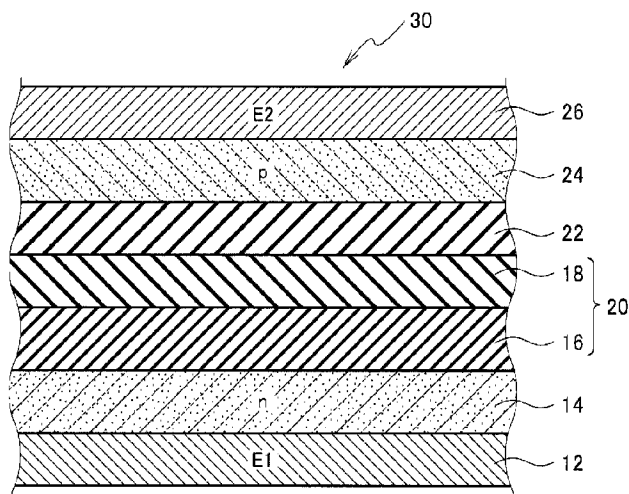




(86) Date de dépôt PCT/PCT Filing Date: 2017/07/24
(87) Date publication PCT/PCT Publication Date: 2018/03/08
(45) Date de délivrance/Issue Date: 2021/02/16
(85) Entrée phase nationale/National Entry: 2019/02/25
(86) N° demande PCT/PCT Application No.: JP 2017/026697
(87) N° publication PCT/PCT Publication No.: 2018/042945
(30) Priorité/Priority: 2016/08/31 (JP2016-168956)

(51) Cl.Int./Int.Cl. *H01M 10/36* (2010.01),
H01M 4/52 (2010.01)
(72) Inventeurs/Inventors:
TONOKAWA, TAKASHI, JP;
KOSAKA, YUTAKA, JP;
TSUNOKUNI, KAZUYUKI, JP;
TAKANO, HIKARU, JP;
CHICHIBU, SHIGEFUSA, JP;
KOJIMA, KAZUNOBU, JP
(73) Propriétaire/Owner:
KABUSHIKI KAISHA NIHON MICRONICS, JP
(74) Agent: GOWLING WLG (CANADA) LLP

(54) Titre : BATTERIE SECONDAIRE
(54) Title: SECONDARY BATTERY



(57) **Abrégé/Abstract:**

A secondary battery (30) includes: a first oxide semiconductor (14) having the first conductivity type; a first charging layer (16) disposed on the first oxide semiconductor layer (14), and composed by including a first insulating material and a second oxide semiconductor having the first conductivity type; a second charging layer (18) disposed on the first charging layer (16); a third oxide semiconductor layer (24) having a second conductivity type disposed on the second charging layer (18); and a hydroxide layer (22) disposed between the first charging layer (16) and the third oxide semiconductor layer (24), and containing a hydroxide of a metal constituting the third oxide semiconductor layer. There is provided a highly reliable secondary battery capable of improving an energy density and increasing battery characteristics (electricity accumulation capacity).

ABSTRACT

A secondary battery (30) includes: a first oxide semiconductor (14) having the first conductivity type; a first charging layer (16) disposed on the first oxide semiconductor layer (14), and composed by including a first insulating material and a second oxide semiconductor having the first conductivity type; a second charging layer (18) disposed on the first charging layer (16); a third oxide semiconductor layer (24) having a second conductivity type disposed on the second charging layer (18); and
5 a hydroxide layer (22) disposed between the first charging layer (16) and the third oxide semiconductor layer (24), and containing a hydroxide of a metal constituting the third oxide semiconductor layer. There is provided a highly reliable secondary battery capable of improving an energy density and increasing battery
10 characteristics (electricity accumulation capacity).

DESCRIPTION**SECONDARY BATTERY**5 **TECHNICAL FIELD**

[0001]

The embodiments described herein relate to a secondary battery.

10 **BACKGROUND ART**

[0002]

As conventional secondary batteries, there have been proposed secondary batteries, in which a first electrode / an insulating material / an n type oxide semiconductor layer / a p
15 type oxide semiconductor layer / a second electrode are layered, since electrolytic solutions and rare elements are not used and thinning thereof can be realized.

[0003]

Moreover, as a structure similar to such secondary batteries,
20 there have been proposed secondary batteries including: a positive electrode including a positive-electrode active material layer containing a nickel oxide or the like as a positive-electrode active material; a solid electrolyte having an aqueous porous structure; and a negative electrode including a
25 negative-electrode active material layer containing a titanium oxide or the like as a negative-electrode active material.

[0004]

Patent Literature 1: Japanese Patent No. 5508542

Patent Literature 2: Japanese Patent No. 5297809

Patent Literature 3: Japanese Patent Application Laid-Open
Publication No. 2015-82445

5 Patent Literature 4: Japanese Patent Application Laid-Open
Publication No. 2016-82125

SUMMARY OF INVENTION

Technical Problem

10 [0005]

The embodiments provide a highly reliable secondary battery capable of improving an energy density and increasing battery characteristics (electricity accumulation capacity).

15 **Solution to Problem**

[0006]

According to one aspect of the embodiments, there is provided a secondary battery comprising: a first oxide semiconductor having a first conductivity type; a first charging layer disposed on the first oxide semiconductor layer, the first charging layer composed by comprising a first insulating material and a second oxide semiconductor, the second oxide semiconductor having the first conductivity type; a third oxide semiconductor layer having a second conductivity type disposed on the first charging layer; and a hydroxide layer disposed between the first charging layer and the third oxide semiconductor layer, the hydroxide layer containing a hydroxide of a metal constituting

20

25

the third oxide semiconductor layer.

Advantageous Effects of Invention

[0007]

5 According to the embodiments, there can be provided the highly reliable secondary battery capable of improving the energy density and increasing the battery characteristics (electricity accumulation capacity).

BRIEF DESCRIPTION OF THE DRAWINGS

[0008]

[Fig. 1] A schematic cross-sectional structure diagram showing a secondary battery according to the embodiments.

[Fig. 2] (a) An energy band diagram before charging of the secondary battery according to the embodiments, and (b) a schematic configuration diagram of each layer corresponding to Fig. 2(a).

[Fig. 3] (a) An energy band diagram during charging (forward bias state) of the secondary battery according to the embodiments, and (b) a schematic configuration diagram of each layer corresponding to Fig. 3(a).

[Fig. 4] (a) An energy band diagram in a fully charged state of the secondary battery according to the embodiments, and (b) a schematic configuration diagram of each layer corresponding to Fig. 4(a).

[Fig. 5] (a) An energy band diagram in a discharged state (state connected to a load) of the secondary battery according to the

embodiments, and (b) a schematic configuration diagram of each layer corresponding to Fig. 5(a).

[Fig. 6] (a) An energy band diagram in a fully discharged state of the secondary battery according to the embodiments, and (b)
5 a schematic configuration diagram of each layer corresponding to Fig. 6(a).

