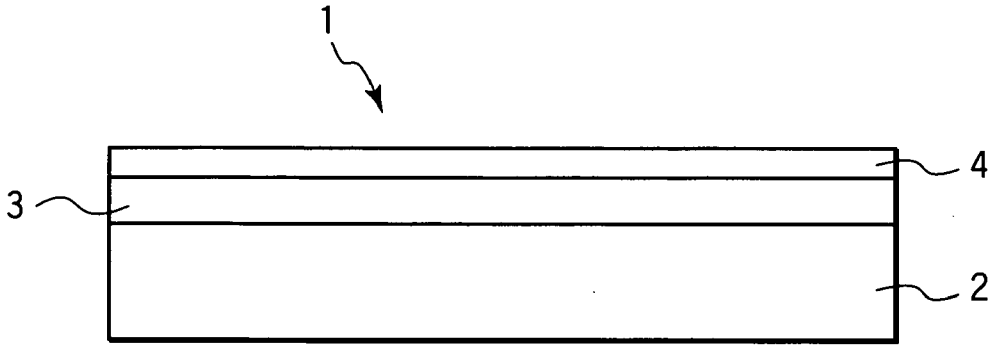

1
3
4
2

FIG. 2

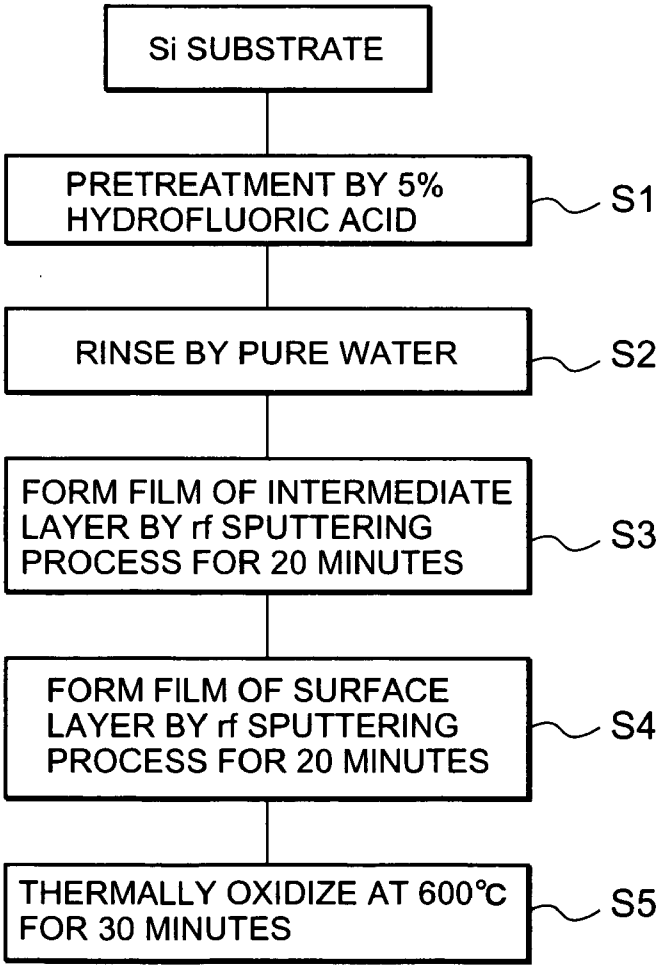

Si SUBSTRATE
PRETREATMENT BY 5% HYDROFLUORIC ACID
S1
RINSE BY PURE WATER
S2
FORM FILM OF INTERMEDIATE LAYER BY rf SPUTTERING PROCESS FOR 20 MINUTES
S3
FORM FILM OF SURFACE LAYER BY rf SPUTTERING PROCESS FOR 20 MINUTES
S4
THERMALLY OXIDIZE AT 600℃ FOR 30 MINUTES
S5

FIG. 3

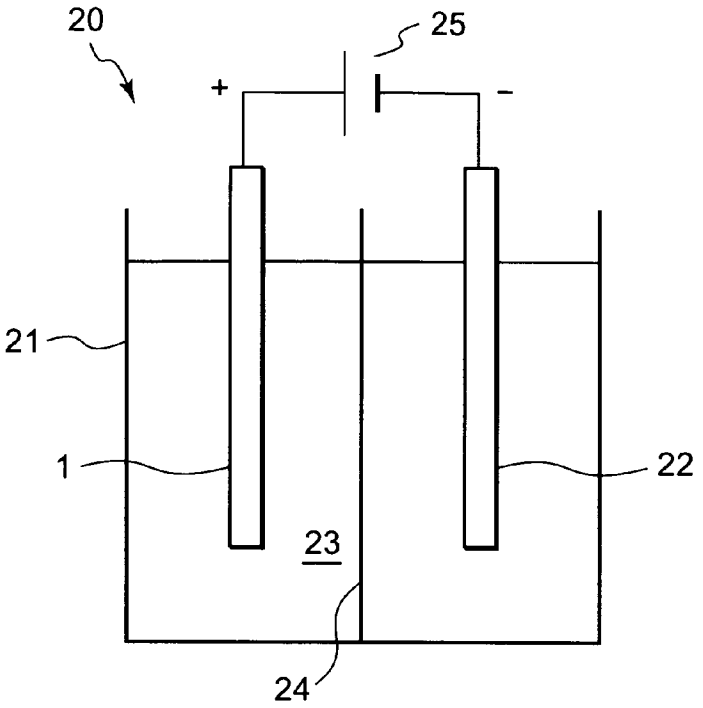

20
25
+
-
21
1
22
23
24

FIG. 4

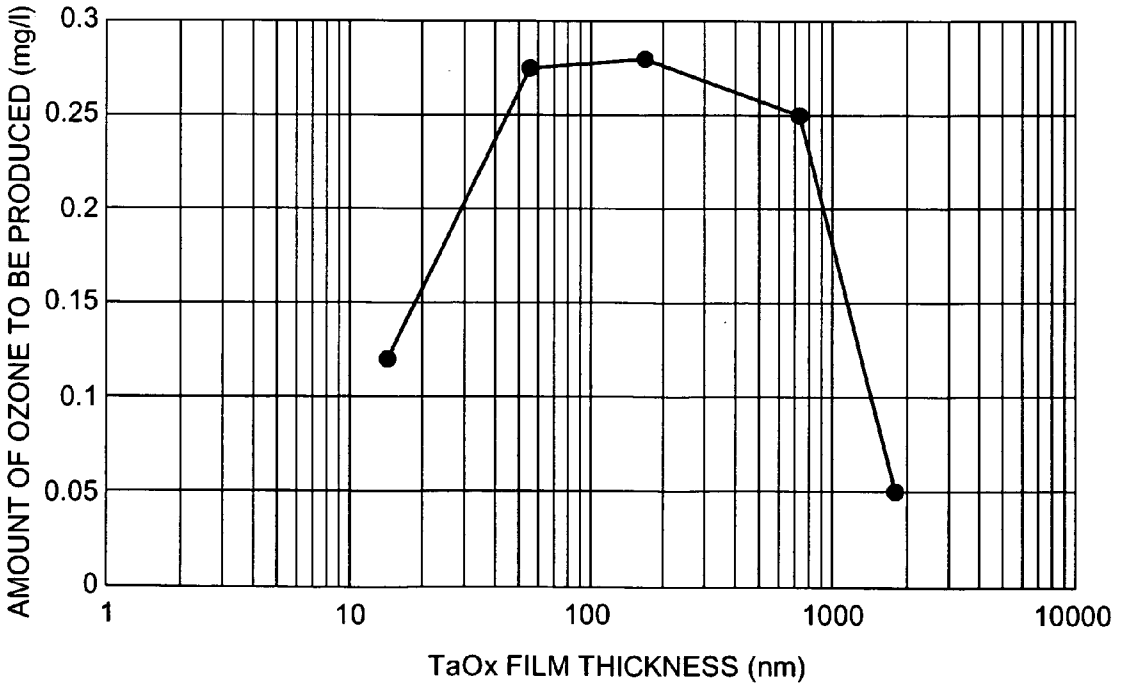

AMOUNT OF OZONE TO BE PRODUCED (mg/l)
0.3
0.25
0.2
0.15
0.1
0.05
0
1
10
100
1000
10000
TaOx FILM THICKNESS (nm)