[Fig. 7] (a) A schematic circuit configuration diagram showing a control system to be applied to an electrical stimulation process of forming a hydroxide layer between a first charging layer and
10 a third oxide semiconductor layer in the secondary battery according to the embodiments, and (b) a waveform example of a pulse voltage V_A to be applied between a first electrode and a second electrode.

[Fig. 8] A diagram showing an experimental result of a relationship
15 between an energy density and an electrical stimulation time in the secondary battery according to the embodiments.

[Fig. 9] An example of a scanning electron microscope (SEM) photograph of a cross section of a sample in which a second charging layer is formed by using silicone oil, in the secondary battery
20 according to the embodiments.

[Fig. 10] An example of an SIMS profile for each element, in the secondary battery according to the embodiments shown in Fig. 9.

[Fig. 11] A diagram showing a relationship of a resistor R between the first electrode and the second electrode and an energy density
25 (a.u.) with respect to an amount of dosage of a conductivity adjusting material (a.u.), in the secondary battery according to the embodiments.

DESCRIPTION OF EMBODIMENTS

[0009]

Next, the embodiments will be described with reference to
5 drawings. In the description of the following drawings, the
identical or similar reference sign is attached to the identical
or similar part. However, it should be noted that the drawings
are schematic and therefore the relation between thickness and
the plane size and the ratio of the thickness differs from an actual
10 thing. Therefore, detailed thickness and size should be
determined in consideration of the following explanation. Of
course, the part from which the relation and ratio of a mutual
size differ also in mutually drawings is included.

[0010]

15 Moreover, the embodiments shown hereinafter exemplify the
apparatus and method for materializing the technical idea; and
the embodiments do not specify the material, shape, structure,
placement, etc. of each component part as the following. The
embodiments may be changed without departing from the spirit or
20 scope of claims.

[0011]

[Embodiments]

Fig. 1 shows a schematic cross-sectional structure of a
25 secondary battery according to the embodiments. Hereinafter, a
secondary battery 30 according to the embodiments will be
explained.

[0012]

As shown in Fig. 1, the secondary battery 30 according to the embodiments includes: a first oxide semiconductor 14 having a first conductivity type; a first charging layer 16 disposed on the first oxide semiconductor layer 14, and composed by including a first insulating material and a second oxide semiconductor having the first conductivity type; a third oxide semiconductor layer 24 having a second conductivity type disposed on the first charging layer 16; and a hydroxide layer 22 disposed between the first charging layer 16 and the third oxide semiconductor layer 24, and containing a hydroxide of a metal constituting the third oxide semiconductor layer 24.

[0013]

Moreover, the secondary battery 30 according to the embodiments may include a second charging layer 18 disposed between the first charging layer 16 and the hydroxide layer 22, as shown in Fig. 1.

[0014]

In the embodiments, the second charging layer 18 may include a second insulating material.

[0015]

Alternatively, the second charging layer 18 may include the second insulating material and a conductivity adjusting material.

[0016]

Alternatively, the first charging layer 16 may include a structure of at least two-layer of which compositions are different from each other. The first charging layer 16 may be

formed by including a silicon oxide (SiO_2) / a titanium oxide (TiO_2),
for example. Specifically, the first charging layer 16 may be
formed by including a layered structure of SiO_2 / TiO_2 , or may be
formed by including a particulate bonding structure in which the
5 periphery of particle-shaped TiO_2 is covered with SiO_2 .
Alternatively, the first charging layer 16 may include a structure
into which TiO_2 and SiO_2 are mixed, or a structure in which TiO_2
is wrapped in a silicon oxide. In the above description, the
compositions of the titanium oxide and the silicon oxide are
10 respectively not limited to TiO_2 and SiO_2 , but may include a
structure in which the composition ratio x , of TiO_x and/or SiO_x
is changed.

[0017]

Moreover, the n type oxide semiconductor may be an oxide
15 of titanium (Ti), tin (Sn), zinc (Zn), or magnesium (Mg).
Accordingly, the first charging layer 16 may be a layered structure
of SiO_2 and an oxide of with Ti, Sn, Zn, or Mg, or may be formed
of a particulate bonding structure in which the periphery of an
oxide of particle-shaped Ti, Sn, Zn, or Mg is covered with SiO_2 .
20 Alternatively, the first charging layer 16 may include a
configuration in which a molecule or molecular group of SiO_2 and
an oxide of Ti, Sn, Zn, or Mg is surrounded by SiO_2 (amorphous).

[0018]

Alternatively, the first charging layer 16 may include a
25 porous structure.

[0019]

Moreover, the second oxide semiconductor may include at

least one oxide selected from the group consist of an oxide of Ti, an oxide of Sn, an oxide of Zn, and an oxide of Mg.

[0020]

Moreover, the conductivity adjusting material may include
5 an oxide of a semiconductor having the first conductivity type or an oxide of a metal.

[0021]

Alternatively, the conductivity adjusting material may include at least one oxide selected from the group of consisting
10 of an oxide of Sn, an oxide of Zn, an oxide of Ti, and an oxide of niobium (Nb).

[0022]

More specifically, the second insulating material may include SiO₂ and the conductivity adjusting material may include
15 SnO_x, in the secondary battery 30 according to the embodiments.

[0023]

Alternatively, the second insulating material may include SiO_x formed as a film from silicone oil, in the secondary battery 30 according to the embodiments.

20 [0024]

Alternatively, the first insulating material may include SiO₂ and the second oxide semiconductor may include TiO₂, in the secondary battery 30 according to the embodiments.

25 [0025]

(Hydroxide Layer)

The hydroxide layer 22 is a layer which reduces a metal

hydroxide and converts an electron hole (h^+) into a hydrogen ion (H^+) by an application of an electric field at the time of charging, and converts the hydrogen ion into the electron hole at the time of discharging.

5 [0026]

If the hydroxide is a nickel hydroxide, the following reaction formula is realized.

[0027]

10 - Nickel Hydroxide Layer -

The nickel hydroxide ($Ni(OH)_2$) is changed to a nickel oxyhydroxide ($NiOOH$) by the applications of the electric field. A reaction of $Ni(OH)_2 + h^+ \rightarrow NiOOH + H^+$ progresses at the time of charging, and a reaction of $NiOOH + H^+ \rightarrow Ni(OH)_2 + h^+$ progresses at the time of discharging. The aforementioned reaction causes electrochromism.

15

[0028]

(First Charging Layer)

20 The first charging layer 16 is a layer which is paired with the hydroxide layer 22 and accumulates hydrogen generated at the time of charging. In the first charging layer 16, a reaction of $M + H_2O + e^- \rightarrow MH + OH^-$ progresses at the time of charging, and a reaction of $MH + OH^- \rightarrow M + H_2O + e^-$ progresses at the time of discharging. If the first charging layer 16 is made porous, efficiency of accumulating the hydrogen can be increased. Moreover, the hydrogen accumulation and electrical conductivity

25

can be optimized if the first charging layer 16 is formed as a plurality of layers. It can be optimized by forming the second oxide semiconductor by using an oxide of Ti, Sn, Zn or Mg.

5 [0029]

(Second Charging Layer)

The second charging layer 18 is a buffer layer for adjusting movement of H^+ and electrons (e^-). The mobility of H^+ and e^- can be further adjusted by adding a conductivity adjusting material.

10 The second charging layer 18 can be thickly formed in a high breakdown voltage electrically by using an oxide of Sn, Zn, Ti, or Nb for the conductivity adjusting material.

[0030]

15 **(P type Oxide Semiconductor Layer)**

The oxide semiconductor layer 24 constitutes a pn junction with respect to the n type semiconductor of the hydroxide layer (NiOOH of the nickel hydroxide layer), and can suppress an electric charge leak at the time of charging. If the p type oxide semiconductor layer 24 is formed by using NiO, it is possible to form $Ni(OH)_2$ layer by electrical stimulation.

[0031]

(N type First Oxide Semiconductor Layer)

25 The n type first oxide semiconductor layer 14 has an electric resistance intermediate between a first electrode 12 and a first charging layer 16, and makes electrical bonding smooth.

[0032]

As shown in Fig. 1, the secondary battery 30 according to the embodiments may include the first electrode 12 and the second electrode 26; the first oxide semiconductor layer 14 may include an n type first oxide semiconductor layer, and may be connected to the first electrode 12; the second oxide semiconductor may include an n type second oxide semiconductor; and the third oxide semiconductor layer 24 may include a p type third oxide semiconductor layer, and may be connected to the second electrode 26.

[0033]

Further in details, the third oxide semiconductor layer 24 may include a nickel oxide (NiO), and the hydroxide layer 22 may include at least any one of a nickel hydroxide (Ni(OH)₂) or nickel oxyhydroxide (NiOOH), in the secondary battery 30 according to the embodiments.

[0034]

Alternatively in the secondary battery 30 according to the embodiments, the third oxide semiconductor layer 24 may include the nickel oxide (NiO); the hydroxide layer 22 may include a laminated structure in which both of the nickel hydroxide (Ni(OH)₂) and the nickel oxyhydroxide (NiOOH) are mixed, and the nickel hydroxide (Ni(OH)₂) may be contacted with the third oxide semiconductor layer 24, and the nickel oxyhydroxide (NiOOH) may be contacted with the second charging layer 18.

[0035]

Moreover, in the secondary battery 30 according to the

embodiments, the third oxide semiconductor layer 24 includes the nickel oxide (NiO); and the hydroxide layer 22 includes the nickel oxyhydroxide (NiOOH) when fully charged, and includes the nickel hydroxide (Ni(OH)₂) when fully discharged.

5 [0036]

Furthermore, the nickel hydroxide (Ni(OH)₂) is changed to the nickel oxyhydroxide (NiOOH) at the time of the charging in which the second electrode 26 is biased to positive with respect to the first electrode 12.

10 [0037]

Moreover, the nickel oxyhydroxide (NiOOH) is changed to the nickel hydroxide (Ni(OH)₂) at the time of discharging via a load connected between the first electrode 12 and the second electrode 26.

15 [0038]

The hydroxide layer 22 may be formed as a film directly on the second charging layer 18, or may be formed by periodically applying a pulse voltage between the p type third oxide semiconductor layer 24 and the n type first oxide semiconductor layer 14, as mentioned below.

[0039]

An electricity accumulation capacity can be increased by forming the nickel hydroxide (Ni(OH)₂) layer between the charging layer 20 (the first charging layer 16 + the second charging layer 18) and the third oxide semiconductor layer 24, in the secondary battery 30 according to the embodiments.

[0040]

Moreover, in the secondary battery 30 according to the embodiments, there may be adopted a configuration in which a layer containing many OH groups $(\text{Ni}(\text{OH})_x)$, $\text{Si}(\text{OH})_x$ is formed to be inserted between the second charging layer 18 and the p type third oxide semiconductor layer 24. The electricity accumulation capacity can be enlarged by including such a configuration, and thereby battery performance can be improved. More specifically, the hydroxide layer 22 is not limited to the nickel hydroxide $(\text{Ni}(\text{OH})_2)$, but may be formed as a mixture layer, e.g. the layer containing many OH groups $(\text{Ni}(\text{OH})_x)$, $\text{Si}(\text{OH})_x$. A compound of Ni, Si, O, H and elements which constitutes the second charging layer 18 may be contained as a structural factor.

[0041]

15 (Energy Band Diagram)

Hereinafter, there will be described an example in which the p type third oxide semiconductor layer 24 is formed of the nickel oxide (NiO), the hydroxide layer 22 is formed of at least any one of the nickel hydroxide $(\text{Ni}(\text{OH})_2)$ or the nickel oxyhydroxide (NiOOH), the first charging layer 16 is formed of $\text{SiO}_2/\text{TiO}_2$, and the second charging layer 18 is formed of SiO_2/SnO .

[0042]

- Before Charging -

25 Fig. 2(a) A shows an energy band diagram before charging of the secondary battery 30 according to the embodiments, and Fig. 2(b) shows a schematic configuration of each layer corresponding

to Fig. 2(a). In the drawings, E_f denotes the Fermi level.

[0043]

The p type third oxide semiconductor layer 24 which is the nickel oxide (NiO) is connected to a second electrode (26) E2, and the first charging layer 16 which is SiO_2 / TiO_2 is connected to a first electrode (12) E1.

[0044]

In a thermal equilibrium state, the energy band diagram before charging of the secondary battery 30 according to the embodiments is shown, as shown in Fig. 2(a), a conduction band of NiO / $\text{Ni}(\text{OH})_2$ / SnO / TiO_2 exists in a level of 1.8 eV / 1.47 eV / 4.3 to 4.5 eV / 4.3 eV with respect to the vacuum level. Moreover, the bandgap energy E_g of NiO / $\text{Ni}(\text{OH})_2$ / SnO / TiO_2 is 4.0 eV / 3.7 eV / 3.8 eV / 3.2 eV. Moreover, the bandgap energy E_g of SiO_2 which constitutes the charging layer 20 is 8.9 eV. Before charging, the hydroxide layer 22 is the nickel hydroxide ($\text{Ni}(\text{OH})_2$).

[0045]

20 - During Charging (Forward Bias State) -

Fig. 3(a) shows an energy band diagram in during charging (forward bias state) of the secondary battery 30 according to the embodiments, and Fig. 3(b) shows a schematic configuration of each layer corresponding to Fig. 3(a).

25 [0046]

Fig. 3(a) shows the energy band diagram in a state where the second electrode E2 is connected to plus (+), the first

electrode E1 is connected to minus (-), and a charging voltage of, for example, approximately 2.8V is applied. In this context, the Fermi level E_f in a state of applying approximately 2.8V is expressed as shown in Fig. 3(a).