FIG. 5

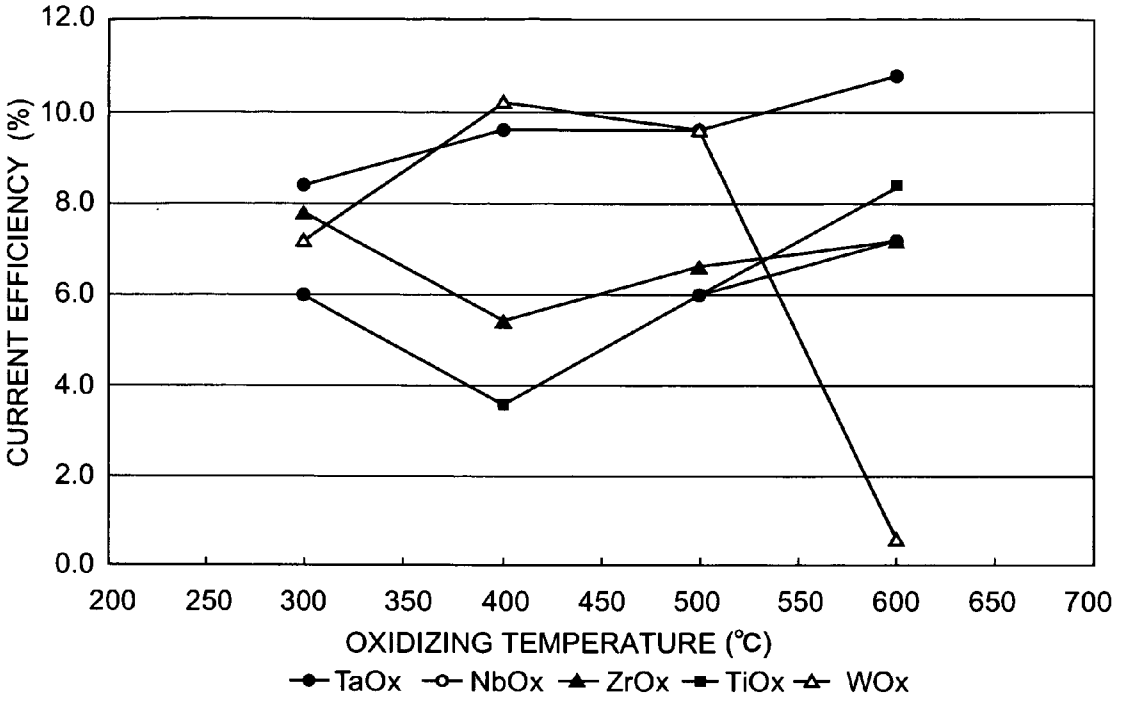

12.0
10.0
8.0
6.0
4.0
2.0
0.0
CURRENT EFFICIENCY (%)
200
250
300
350
400
450
500
550
600
650
700
OXIDIZING TEMPERATURE (℃)
TaOx
NbOx
ZrOx
TiOx
WOx