5 [0047]

Since the nickel oxyhydroxide (NiOOH) is generated from the nickel hydroxide (Ni(OH)_2) in the hydroxide layer 22C during charging in the secondary battery 30 according to the embodiments, the hydroxide layer 22C during charging is represented by a layered
 10 structure of the nickel hydroxide (Ni(OH)_2) / the nickel oxyhydroxide (NiOOH), as shown in Figs. 3(a) and 3(b). The nickel hydroxide (Ni(OH)_2) layer is mainly disposed at the nickel oxide layer (NiO) side, and the nickel oxyhydroxide (NiOOH) layer is disposed at the second charging layer 18 side.

15 [0048]

Since approximately 2.8V is applied as a positive voltage between the second electrode E2 and the first electrode E1 during charging, an electron e^- is injected into the n type oxide semiconductor (TiO_2) of the charging layer 20 from the first
 20 electrode E1, and a hole h^+ is injected into the p type oxide semiconductor layer (NiO) 24 from the second electrode E2, inside the secondary battery 30.

[0049]

Due to assist of water or water vapor component (H_2O), an
 25 reaction of $\text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + e^-$ progresses at the positive electrode side, whereas an reaction of $\text{M} + \text{H}_2\text{O} + e^- \rightarrow \text{MH} + \text{OH}^-$ progresses at the negative electrode side. In this context,

M denotes a metallic element in the charging layer 20.

[0050]

As a result, since a reaction of $\text{Ni}(\text{OH})_2 + \text{h}^+ \rightarrow \text{NiOOH} + \text{H}^+$ progresses in the hydroxide layer 22C during the charging, hydrogen accumulation due to the assist of the water or water vapor component (H_2O) is realized in the charging layer 20 in accordance with the synthesis between the hydrogen ion H^+ and the electron e^- , as shown in Fig. 3(a). In this case, the hydrogen H is coupled to dangling bonds of Ti, Si, etc., in the charging layer 20, in the hydrogen accumulation. It is also possible to be coupled in OH form.

[0051]

- Full Charge -

Fig. 4(a) shows an energy band diagram in a fully charged state of the secondary battery 30 according to the embodiments, and Fig. 4(b) shows a schematic configuration of each layer corresponding to Fig. 4(a). A conduction band of NiO / NiOOH exists at a level of $1.8\text{eV} + 2.8\text{ eV} / \Delta\text{eV} + 2.8\text{eV}$ with respect to the vacuum level. Moreover, the bandgap energy E_g of NiOOH is 1.75 eV.

[0052]

In an opened state after full charging in which fully hydrogen accumulation is performed in the charging layer 20, a holding voltage slightly lower than that at the time of the charging (2.8V) is held between the second electrode E2 and the first electrode E1.

[0053]

Moreover, in the fully charged state of the secondary battery 30 according to the embodiments, the nickel hydroxide (Ni(OH)_2) layer 22 is changed to the nickel oxyhydroxide (NiOOH) layer 22F, and then energy accumulation as chemical potential of unstable NiOOH is performed.

[0054]

- During Discharging -

Fig. 5(a) shows an energy band diagram in a discharged state (state connected to a load) of the secondary battery 30 according to the embodiments, and Fig. 5(b) shows a schematic configuration of each layer corresponding to Fig. 5(a). More specifically, the energy band diagram in the discharged state (state connected to the load) where a load 42 is connected between the second electrode E2 and the first electrode E1 is expressed as shown in Fig. 5(a). In this case, the Fermi level E_f in a state of applying approximately 2.8V gradually increases in accordance with a discharged state, as shown in Fig. 5(a). In the discharged state (state connected to the load) of the secondary battery 30 according to the embodiments, the reverse reaction of the above-mentioned charging operation occurs.

[0055]

Since the nickel hydroxide (Ni(OH)_2) is generated from the nickel oxyhydroxide (NiOOH) in the hydroxide layer 22D during discharging, in the secondary battery 30 according to the embodiments, the hydroxide layer 22D during discharging is

represented by a layered structure of the nickel hydroxide (Ni(OH)_2) / the nickel oxyhydroxide (NiOOH), as shown in Figs. 5(a) and 5(b). The nickel hydroxide (Ni(OH)_2) layer is mainly formed at the nickel oxide layer (NiO) side, and the nickel oxyhydroxide (NiOOH) layer is formed at the second charging layer side.

[0056]

Since the load 42 is externally connected between the second electrode E2 and the first electrode E1 during discharging, the electron e^- is discharged to the first electrode E1 from the n type oxide semiconductor (TiO_2) of the charging layer 20, and the hole h^+ is discharged to the second electrode E2 from the p type oxide semiconductor layer (NiO) 24, inside the secondary battery 30.

15 [0057]

Due to assist of water or water vapor component (H_2O), an reaction of $\text{NiOOH} + \text{H}_2\text{O} + e^- \rightarrow \text{Ni(OH)}_2 + \text{OH}^-$ progresses at the positive electrode side, whereas an reaction of $\text{MH} + \text{OH}^- \rightarrow \text{M} + \text{H}_2\text{O} + e^-$ progresses at the negative electrode side.

20 [0058]

As a result, since a reaction of $\text{NiOOH} + \text{H}^+ \rightarrow \text{Ni(OH)}_2 + h^+$ progresses in the hydroxide layer 22D during the discharging, release of the hydrogen accumulation state due to the assist of the water or water vapor component (H_2O) is realized in the charging layer 20 in accordance with separation between the hydrogen ion H^+ and the electron e^- , as shown in Fig. 5(a).

[0059]

- Fully Discharged State -

Fig. 6(a) shows an energy band diagram in a fully discharged state of the secondary battery 30 according to the embodiments, and Fig. 6(b) shows a schematic configuration of each layer corresponding to Fig. 6(a).

[0060]

In the fully discharged state, the nickel oxyhydroxide (NiOOH) is changed to the nickel hydroxide (Ni(OH)₂) layer 22.

10 [0061]

In the fully discharged state, the energy band diagram of the secondary battery 30 according to the embodiments is expressed as shown in Fig. 6(a), and a conduction band of NiO / Ni(OH)₂ / SnO / TiO₂ exists in a level of 1.8 eV / 1.47 eV / 4.3 to 4.5 eV / 4.3 eV with respect to the vacuum level. Moreover, the bandgap energy E_g of NiO / Ni(OH)₂ / SnO / TiO₂ is 4.0 eV / 3.7 eV / 3.8 eV / 3.2 eV. Moreover, the bandgap energy E_g of SiO₂ which constitutes the charging layer 20 is 8.9 eV. In the fully discharged state, the hydroxide layer 22 is the nickel hydroxide (Ni(OH)₂).

[0062]

In the fully discharged state, it has recovered to a state equivalent to the above-mentioned thermal equilibrium state before the charging.

25

[0063]

(Fabrication Method)

A fabrication method of the secondary battery 30 according to the embodiments includes: forming a first oxide semiconductor 14 having a first conductivity type; forming a first charging layer 16 composed by including a first insulating material and a second oxide semiconductor having the first conductivity type on the first oxide semiconductor layer 14; forming a second charging layer 18 on the first charging layer 16; forming a third oxide semiconductor layer 24 having a second conductivity type on the second charging layer 18; and forming a hydroxide layer 22 containing a hydroxide of a metal constituting the third oxide semiconductor layer 24 between the first charging layer 16 and the third oxide semiconductor layer 24.

15 [0064]

- n type Oxide Semiconductor Layer 14 -

A TiO_2 layer is formed as a film on the first electrode 12 which constitutes a lower electrode, for example by a sputtering deposition method. In this case, Ti or TiO can be used as a target. The layer thickness of the n type oxide semiconductor layer 14 is approximately 50 nm to approximately 200 nm, for example. A tungsten (W) electrode or the like can be applied to the first electrode 12, for example.

25 [0065]

- First Charging Layer 16 -

A chemical solution is formed by stirring titanium fatty

acid and silicone oil with a solvent. The aforementioned chemical solution is coated on the n type oxide semiconductor layer 14 by means of a spin coater. The rotational frequency thereof is approximately 500 to approximately 3000 rpm. It is dried on a hot plate after the coating. The drying temperature on the hot plate is approximately 30°C to approximately 200°C, for example, and the drying time thereon is approximately 5 minutes to approximately 30 minutes, for example. It is fired after the drying. In the firing performed after the drying, it is fired in the atmosphere using a baking furnace. The firing temperature is approximately 300°C to approximately 600°C, and the firing time is approximately 10 minutes to approximately 60 minutes.

[0066]

Consequently, aliphatic acid salt is decomposed and then a fine particle layer of a titanium dioxide covered with a silicone insulating film is formed. The above-mentioned fabrication (preparation) method of forming the titanium dioxide layer covered with the silicone insulating film is a coating and thermodecomposition method. More specifically, the aforementioned layer has a structure where a metallic salt of the titanium dioxide coated with silicone is embedded in the silicone layer. After the firing, UV irradiation by means of a low pressure mercury lamp is implemented. The UV irradiation time is approximately 10 minutes to approximately 100 minutes.

25

[0067]

- Second Charging Layer (Buffer Layer) 18 (Method 1) -

A chemical solution is formed by stirring tin fatty acid and silicone oil with a solvent. The aforementioned chemical solution is coated on the first charging layer 16 by means of the spin coater. The rotational frequency thereof is approximately 500 to approximately 3000 rpm. It is dried on a hot plate after the coating. The drying temperature on the hot plate is approximately 30°C to approximately 200°C, for example, and the drying time thereon is approximately 5 minutes to approximately 30 minutes, for example. Furthermore, it is fired after the drying. In the firing performed after the drying, it is fired in the atmosphere using a baking furnace. The firing temperature is approximately 300°C to approximately 600°C, and the firing time is approximately 10 minutes to approximately 60 minutes. After the firing, UV irradiation by means of a low pressure mercury lamp is implemented. The UV irradiation time is approximately 10 minutes to approximately 100 minutes. The layer thickness of the second charging layer (buffer layer) 18 after the UV irradiation is approximately 100 nm to approximately 300 nm, for example.

[0068]

- Second Charging Layer (Buffer Layer) 18 (Method 2) -

A chemical solution is formed by stirring silicone oil with a solvent. The aforementioned chemical solution is coated on the first charging layer 16 by means of the spin coater. The rotational frequency thereof is approximately 500 to approximately 3000 rpm. It is dried on a hot plate after the

coating. The drying temperature on the hot plate is approximately 50°C to approximately 200°C, for example, and the drying time thereon is approximately 5 minutes to approximately 30 minutes, for example. Furthermore, it is fired after the drying. In the firing performed after the drying, it is fired in the atmosphere using a baking furnace. The firing temperature is approximately 300°C to approximately 600°C, and the firing time is approximately 10 minutes to approximately 60 minutes. After the firing, UV irradiation by means of a low pressure mercury lamp is implemented. The UV irradiation time is approximately 10 minutes to approximately 60 minutes. The layer thickness of the second charging layer (buffer layer) after the UV irradiation is approximately 10 nm to approximately 100 nm, for example.

[0069]

- p type Third Oxide Semiconductor Layer 24 -

A NiO layer is formed as a film on the second charging layer 18, for example by a sputtering deposition method. In this case, Ni or NiO can be used as a target. The layer thickness of the p type oxide semiconductor layer 24 is approximately 200 nm to approximately 1000 nm, for example.

[0070]

- Second Electrode 26 -

The second electrode 26 as an upper electrode is formed by forming Al as a film by means of a sputtering deposition method or a vacuum evaporation method, for example. The second electrode

26 can be formed on the p type third oxide semiconductor layer (NiO) 24 using Al target. The second electrode 26 may be formed only on a specified region using a stainless steel mask, for example.

5

[0071]

- $\text{Ni}(\text{OH})_2$ -

It is formed through an electrical stimulation process which performs an electrical treatment after the formation of the second
10 electrode 26.

[0072]

Plus and negative voltages are alternately applied to the second electrode 26, using the first electrode 12 as a ground (earth) potential. An atmosphere is the atmospheric air and
15 humidity is approximately 20% to approximately 60%, for example.

[0073]

Fig. 7(a) shows a schematic circuit configuration of a control system to be applied to the electrical stimulation process for forming a hydroxide layer between the charging layer 20 and
20 the third oxide semiconductor layer 24, in the secondary battery 30 according to the embodiments. Fig. 7(b) shows a waveform example of a pulse voltage V_A to be applied between the first electrode 12 and the second electrode 26. In Fig. 7(a), a connecting relationship between the circuits is expressed by the
25 thick line and a signal flow is expressed by the thin line.

[0074]

As shown in Fig. 7(a), the pulse voltage V_A to be applied

to the second electrode 26 of the secondary battery 30 with which the first electrode 12 is grounded (earthed) is supplied from a voltage source 32 through an ammeter 34, a voltmeter 36, and a resistor 38. The voltage source 32 can be controlled by the control device 40. Moreover, since a value of the ammeter 34 and a value of the voltmeter 36 are fed back to the control device 40, the pulse voltage V_A shown in Fig. 7(b) can be supplied from the voltage source 32 controlled by the control device 40.

[0075]

10 As shown in Fig. 7(b), one cycle TC is set to 3V (5 seconds) $\rightarrow$ -3V (2 seconds) $\rightarrow$ 5V (0.5 seconds) $\rightarrow$ -0.4V (4.5 seconds), for example, and the pulse voltage V_A is applied thereto in approximately 300 to approximately 5000 cycles. Thereby, the $\text{Ni}(\text{OH})_2$ layer 22 can be formed between the second charging layer 18 and the third oxide semiconductor layer (NiO) 24. In addition, it is detected from a measured result of a Secondary Ion Mass Spectroscopy (SIMS) that substances containing Si, O, H, and Ni also exists in the $\text{Ni}(\text{OH})_2$ layer 22.

[0076]

20 Also in a structure including only the first charging layer 16 and not including the second charging layer 18 as the charging layer 20, the hydroxide layer can be formed between the first charging layer 16 and the third oxide semiconductor layer 24 through the above-mentioned electrical stimulation process.