FIG. 6

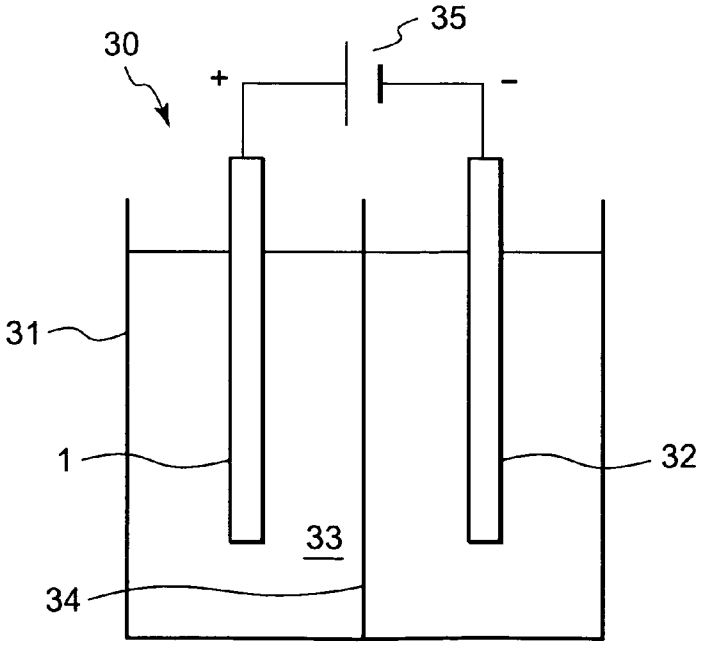

30
35
+
-
31
1
32
33
34

FIG. 7

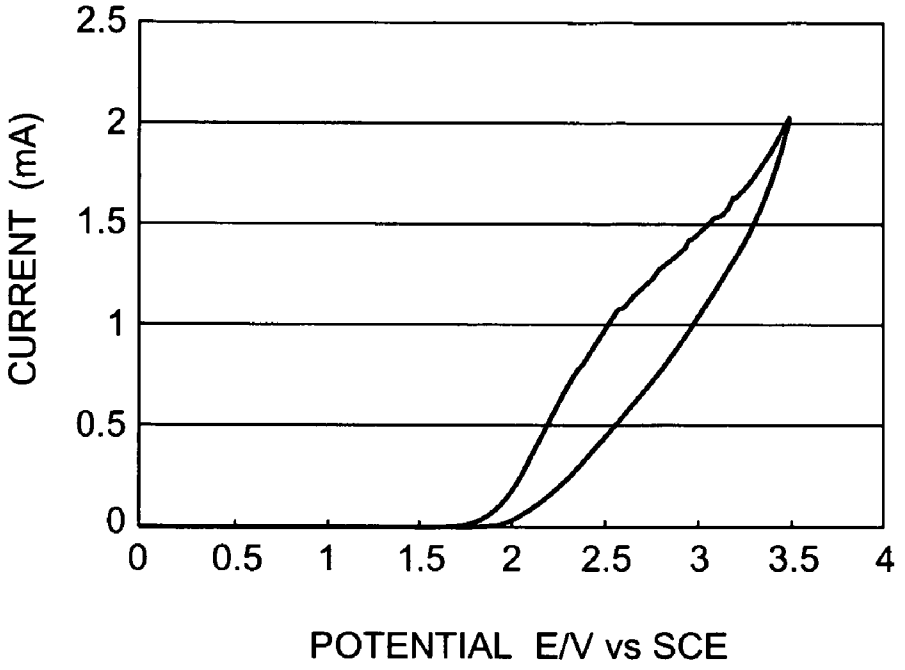
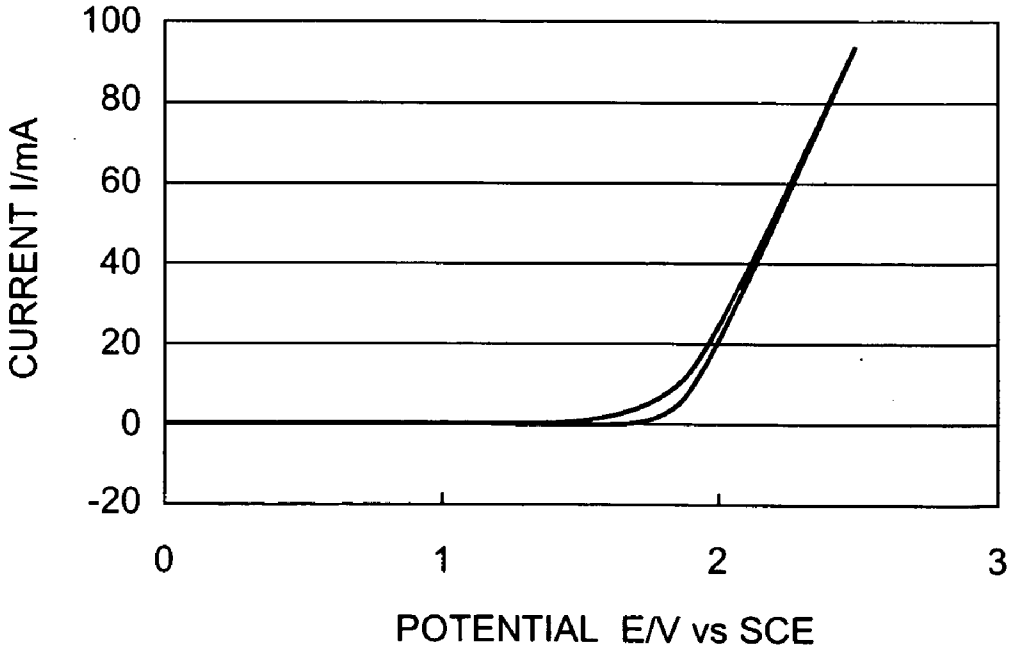

2.5
2
1.5
1
0.5
0
CURRENT (mA)
0
0.5
1
1.5
2
2.5
3
3.5
4
POTENTIAL E/V vs SCE

FIG. 8


100
80
60
40
20
0
-20
CURRENT I/mA
0
1
2
3
POTENTIAL E/V vs SCE

ELECTROLYZING ELECTRODE AND PRODUCTION METHOD OF PERSULFURIC ACID-DISSOLVING LIQUID BY USE OF THE ELECTRODE

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to an electrolyzing electrode for use in an industrial or household electrolysis process and a method of producing a persulfuric acid-dissolving liquid by use of the electrolyzing electrode.

[0003] 2. Description of the Related Art

[0004] In general, ozone is a substance having a very strong oxidizing power. There is expected broad utilization of water in which ozone has been dissolved, so-called ozone water in a cleaning and sterilizing treatment, such as application of ozone water to water supply and sewage systems or foods or application of ozone water to a cleaning treatment in a semiconductor device manufacturing process or the like. As a method of producing ozone water, there are known: a method of dissolving, in water, ozone produced by ultraviolet irradiation or electric discharge; a method of producing ozone in water by electrolysis of water and the like.

[0005] In Japanese Patent Application Laid-Open No. 11-77060, there is disclosed an ozone water producing device including: ozone producing means for producing an ozone gas by use of an ultraviolet lamp; and a tank which stores water. In the device, the produced ozone gas is supplied to water in the tank to thereby produce ozone water. In Japanese Patent Application Laid-Open No. 11-333475, there is disclosed an ozone water producing device which mixes, at a predetermined ratio by a mixing pump, an ozone gas produced by an electric discharge type of ozone gas producing device and water in order to dissolve the ozone gas in water with a good efficiency.

[0006] However, in the above-described ozone water producing method in which the ozone gas is produced by the ultraviolet lamp or the electric discharge system as described above to dissolve this ozone gas in water, there is required the ozone gas producing device or an operation for dissolving the ozone gas in water, and the device easily becomes complicated. In this method, since the produced ozone gas is dissolved in water, there is a problem that it is difficult to produce ozone water having a desired concentration with a high efficiency.

[0007] In Japanese Patent Application Laid-Open No. 2002-80986, as a method for solving the above problem, there is disclosed a method of producing ozone in water by electrolysis of water to obtain ozone water. In such method, there is used an ozone producing electrode including: an electrode substrate constituted of a porous or net-like material; and an electrode catalyst containing an oxide of a platinum group element or the like.

[0008] On the other hand, as a substance having a very strong oxidizing power, a persulfuric acid is known. This persulfuric acid is an oxidizing agent which is broadly used in cleaning a semiconductor or as a polymerization initiator, an oxidizing agent, a bleaching agent, a photograph treating agent, an oxidizing agent for a reagent chemical such as manganese or chromium, an analysis reagent or the like. In general, a sulfuric acid is used in cleaning a semiconductor. However, the persulfuric acid has an oxidizing power which is stronger than that of the sulfuric acid. Therefore, the cleaning can efficiently be performed with a less amount of persulfuric acid having a concentration which is lower than that of the sulfuric acid.

[0009] A method of manufacturing the persulfuric acid is generally performed by an electrochemical technology in many cases, and a platinum ribbon is used as, for example, an electrode for manufacturing the persulfuric acid. However, in an electrolysis treatment using the platinum ribbon, wear on the electrode increases in accordance with electrolysis conditions. The treatment also has a disadvantage due to mixed impurities or a disadvantage that the electrode has to be changed frequently.

[0010] To solve the problem, in Japanese Patent Application Laid-Open No. 2001-192874, there is disclosed a developed method in which conductive diamond carried on a substrate is used as an electrode for manufacturing the persulfuric acid.

[0011] In the above-described method of producing ozone water by the electrolysis of water, 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 contain any organic substance. However, the element has a low ozone production efficiency for the ozone producing electrode, and it is difficult to produce ozone water by a high-efficiency electrolysis method. When ozone water is produced by the electrolysis method using such conventional ozone producing electrode, electrolysis at a high current density is required for producing ozone, and there is a problem in energy consumption or electrode life.

[0012] Moreover, in the electrode for manufacturing the persulfuric acid, in which conductive diamond is used as described above, there is a problem that production costs of the electrode itself soar, and there has been a demand for development of an electrode material capable of producing the persulfuric acid inexpensively.

[0013] In consequence, the present invention has been developed in order to solve the conventional technical problem, and there are provided: an electrolyzing electrode, capable of producing ozone water with a high efficiency by electrolysis of water at a low current density; and a production method of a persulfuric acid-dissolving liquid by use of the electrode.

SUMMARY OF THE INVENTION

[0014] In a first aspect of the present invention, an electrolyzing electrode comprises: a substrate; and a surface layer formed on the surface of the substrate and including a dielectric material, the surface layer being formed to have a thickness which is larger than 0 and is 2000 nm or less.

[0015] In the electrolyzing electrode of a second aspect of the present invention, in the above invention, the substrate is a conductive substrate.

[0016] In the electrolyzing electrode of a third aspect of the present invention, in the above invention, on the substrate, there is formed an intermediate layer positioned on an inner side of the surface layer, formed on the surface of the

substrate, and containing at least one of an oxidization retarding metal, a metal oxide having conductivity and a metal having conductivity even when oxidized.

[0017] In the electrolyzing electrode of a fourth aspect of the present invention, in the above invention, the dielectric material included in the surface layer is an oxide.

[0018] In the electrolyzing electrode of a fifth aspect of the present invention, in the above invention, the oxide is tantalum oxide or aluminum oxide.

[0019] In the electrolyzing electrode of a sixth aspect of the present invention, in the above invention, the surface layer is constituted by forming a surface layer constituting material on the surface of the substrate by a sputtering process.

[0020] In the electrolyzing electrode of a seventh aspect of the present invention, in the third, fourth, fifth or sixth invention, the intermediate layer is constituted by forming an intermediate layer constituting material on the surface of the substrate by the sputtering process.

[0021] A method of producing a persulfuric acid-dissolving liquid in an eighth aspect of the present invention is a production method of a persulfuric acid-dissolving liquid by electrolyzing an aqueous solution containing sulfate ions to produce a persulfuric acid-dissolving liquid, wherein the electrolyzing electrode of each of the above inventions is used as an anode.

[0022] According to the first aspect of the present invention, the electrolyzing electrode comprises: the substrate; and the surface layer formed on the surface of the substrate and including the dielectric material, and the surface layer is formed to have a thickness which is larger than 0 and is 2000 nm or less. Therefore, when electrolysis is performed by the electrolyzing electrode, ozone can be produced efficiently at a low current density.

[0023] Especially the surface layer constituted of the dielectric material formed on the surface of the substrate has a thickness which is larger than 0 and is 2000 um or less. Therefore, electrons can move in the electrode via an impurity level in the surface layer or the Fowler-Nordheim tunneling. Accordingly, in an electrode reaction in the anode, an empty level in the vicinity of a bottom of a conduction band in an energy level can receive the electrons from an electrolyte, the energy level being higher as much as about a half of a band gap than the Fermi level. When the movement of the electrons is excited in a higher energy level, ozone can efficiently be produced at a lower current density.

[0024] According to the electrolyzing electrode of the second aspect of the present invention, in the above invention, since the substrate is the conductive substrate, the electrode reaction can be excited by the electrons which have moved in the surface layer. In consequence, ozone can efficiently be produced.

[0025] According to the electrolyzing electrode of the third aspect of the present invention, in the above invention, on the substrate, there is formed the intermediate layer positioned on the inner side of the surface layer, formed on the surface of the substrate, and containing at least one of the oxidization retarding metal, the metal oxide having conductivity and the metal having the conductivity even when oxidized. Therefore, the electrons can effectively move in the surface layer as described above. Therefore, the electrode reaction can occur in the high energy level on the surface of the surface layer. In consequence, ozone can efficiently be produced with a lower current density.

[0026] Especially, according to such invention, on the surface of the substrate, there is formed the intermediate layer including any of the oxidization retarding metal, the metal oxide having the conductivity and the metal having the conductivity even when oxidized. Therefore, in a case where the electrolysis is performed by the electrode, it is possible to avoid a disadvantage that the intermediate layer is oxidized and become an insulator. This can improve durability of the electrode. Moreover, as compared with a case where the whole substrate is constituted of a material constituting the intermediate layer, production costs can reduced, and ozone can similarly efficiently be produced.

[0027] Moreover, according to the fourth aspect of the present invention, in the above invention, the dielectric material included in the surface layer is an oxide. Especially, as in the fifth aspect of the present invention, the oxide is tantalum oxide or aluminum oxide. Therefore, ozone can further effectively be produced at a low current density.

[0028] According to the sixth aspect of the present invention, in the above invention, the surface layer is constituted by forming the surface layer constituting material on the surface of the substrate by the sputtering process. Therefore, the surface layer can uniformly be formed on the surface of the substrate. Since it is possible to constitute the surface layer having a homogeneous thickness on the whole surface of the substrate, electron can uniformly be conducted to the whole surface of the electrode, and it is possible to improve an ozone production efficiency.

[0029] According to the seventh aspect of the present invention, in the third, fourth, fifth or sixth invention, the intermediate layer is constituted by forming the intermediate layer constituting material on the surface of the substrate by the sputtering process. Accordingly, the intermediate layer can uniformly be formed on the surface of the substrate. Therefore, it is possible to uniformly constitute even the surface layer to be formed on an outer side of the intermediate layer. In consequence, the electron can uniformly be conducted to the whole surface of the electrode, and it is possible to improve the ozone production efficiency.

[0030] A method of producing a persulfuric acid-dissolving liquid in the eighth aspect of the present invention is a production method of a persulfuric acid-dissolving liquid by electrolyzing the aqueous solution containing the sulfate ions to produce a persulfuric acid-dissolving liquid. Since the electrolyzing electrode of each of the above inventions is used as the anode, the persulfuric acid-dissolving liquid can efficiently be produced. That is, when the electrolyzing electrode of the present invention is used, an overvoltage rises with respect to an oxygen producing reaction. When the electrolytic treatment is performed in the presence of the sulfate ions, the production of persulfate ions by the oxidation of the sulfate ions proceeds in preference to the progress of the oxygen producing reaction.

[0031] In consequence, when water containing the sulfate ions is electrolyzed using the electrolyzing electrode of each of the above inventions as the anode, it is possible to produce

a persulfuric acid-dissolving liquid for use on the spot. Therefore, the persulfuric acid having a strong oxidizing power can easily be produced for use, which improves convenience.

BRIEF DESCRIPTION OF THE DRAWINGS

[0032] **FIG. 1** is a schematic sectional view of an electrolyzing electrode in the present invention;

[0033] **FIG. 2** is a flowchart of a method of manufacturing the electrolyzing electrode in the present invention;

[0034] **FIG. 3** is a schematic explanatory view of an ozone water producing device in the present invention;

[0035] **FIG. 4** is a diagram showing an amount of ozone to be produced with respect to a thickness of a surface layer of the electrode of the present invention in the ozone water producing device of **FIG. 3**;

[0036] **FIG. 5** is a diagram showing a current efficiency of an object which is ozone with respect to an annealing temperature of each electrolyzing electrode;

[0037] **FIG. 6** is a schematic sectional view of a persulfuric acid-dissolving liquid producing device;

[0038] **FIG. 7** is a current-potential curve in a case where an electrolytic solution including sulfate ions is electrolyzed; and

[0039] **FIG. 8** is a current-potential curve in a case where an electrolytic solution containing a perchloric acid is electrolyzed.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0040] There will be described hereinafter preferable embodiments of an electrolyzing electrode in the present invention with reference to the drawings. **FIG. 1** is a cross sectional view of an electrolyzing electrode **1** in the present invention.

[0041] As shown in **FIG. 1**, the electrolyzing electrode **1** is constituted of: a substrate **2**; an intermediate layer **3** formed on the surface of the substrate **2**; and a surface layer **4** formed on the surface of the intermediate layer **3**.

[0042] In the present invention, the substrate **2** is made of, as a conductive material, a valve metal such as tantalum (Ta), zirconium (Zr) or niobium (Nb), an alloy of two or more of the valve metals, silicon (Si) or the like. Since it is especially preferable that the surface of the substrate **2** for use in the present embodiment is flat, there is used silicon having its surface treated to be flat.