25 [0077]

The pulse voltage waveform shown in Fig. 7(b) is merely one example, and the voltage, the number of pulses per cycle, the order

of the positive / negative voltages, and the like can be appropriately selected in accordance with the configuration of the secondary battery 30. It is also possible to select a pulse waveform applying of no negative voltage.

5

[0078]

(Relationship between Energy Density and Electrical Stimulation Time)

Fig. 8 shows an experimental result of a relationship
10 between an energy density and an electrical stimulation time, in the secondary battery 30 according to the embodiments. In the embodiments, the electrical stimulation time corresponds to a time period of applying the pulse voltage V_A of one cycle $TC = 12$ seconds for a plurality of the cycles.

15 [0079]

As shown in Fig. 8, there is a tendency that the energy density increases as the electrical stimulation time increases. It is confirmed that the layer thickness of the hydroxide ($Ni(OH)_x$) layer 22 increases with elapsing of the electrical stimulation
20 time.

[0080]

In embodiments, the nickel hydroxide ($Ni(OH)_2$) layer 22 is formed between the charging layer 20 and the third oxide semiconductor layer (NiO) 24. As a result, since the reaction of
25 $Ni(OH)_2 + h^+ \rightarrow NiOOH + H^+$ progresses at the time of charging, and the reaction of $NiOOH + H^+ \rightarrow Ni(OH)_2 + h^+$ progresses at the time of discharging, there can be provided the secondary battery 30

with the increased electricity accumulation capacity.

[0081]

(Experimental Results)

5 Fig. 9 shows an example of a cross section SEM photograph of a sample in which the second charging layer 18 is made only using silicone oil and is subjected to the electrical stimulation process, in the secondary battery 30 according to the embodiments.

[0082]

10 The hydroxide ($\text{Ni}(\text{OH})_2$) layer 22 is clearly formed between the second charging layer (buffer layer) 18 and the third oxide semiconductor layer (NiO) 24 which are formed only of silicone oil.

15 [0083]

(SIMS Analysis)

 In the secondary battery 30 according to the embodiments shown in Fig. 9, mass spectrometry of each element is implemented by digging from a front side surface of the third oxide
20 semiconductor layer (NiO) 24 to obtain an SIMS profile for each element.

[0084]

 In the sample not subjected to the electrical stimulation process (curved line WO in Fig. 10), a region having a peak of
25 Si near the depth 5 (a.u.) corresponds to the second charging layer (buffer layer) 18 made by only using the silicone oil. A peak of H is observed at an interface between the buffer layer 18 and

the third oxide semiconductor layer (NiO) 24 (a portion of which the depth is the vertical line A).

[0085]

On the other hand, in a sample which subjected to the electrical stimulation process (the curved line W in Fig. 10), there is a region with a large amount of H in a depth portion on the left-hand side of the vertical line A, and therefore it is estimated it is due to the presence of the hydroxide (Ni(OH)₂) layer 22.

10 [0086]

The hydroxide (Ni(OH)₂) layer 22 is a layer electrochemically formed through the electrical stimulation process. Therefore, there is also introduction of Si from SiO_x of the underlying second charging layer (buffer layer) 18, and the presence of Si can be confirmed also from the SIMS profile (the curved line W in Fig. 10).

[0087]

Fig. 11 shows a relationship of the resistor R between the first electrode and the second electrode and an energy density (a.u.) with respect to an amount of dosage of a conductivity adjusting material (a.u.), in the secondary battery 30 according to the embodiments. The energy density (a. u.) corresponds to the discharge capacity of the secondary battery 30.

[0088]

25 In Fig. 11, the amount of dosage of conductivity adjusting material corresponds to a value related to an additive amount of SnO_x in the second charging layer (buffer layer) 18. As shown in

Fig. 11, the optimum values of the resistor R between the first electrode and the second electrode (a.u.) and the energy density (a.u.) exist with respect to the value related to the additive amount of SnO_x in the second charging layer 18.

5 [0089]

In the secondary battery 30 according to the embodiments, the second charging layer (buffer layer) 18 composed by including the insulating material and the conductivity adjusting material can be optimize the energy density by controlling the additive
10 amount of the conductivity adjusting material.

[0090]

(Laminated Structure)

For example, a structure of the secondary battery 30
15 according to the embodiments is made in a sheet shape by using stainless steel foil as a substrate. Subsequently, this sheet may be laminated to produce the secondary battery 30 with a required capacity.

[0091]

20 For example, a secondary battery with a required capacity can be manufactured by opposing two sheets of the second electrodes (upper electrodes), inserting an electrode (thin metal foil) therebetween, and laminating the two sheets in multiple layers. It may be sealed with a laminate or the like after the laminating.

25

[0092]

[Other embodiments]

As explained above, the embodiments have been described, as a disclosure including associated description and drawings to be construed as illustrative, not restrictive. This disclosure
 5 makes clear a variety of alternative embodiments, working examples, and operational techniques for those skilled in the art.

[0093]

Such being the case, the embodiments cover a variety of embodiments, whether described or not.

10

INDUSTRIAL APPLICABILITY

[0094]

The secondary battery of the embodiments can be utilized for various consumer equipment and industrial equipment, and can
 15 be applied to wide applicable fields, such as secondary batteries for system applications capable of transmitting various kinds of sensor information with low power consumption, e.g. communication terminals and secondary batteries for wireless sensor networks.

20 **Reference Signs List**

[0095]

12: First electrode (E1)

14: First oxide semiconductor layer (TiO₂ layer)

16: First charging layer (TiO₂ / SiO₂)

25 18: Second charging layer (buffer layer)

20: Charging layer (16 / 18)

22: Hydroxide layer (Ni(OH)₂ layer)

22C, 22D: $\text{Ni}(\text{OH})_2$ / NiOOH layer
22F: NiOOH layer
24: Third oxide semiconductor layer (NiO layer)
26: Second electrode (E2)
5 30: Secondary battery
32: Voltage source
34: Ammeter
36: Voltmeter
38: Resistor
10 40: Control device
42: Load
VA: Pulse voltage
R: Resistor between first electrode and second electrode

[Claims]

[Claim 1]

A secondary battery comprising:

5 a first oxide semiconductor having a first conductivity type;

 a first charging layer disposed on the first oxide semiconductor layer, the first charging layer comprising a first insulating material and a second oxide semiconductor,
10 the second oxide semiconductor having the first conductivity type;

 a third oxide semiconductor layer having a second conductivity type disposed on the first charging layer; and

 a hydroxide layer disposed between the first charging
15 layer and the third oxide semiconductor layer, the hydroxide layer containing a hydroxide of a metal constituting the third oxide semiconductor layer.

[Claim 2]

20 The secondary battery according to claim 1 further comprising

 a second charging layer disposed between the first charging layer and the hydroxide layer.

25 [Claim 3]

 The secondary battery according to claim 2, wherein

 the second charging layer comprises a second insulating material.

[Claim 4]

The secondary battery according to claim 2, wherein
the second charging layer comprises a second insulating
material and a conductivity adjusting material.

5

[Claim 5]

The secondary battery according to any one of claims 1-
4, wherein
the first charging layer comprises a porous structure.