[0043] The intermediate layer **3** is made of: a metal which is difficult to oxidize, such as platinum or gold (Au); a metal oxide having conductivity, such as iridium oxide, palladium oxide or ruthenium oxide; a superconductive oxide; or a metal having conductivity even when oxidized, such as 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 intermediate layer **3** formed beforehand as the oxide, and includes the metal oxide oxidized by electrolysis. In the present embodiment, it is assumed that the intermediate layer **3** is made of platinum. It is to be noted that in a case where the substrate **2** is made of platinum, needless to say, even the surface of the substrate **2** is made of platinum, and the intermediate layer **3** does not have to be especially constituted. However, when such substrate **2** is made of platinum, cost rise is incurred. Therefore, it is industrially preferable that the substrate **2** is constituted of an inexpensive material, and the intermediate layer **3** made of a noble metal or the like is formed on the surface of the substrate **2**.

[0044] Moreover, the surface layer **4** is constituted of a dielectric material into a layer on the surface of the substrate **2** together with the intermediate layer **3** so as to coat the intermediate layer **3**. This surface layer **4** is formed into a predetermined thickness which is larger than 0 and is 2000 nm or less in the present embodiment. It is to be noted that the thickness of the surface layer **4** will be described later in detail. It is further preferable that the thickness is 40 nm or more and is less than 1000 nm.

[0045] As the dielectric material constituting the surface layer **4**, there is used tantalum oxide, aluminum oxide, titanium oxide, tungsten oxide or niobium oxide.

[0046] Moreover, the surface layer **4** may be made of: an oxide containing two or more types of metal elements represented by a perovskite oxide such as barium titanate ($BaTiO_3$); or a mixture of two or more types of oxides having different crystal structure, such as a mixture of titanium oxide and tantalum oxide. In this case, instead of such oxide, there may be used an oxide containing the above noble metal or the noble-metal oxide.

[0047] Here, tantalum oxide indicates a general substance constituted by combining tantalum with oxygen, and examples of tantalum oxide include: crystalline TaO or Ta_2O_5; such oxide in which a slight oxygen defect is produced, such as TaO_{1-X} or Ta_2O_{5-x}; and amorphous TaO_X. Examples of aluminum oxide include Al_2O_3 and AlO_X. Examples of titanium oxide include TiO_2, Ti_2O_3 and TiO_X. Examples of tungsten oxide include WO_3 and WO_X. It is to be noted that as another dielectric material forming the surface layer **4**, there is applicable Na_2O, NaO_X, MgO, MgO_X, SiO_2, SiO_X, K_2O, KO_X, CaO, CaO_X, Sc_2O_3, ScO_X, V_2O_5, VO_X, CrO_2, CrO_X, Mn_3O_4, MnO_X, Fe_2O_3, FeO_X, CoO, CoO_X, NiO, NiO_X, CuO, CuO_X, ZnO, ZnO_X, GaO, GaO_X, GeO_2, GeO_X, Rb_2O_3, RbO_X, SrO, SrO_X, Y_2O_3, YO_X, ZrO_2, ZrO_X, Nb_2O_5, NbO_X, MoO_3, MoO_X, In_2O_3, InO_X, SnO_2, SnO_X, Sb_2O_5, SbO_X, Cs_2O_5, CsO_X, BaO, BaO_X, La_2O_3, LaO_X, CeO_2, CeO_X, PrO_2, PrO_X, Nd_2O_3, NdO_X, Pm_2O_3, PmO_X, Sm_2O_3, SmO_X, Eu_2O_3, EuO_X, Gd_2O_3, GdO_X, Tb_2O_3, TbO_X, Dy_2O_3, DyO_X, Ho_2O_3, HoO_X, Er_2O_3, ErO_X, Tm_2O_3, TmO_X, Yb_2O_3, YbO_X, Lu_2O_3, LuO_X, HfO_2, HfO_X, PbO_2, PbO_X, Bi_2O_3, BiO_X or the like.

[0048] Next, there will be described a method of manufacturing the electrolyzing electrode of the present invention with reference to a flowchart of **FIG. 2**. As the substrate **2**, silicon is used. As silicon, silicon having a very flat surface is used. It is to be noted that in the present embodiment, silicon is used as the substrate **2**. Alternatively, there may be used the above-described conductive material preferably having its surface treated to be flat.

[0049] First, in step **S1**, the silicon substrate **2** is pretreated with 5% hydrofluoric acid, and a natural silicon oxide film formed on the surface of the substrate **2** is removed. This brings the surface of the substrate **2** into a flatter state.

Thereafter, in step S2, the surface of the substrate **2** is rinsed with pure water. Subsequently, in steps S3 and S4, the substrate is introduced into a chamber of an existing sputtering device, and films are formed on the substrate.

[0050] In the present embodiment, the intermediate layer **3** and the surface layer **4** are formed onto the substrate **2** by an RF sputtering process. In the present embodiment, since the intermediate layer **3** is made of platinum, Pt (80 mmφ) which is an intermediate layer constituting material is used as a first target. An RF power is set to 100 W, an Ar gas pressure is set to 0.9 Pa, a distance between the substrate **2** and the target is set to 60 mm, and the film is formed at room temperature for 20 minutes (step S3). Accordingly, the intermediate layer **3** having a thickness of about 100 nm is formed on the surface of the substrate **2**.

[0051] Next, the surface layer **4** is formed on the surface of the substrate **2** on which the intermediate layer **3** has been formed. In the present embodiment, since the surface layer **4** is made of tantalum, the target is changed to Ta which is a surface layer constituting material. Conditions similar to the above conditions are set. That is, the RF power is set to 100 W, the Ar gas pressure is set to 0.9 Pa, the distance between the substrate **2** and the target is set to 60 mm, and the film is formed at room temperature for 5 to 180 minutes (step S4). Accordingly, the surface layer **4** having a thickness of about 7 nm to 1000 nm is formed on the surface of the intermediate layer **3** of the substrate **2**. It is to be noted that film thicknesses of the intermediate layer **3** and the surface layer **4** are obtained by acquiring carried amounts of Pt and Ta by evaluation with a X-ray fluorescence and converting the amounts into the thicknesses.

[0052] Consequently, it is possible to form the intermediate layer **3** and the surface layer **4** into appropriate thicknesses and amounts with high in-plane homogeneity. The intermediate layer **3** and the surface layer **4** can be formed with a high adhesion. In consequence, durability of the electrolyzing electrode **1** can be improved.

[0053] Thereafter, in step S5, the substrate **2**, on which the intermediate layer **3** and the surface layer **4** have been formed, is thermally annealed at 600° C. in a muffle furnace for 30 minutes in air atmosphere, and the electrolyzing electrode **1** is obtained. Accordingly, the tantalum metal constituting the surface layer **4** formed on the surface of the intermediate layer **3** is homogeneously oxidized. It is to be noted that the tantalum metal is oxidized by the annealing to constitute tantalum oxide. Therefore, the surface layer **4** has a thickness of about 14 nm to 2000 nm. In the present embodiment, after forming the intermediate layer **3** and the surface layer **4** by the sputtering process, the layers are annealed, and the surface of the electrode **1** is oxidized. However, when the electrode **1** is used in electrolysis, the surface of the electrode is oxidized. Therefore, it is assumed that the annealing does not have to be executed.