10

[Claim 6]

The secondary battery according to any one of claims 1-
5, wherein
the second oxide semiconductor comprises at least one
oxide selected from the group consisting of an oxide of Ti, an
oxide of Sn, an oxide of Zn, and an oxide of Mg.

15

[Claim 7]

The secondary battery according to claim 4, wherein
the conductivity adjusting material comprises an oxide
of a semiconductor having the first conductivity type or an
oxide of a metal.

20

[Claim 8]

The secondary battery according to claim 4 or 7, wherein
the conductivity adjusting material comprises at least one
oxide selected from the group consisting of an oxide of Sn, an
oxide of Zn, an oxide of Ti, and an oxide of Nb.

25

[Claim 9]

The secondary battery according to claim 4, wherein
the second insulating material comprises SiO_2 , and the
conductivity adjusting material comprises SnO_x .

5

[Claim 10]

The secondary battery according to claim 4, wherein
the second insulating material comprises SiO_x formed as a
film from silicone oil.

10

[Claim 11]

The secondary battery according to any one of claims 1-10,
wherein

the first insulating material comprises SiO_2 , and the
15 second oxide semiconductor comprises TiO_2 .

[Claim 12]

The secondary battery according to any one of claims 4 or
7-9, wherein

20 an energy density is adjusted by controlling an additive
amount of the conductivity adjusting material.

[Claim 13]

The secondary battery according to any one of claims 1-12,
25 wherein

the third oxide semiconductor layer comprises nickel
oxide (NiO), and

the hydroxide layer comprises at least any one of nickel
hydroxide ($\text{Ni}(\text{OH})_2$) and nickel oxyhydroxide (NiOOH).

30

[Claim 14]

The secondary battery according to any one of claims 2 - 4, 7 - 10, and 12, wherein:

the third oxide semiconductor layer comprises nickel oxide
5 (NiO); and

the hydroxide layer comprises a laminated structure in which both of nickel hydroxide ($\text{Ni}(\text{OH})_2$) and nickel oxyhydroxide (NiOOH) are mixed, and the nickel hydroxide ($\text{Ni}(\text{OH})_2$) is contacted with the third oxide semiconductor layer, and the nickel oxyhydroxide
10 (NiOOH) is contacted with the second charging layer.

[Claim 15]

The secondary battery according to claim 13, wherein:

the third oxide semiconductor layer comprises nickel oxide
15 (NiO); and

the hydroxide layer comprises the nickel oxyhydroxide (NiOOH) when fully charged, and comprises the nickel hydroxide ($\text{Ni}(\text{OH})_2$) when fully discharged.

20 [Claim 16]

The secondary battery according to claim 13, wherein

the nickel hydroxide ($\text{Ni}(\text{OH})_2$) is changed to the nickel oxyhydroxide (NiOOH) at a time of charging.

25 [Claim 17]

The secondary battery according to claim 13, wherein

the nickel oxyhydroxide (NiOOH) is changed to the nickel hydroxide ($\text{Ni}(\text{OH})_2$) at a time of discharging.

[Claim 18]

The secondary battery according to claim 14, wherein
the first charging layer comprises a porous structure.

5 [Claim 19]

The secondary battery according to claim 14 or 18,
wherein

the second oxide semiconductor comprises at least one
oxide selected from the group consisting of an oxide of Ti, an
10 oxide of Sn, an oxide of Zn, and an oxide of Mg.

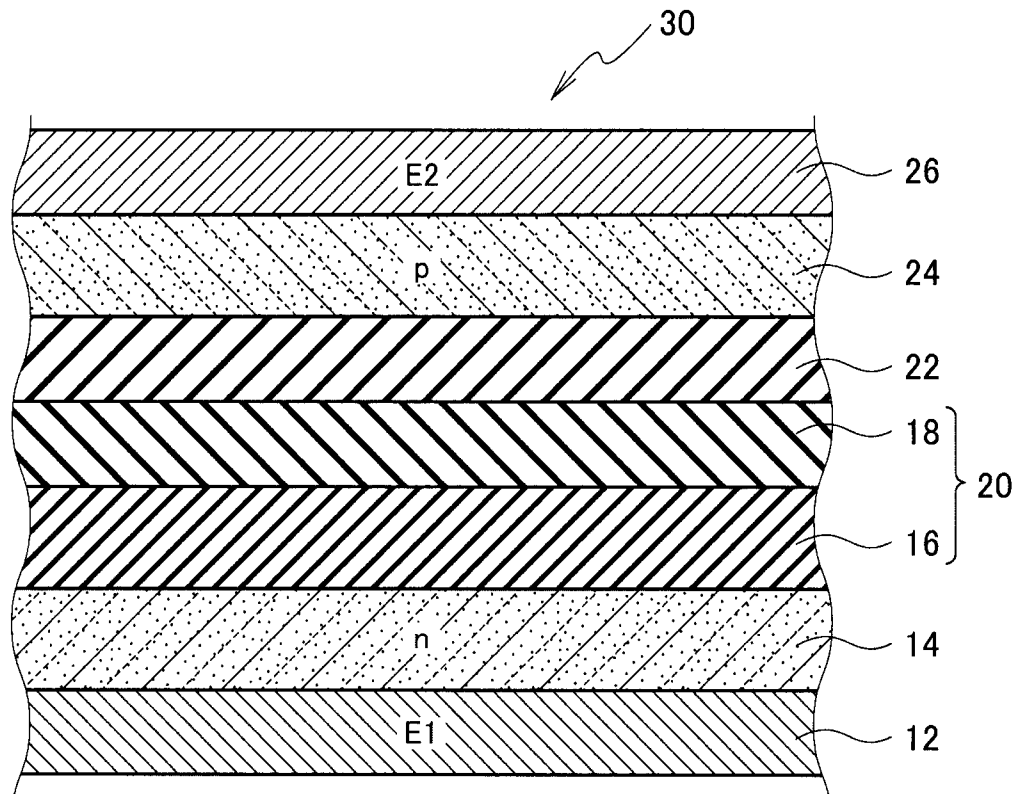
[Claim 20]