[0054] The surface layer **4** of the electrolyzing electrode **1** obtained as described above is entirely oxidized. The intermediate layer **3** forms platinum silicide together with silicon of the substrate **2**. Moreover, silicon stops at the intermediate layer **3**, and is not diffused in the surface layer **4**. Similarly, platinum constituting the intermediate layer **3** does not reach the inside of the surface layer **4**. Furthermore, the surface layer **4** is very homogeneously distributed on the surface of the intermediate layer **3**, and the layer is uniformly on the whole surface of the intermediate layer **3**. Since the surface of the electrolyzing electrode **1** is thus uniformly coated with the surface layer **4**, the substrate **2** and the intermediate layer **3** are not exposed. Since any gap or crack is not formed in the surface layer **4**, an electrolyte as an object of an electrolysis treatment does not directly reach the intermediate layer **3** or the substrate **2** under the surface layer. Therefore, it is possible to avoid a disadvantage that the substrate **2** is corroded during the electrolysis.

[0055] It is to be noted that in the present embodiment, since the surface layer **4** is constituted of the only dielectric material, the use of a noble metal or a noble-metal oxide in the surface layer **4** can be reduced. This can reduce costs.

[0056] Next, there will be described ozone production by electrolysis using the electrolyzing electrode **1** manufactured in the above embodiment with reference to **FIG. 3**. **FIG. 3** is a schematic explanatory view of an ozone water producing device **20** to which the electrolyzing electrode **1** of the present embodiment has been applied. The ozone water producing device **20** includes: a treatment tank **21**; the above-described electrolyzing electrode **1** as the anode; an electrode **22**; a cation exchange film **24**; and a power supply **25** which applies a direct current to the electrodes **1** and **22**. In this treatment tank **21**, model tap water **23** is pooled as an electrolytic solution.

[0057] The electrolyzing electrode **1** is prepared by the above manufacturing method. As the electrolyzing electrodes **1** for use in the ozone water producing device **20**, there are used electrodes having five types of thicknesses of the surface layers **4** in total: about 14 nm; about 56 nm; about 170 nm; about 730 nm; and about 1800 nm. Accordingly, there are measured amounts of ozone to be produced in a case where the electrolyzing electrodes **1** are used as the anodes, respectively, and each electrolyzing electrode **1** is evaluated.

[0058] On the other hand, platinum is used in the electrode **22** as a cathode. In addition, there may be constituted: an insoluble electrode obtained by platinum on the substrate of the silicon substrate **2**; a platinum-iridium based electrolyzing electrode; a carbon electrode or the like.

[0059] The cation exchange film **24** is a fluororesin-based film having durability against an oxidizing agent such as hydrogen peroxide. As a typical cation exchange film, there is a perfluoro sulfonic acid-based film such as trade name Nafion 115, 117, 315 or 350 manufactured by DuPont. It is assumed that in the present embodiment, Nafion is used as the cation exchange film **24**.

[0060] Moreover, in the present embodiment, the electrolytic solution to be electrolyzed is an aqueous solution obtained by simulating tap water. A component composition of model tap water **23** is: 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; and 16.5 ppm of CO_3^{2-}.

[0061] According to the above constitution, 300 ml in total of model tap water **23** at water temperature of +15° C. is stored in the treatment tank **21**: 150 ml of water is stored in each of an anode side and a cathode side defined by the cation exchange film **24** in the treatment tank. The electrolyzing electrode **1** and the electrode **22** are submerged into model tap water on the anode side and that on the cathode side, respectively, with the cation exchange film **24** being

sandwiched between the opposite sides. It is to be noted that in the present embodiment, each of areas of the electrolyzing electrode **1** and the electrode **22** is 40 mm×20 mm (submerged portion of 35 mm×15 mm), and a distance between the electrodes is set to 10 mm. Furthermore, the power supply **25** applies each constant current of 100 mA to the electrolyzing electrode **1** and the electrode **22** at a current density of about 20 mA/cm^2.

[**0062**] It is to be noted that in the present embodiment, the amount of ozone to be produced by the electrolyzing electrode **1** is obtained by measuring, by a colorimetric method, a concentration of ozone in model tap water **23** after the electrolysis performed for one minute on the above conditions.

[**0063**] Next, there will be described the amount of ozone to be produced with respect to the thickness of the surface layer **4** of the electrolyzing electrode **1** in the present embodiment with reference to **FIG. 4**. **FIG. 4** shows the amount of ozone to be produced by each electrolyzing electrode **1** on the same conditions among the five types of electrolyzing electrodes in the present embodiment. In **FIG. 4**, the ordinate indicates the amount of ozone to be produced (mg/l), and the abscissa indicates the thickness (nm) of the surface layer **4** of the electrolyzing electrode **1**.

[**0064**] According to experiment results of **FIG. 4**, in a case where the thickness of the surface layer **4** of the electrolyzing electrode **1** was about 1800 nm, the amount of ozone to be produced was 0.05 mg/l. When the thickness was about 14 nm, the amount of ozone to be produced was as small as 0.12. However, the amount of ozone to be produced rapidly increased in a case where the thickness as 40 nm or more and below 1000 nm. In the experiment results, when the thickness of the surface layer **4** was about 56 nm, the amount of ozone to be produced was 0.275 mg/l. When the thickness was about 170 nm, the amount was 0.28 mg/l. When the thickness was about 730 nm, the amount was 0.25 mg/l.

[**0065**] On the other hand, experimental results will be described with reference to **FIG. 5** in a case where substances constituting the surface layer **4** of the electrolyzing electrode **1** are niobium oxide, zirconium oxide, titanium oxide and tungsten oxide in addition to tantalum oxide. **FIG. 5** shows experimental results of the five types of substances, indicating a current efficiency with respect to ozone as an object at an annealing (the step **S5**) temperature.

[**0066**] It is to be noted that in the above experiment, the annealing temperatures are 300° C., 400° C., 500° C. and 600° C. while the thickness of each surface layer **4** is around 50 nm. Four types of each substance are used, and the current efficiency with respect to ozone as the object is measured in a case where each electrolyzing electrode **1** is used as the anode, whereby evaluating each electrolyzing electrode **1**.

[**0067**] Moreover, platinum is used in the electrode **22** as the cathode in the same manner as in the experiment of **FIG. 4**, and Nafion is used in the cation exchange film **24**. As the electrolytic solution to be electrolyzed, model tap water **23** is used in the same manner as in the aqueous solution.

[**0068**] According to the above constitution, 300 ml in total of model tap water **23** at water temperature of +15° C. is stored in the treatment tank **21**: 150 ml of water is stored in each of the anode side and the cathode side defined by the cation exchange film **24** in the treatment tank. The electrolyzing electrode **1** and the electrode **22** are submerged into model tap water on the anode side and that on the cathode side, respectively, with the cation exchange film **24** being sandwiched between the opposite sides. It is to be noted that in the present embodiment, each of areas of the electrolyzing electrode **1** and the electrode **22** is 2.25 cm^2, and a distance between the electrodes is set to 10 mm. Furthermore, the power supply **25** applies each constant current of 50 mA to the electrolyzing electrode **1** and the electrode **22** at a current density of about 20 mA/cm^2. The electrolysis is performed for one minute on the above conditions, and there is measured each current efficiency with respect to ozone as the object, whereby evaluating each electrolyzing electrode **1**.

[**0069**] According to experiment results of **FIG. 5**, in a case where the surface layer **4** of the electrolyzing electrode **1** was made of tantalum oxide, the current efficiency was 8.4% with respect to ozone as the object at an annealing temperature of 300° C., the current efficiency at 400° C. was 9.6%, the current efficiency at 500° C. was 9.6%, and the current efficiency at 600° C. was 10.8%. In a case where the surface layer **4** of the electrolyzing electrode **1** was made of niobium oxide, the current efficiency was 6.0% with respect to ozone as the object at an annealing temperature of 300° C., the current efficiency at 500° C. was 6.0%, and the current efficiency at 600° C. was 7.2%. In a case where the surface layer **4** of the electrolyzing electrode **1** was made of zirconium oxide, the current efficiency was 7.8% with respect to ozone as the object at an annealing temperature of 300° C., the current efficiency at 400° C. was 5.4%, the current efficiency at 500° C. was 6.6%, and the current efficiency at 600° C. was 7.2%. In a case where the surface layer **4** of the electrolyzing electrode **1** was made of titanium oxide, the current efficiency was 6.0% with respect to ozone as the object at an annealing temperature of 300° C., the current efficiency at 400° C. was 3.6%, the current efficiency at 500° C. was 6.0%, and the current efficiency at 600° C. was 8.4%. In a case where the surface layer **4** of the electrolyzing electrode **1** was made of tungsten oxide, the current efficiency was 7.2% with respect to ozone as the object at an annealing temperature of 300° C., the current efficiency at 400° C. was 10.2%, the current efficiency at 500° C. was 9.6%, and the current efficiency at 600° C. was 0.6%.

[**0070**] From the above experiment results, it is seen that the electrolytic solution can be electrolyzed as described above even in a case where the surface layer **4** constituting the surface of the electrolyzing electrode **1** is made of tantalum oxide, niobium oxide, zirconium oxide, titanium oxide or tungsten oxide which is not a metal. The reason is that the surface layer **4** made of tantalum oxide, niobium oxide, zirconium oxide, titanium oxide or tungsten oxide has a comparatively small thickness of, for example, about 40 nm, and therefore the electrons in the surface layer **4** move via the impurity level or the Fowler-Nordheim tunnel to the intermediate layer **3** constituted of the conductive material.

[**0071**] Moreover, in the experiment shown in **FIG. 4** described above, the voltage between the electrodes during the electrolysis was about 90 V (there was used the electrode including the surface layer **4** having a thickness of 56 nm). This does not indicate a remarkably large value, where as the voltage between the electrodes during the electrolysis is

about 75 V in a case where the electrolyzing electrode **1** is made of platinum silicide. In a case where the electrolyzing electrode **1** of the present invention is used, the ozone production efficiency is high as compared with a case where the electrode made of platinum silicide is used.

[**0072**] In a case where the metal electrode is usually used as the electrolyzing electrode, the electrode reaction in the anode occurs, when the empty level directly above the Fermi level receives the electrons from the electrolyte. On the other hand, in a case where the electrolyzing electrode **1** including the surface layer **4** constituted of the dielectric material in the present invention is used, the reaction occurs, when the empty level in the vicinity of the bottom of the conduction band receives the electrons from the electrolyte, the bottom of the conduction band being located at an energy level which is higher as much as about a half of a band gap than the Fermi level.

[**0073**] Therefore, in a case where the electrolyzing electrode **1** of the present invention is used, the movement of the electron in a higher energy level is caused to excite the electrode reaction as compare with a case where the platinum silicide electrode is used. Therefore, it is considered that the ozone production efficiency rises.

[**0074**] In consequence, there can be obtained the electrode capable of producing ozone at a high efficiency even with a low current density, in a case where the surface layer **4** constituted of the dielectric material in the electrolyzing electrode **1** is formed to have a thickness which is larger than 0 and is 2000 nm or less. Especially in a case where the surface layer **4** is formed to have a thickness which is 40 nm or more and is below 1000 nm, even when the current density is remarkably low, ozone can be produced with a high efficiency.

[**0075**] Moreover, in the present embodiment, in a case where the substrate **2** on which the intermediate layer **3** and the surface layer **4** are to be formed is constituted of a material having a flat surface, the intermediate layer **3** and the surface layer **4** can homogeneously be formed on the surface of the substrate **2**. Therefore, since the thickness of each layer **3** or **4** is set to be homogeneous with respect to the surface of the electrode, uniform electric conduction can be realized with respect to the whole surface of the electrolyzing electrode **1**. In consequence, fluctuations of the electric conduction to the whole surface of the electrode can be reduced, and the ozone production efficiency can be improved.

[**0076**] Furthermore, in the present embodiment, since the intermediate layer **3** and the surface layer **4** are formed on the surface of the substrate **2** by the sputtering process, the layers can more homogeneously be formed on the surface of the substrate **2**. Accordingly, the intermediate layer **3** and the surface layer **4** having a uniform thickness can be formed on the whole surface of the substrate **2**. Therefore, electron can uniformly be conducted to the whole surface of the electrode, and the ozone production efficiency can be improved. In this case, even if the treatment for flattening the surface of the substrate **2** is slightly insufficient, the sputtering process can form the layer having a uniform thickness on the whole surface on which the layer is to be formed. Therefore, the electron can uniformly be conducted to the whole surface of the electrode.

[**0077**] It is to be noted that a method of forming the intermediate layer **3** and the surface layer **4** is not limited to the sputtering process as in the present embodiment, and there may be used, for example, a CVD process, an evaporation process, an ion plating process, a plating process or the like.

[**0078**] It is to be noted that as the material of the surface layer **4** for use in the experiment, there is used tantalum oxide, niobium oxide, zirconium oxide, titanium oxide or tungsten oxide. However, even when aluminum oxide or the like is used, a remarkably high ozone production efficiency is seen at a low current density.

[**0079**] Moreover, as described above, in the present embodiment, on the substrate **2** made of silicon, there is formed the intermediate layer **3** containing any of at least an oxidation retarding metal, a metal oxide having conductivity and a metal having the conductivity even when oxidized. Further on the surface of the intermediate layer **3**, the surface layer **4** is constituted as described above to thereby form the electrolyzing electrode **1**. However, in a case where the substrate **2** is constituted of a material similar to that of the intermediate layer **3**, that is, the material containing any of at least the oxidation retarding metal, the metal oxide having the conductivity and the metal having the conductivity even when oxidized, if the intermediate layer **3** is not especially formed, it is possible to constitute an electrode similarly capable of efficiently producing ozone. However, when the substrate **2** is coated with the intermediate layer **3** constituted of the above material as in the present invention, it is possible to realize the electrode **1** similarly capable of efficiently producing ozone at a small production cost.

[**0080**] Next, there will be described production of persulfuric acid (peroxodisulfuric acid: $H_2S_2O_8$) by electrolysis using the electrolyzing electrode **1** manufactured in the above embodiment with reference to **FIG. 6**. **FIG. 6** is a schematic explanatory view of a persulfuric acid-dissolving liquid producing device **30** to which the electrolyzing electrode **1** of the present embodiment has been applied. The persulfuric acid-dissolving liquid producing device **30** includes: a treatment tank **31**; the above-described electrolyzing electrode **1** as an anode; an electrode **32** as a cathode; a cation exchange film **34**; and a power supply **35** which applies a direct current to the electrodes **1** and **32**. In this treatment tank **31**, a 0.1 M sulfuric acid (electrolytic solution **33**) is stored as an electrolytic solution containing sulfate ions on both anode and cathode sides with the cation exchange film **34** being sandwiched between opposite sides.

[**0081**] The electrolyzing electrode **1** is prepared by the above manufacturing method. In the electrolyzing electrodes **1** for use in the persulfuric acid-dissolving liquid producing device **30**, tantalum oxide is used as an oxide which is a dielectric material to be included in the surface layer **4**, and the surface layer **4** is formed into a film thickness which is larger than 0 and is 2000 nm or less, preferably 40 nm or more and below 1000 nm. It is to be noted that in the present embodiment, the surface layer having a thickness of about 56 nm is used.

[**0082**] On the other hand, platinum is used in the electrode **32** as the cathode. In addition, there may be constituted: an insoluble electrode obtained by platinum on the substrate of the silicon substrate **2**; a platinum-iridium-based electrolyzing electrode; a carbon electrode or the like.

[**0083**] The cation exchange film **34** is a fluororesin-based film having durability against a predetermined oxidizing

agent. As a typical cation exchange film, there is a perfluoro sulfonic acid-based film such as trade name Nafion 115, 117, 315 or 350 manufactured by DuPont. It is assumed that in the present embodiment, Nafion is used as the cation exchange film **34**.

[**0084**] According to the above constitution, in this treatment tank **31**, a 0.1 M sulfuric acid (electrolytic solution **33**) is stored on the anode side and the cathode side defined by the cation exchange film **34**, and the electrolyzing electrode **1** and the electrode **32** are submerged into the electrolytic solution **33** on the anode side and the electrolytic solution **33** on the cathode side, respectively, with the cation exchange film **34** being sandwiched between the opposite sides. Thereafter, the power supply **35** applies a direct current to the electrodes **1** and **32** to electrolyze the electrolytic solution **33**.

[**0085**] When water is electrolyzed using the electrolyzing electrode, an oxygen gas is usually produced on the anode side (reaction A). When a material of the electrolyzing electrode is selected, in addition to oxygen, ozone or hydrogen peroxide is produced (reactions B and C). The reactions A to C will be described:

[**0086**] Reaction A $2H_2O \rightarrow O_2+4H^++4e^-$;

[**0087**] Reaction B $3H_2O \rightarrow O_3+6H^++6e^-$; and

[**0088**] Reaction C $2H_2O \rightarrow H_2O_2+2H^++2e^-$.

[**0089**] In the present invention, when the electrolytic solution **33** containing sulfate ions is electrolyzed using the electrolyzing electrode **1**, the persulfuric acid is produced (reaction D). It is to be noted that even in the electrolytic solution **33** contains sulfite ions, persulfate ions are similarly produced (reaction E). The reactions D and E will be described hereinafter.

[**0090**] Reaction D $2SO_4^{2-} \rightarrow S_2O_8^{2-}+2e^-$; and

[**0091**] Reaction E $2HSO_4^- \rightarrow S_2O_8^{2-}+2H^++2e^-$.

[**0092**] Since the electrolyzing electrode usually has a small potential window, an anode-side reaction having a low theoretical electrolytic voltage, especially an oxygen producing reaction preferentially occurs. On the other hand, since the electrolyzing electrode **1** of the present embodiment has an excessively large potential window, and an active overvoltage is very high with respect to the oxygen producing reaction, a target oxidation reaction occurs in preference to the oxygen producing reaction. That is, in the present embodiment, the oxidation reaction of the sulfate ions contained in the electrolytic solution **33** proceeds. Accordingly, when the aqueous solution containing the sulfate ions is electrolyzed, a persulfuric acid-dissolving liquid can be obtained.

[**0093**] On the other hand, **FIG. 7** shows a current-potential curve (cyclic voltammogram) at a time when a potential of the electrolyzing electrode **1** constituting the anode is changed with time by use of a potentiostatic electrolysis device (potentiostat), thereby electrolyzing the electrolytic solution **33** by the electrolyzing electrode **1**. **FIG. 8** shows, in contrast to **FIG. 7**, a current-potential curve at a time when an electrolytic solution containing a perchloric acid is electrolyzed.

[**0094**] According to the current-potential curve shown in **FIG. 7** in a case where the electrolytic solution **33** containing the sulfate ions is electrolyzed, an oxygen production peak is indicated in the vicinity of a potential of 3.5 V, and a chemical reaction peak is indicated in the vicinity of 2.5 V before reaching the oxygen production peak. It is seen that since the electrolytic solution **33** does not contain any substance other than the sulfuric acid and water, the oxidation reaction of the sulfate ions occurs. It is to be noted that the current-potential curve of **FIG. 8** shows the case where the electrolytic solution containing the perchloric acid is electrolyzed. This current-potential curve does not indicate any chemical reaction peak other than the oxygen production peak. The comparison between **FIGS. 7 and 8** clearly indicates that **FIG. 7** shows the chemical reaction peak in addition to the oxygen production peak.

[**0095**] Therefore, the potential of the electrolyzing electrode **1** constituting the anode is fixed in the vicinity of 2.5 V in which the chemical reaction peak is indicated, and the solution containing the sulfate ions, that is, the electrolytic solution **33** is electrolyzed. Accordingly, the persulfuric acid can be produced with a high current efficiency.

[**0096**] As described above, in a place where the persulfuric acid having a very strong oxidizing power is to be used, when the aqueous solution containing the sulfate ions is electrolyzed, the persulfuric acid can efficiently be produced. Therefore, it is possible to avoid a risk in transporting or storing the persulfuric acid. In consequence, the persulfuric acid, having an oxidizing power which is much stronger than that of the sulfuric acid or the like, can easily be used in cleaning a semiconductor or used as a polymerization initiator, an oxidizing agent, a bleaching agent, a photograph treating agent, an oxidizing agent for a reagent chemical such as manganese or chromium, an analysis reagent or the like. Especially, in a case where the persulfuric acid-dissolving liquid is used in cleaning the semiconductor, a purpose can be achieved with a concentration and an amount which are less than those in a conventional method. In consequence, an amount of a solution required for the cleaning can be reduced, and waste water disposal can be simplified.

[**0097**] Moreover, in the present embodiment, the electrolyzing electrode **1** which can realize the production of the persulfuric acid is made of silicon constituting the substrate **2**, platinum constituting the intermediate layer **3**, and tantalum oxide constituting the surface layer **4**. Therefore, the electrolyzing electrode can be manufactured inexpensively as compared with a conventional electrode using conductive diamond. In consequence, production costs can be reduced.

What is claimed is:

1. An electrolyzing electrode comprising:

a substrate; and

a surface layer formed on the surface of the substrate and including a dielectric material,

the surface layer being formed to have a thickness which is larger than 0 and is 2000 nm or less.

2. The electrolyzing electrode according to claim 1, wherein the substrate is a conductive substrate.

3. The electrolyzing electrode according to claim 1 or 2, wherein on the substrate, there is formed an intermediate layer positioned on an inner side of the surface layer, formed on the surface of the substrate, and containing at least one of

an oxidization retarding metal, a metal oxide having conductivity and a metal having conductivity even when oxidized.

4. The electrolyzing electrode according to claim 1, 2 or **3**, wherein the dielectric material included in the surface layer is an oxide.

5. The electrolyzing electrode according to claim 4, wherein the oxide is tantalum oxide or aluminum oxide.

6. The electrolyzing electrode according to claim 1, 2, **3**, **4** or **5**, wherein the surface layer is constituted by forming a surface layer constituting material on the surface of the substrate by a sputtering process.

7. The electrolyzing electrode according to claim 3, 4, **5** or **6**, wherein the intermediate layer is constituted by forming an intermediate layer constituting material on the surface of the substrate by the sputtering process.

8. A production method of a persulfuric acid-dissolving liquid by electrolyzing an aqueous solution containing sulfate ions to produce a persulfuric acid-dissolving liquid,

wherein the electrolyzing electrode according to any one of claims 1 to 7 is used as an anode.

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