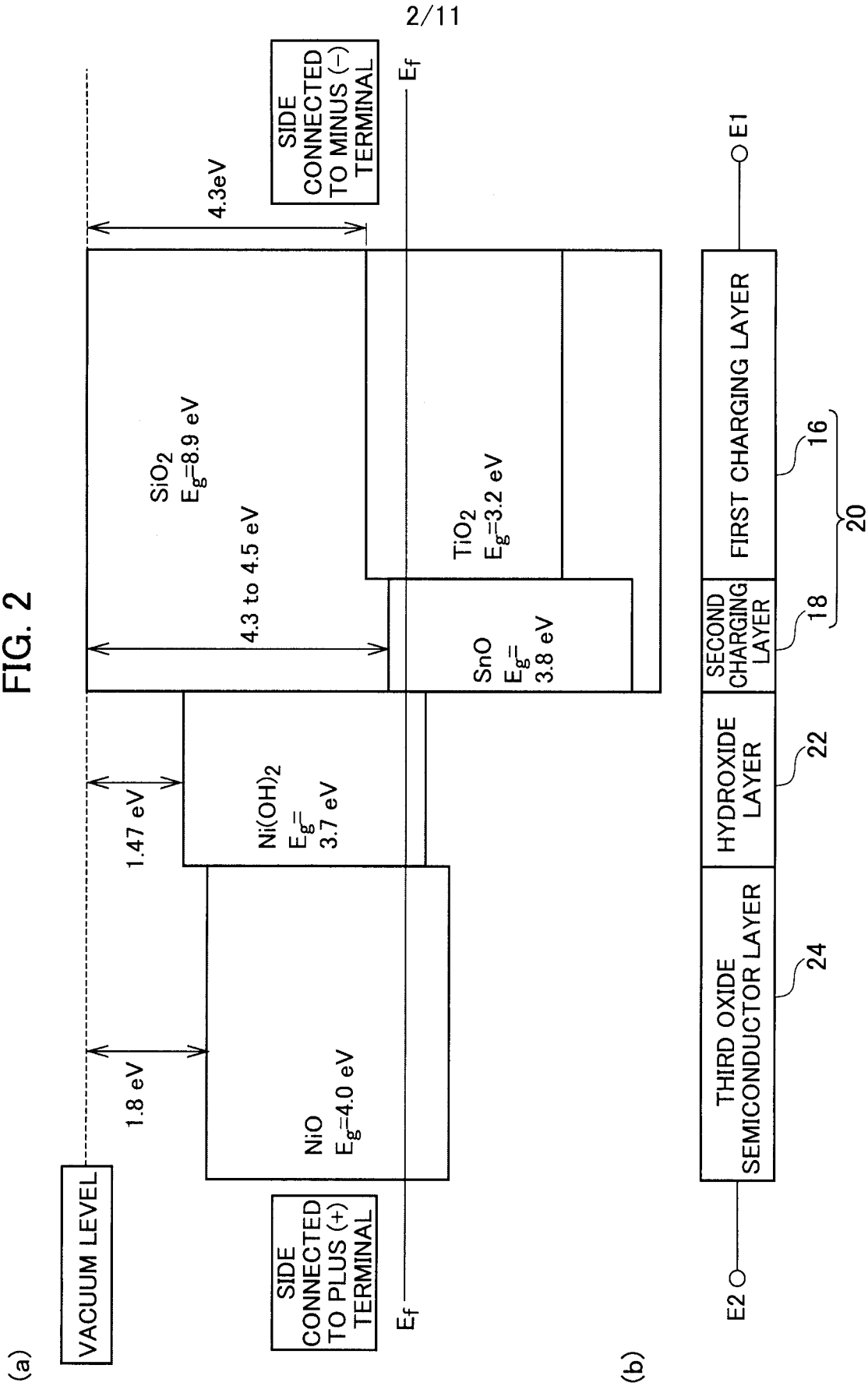
The secondary battery according to any one of claims 14,
18 and 19, wherein

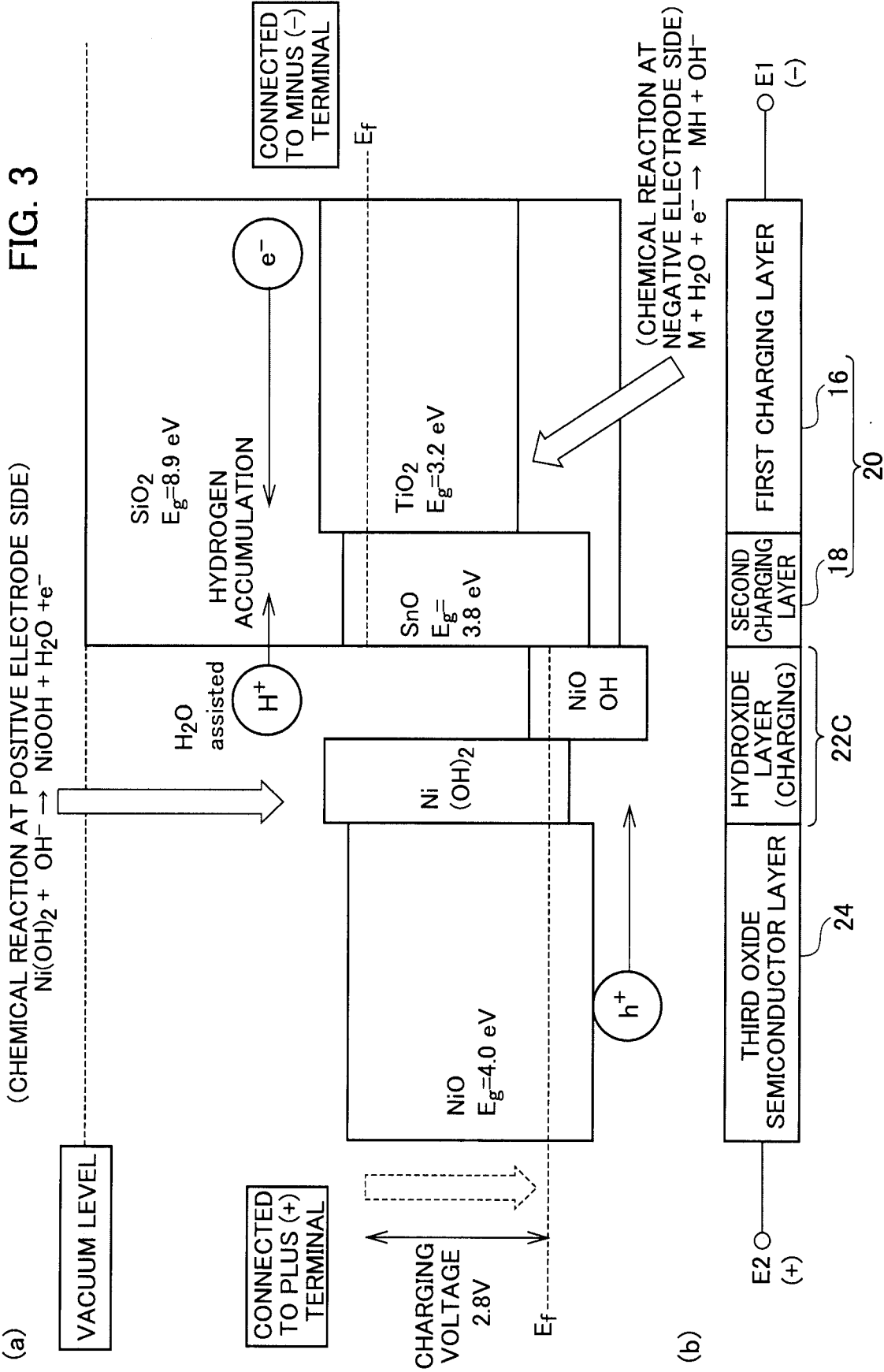
15 the first insulating material comprises SiO_2 , and the
second oxide semiconductor comprises TiO_2 .

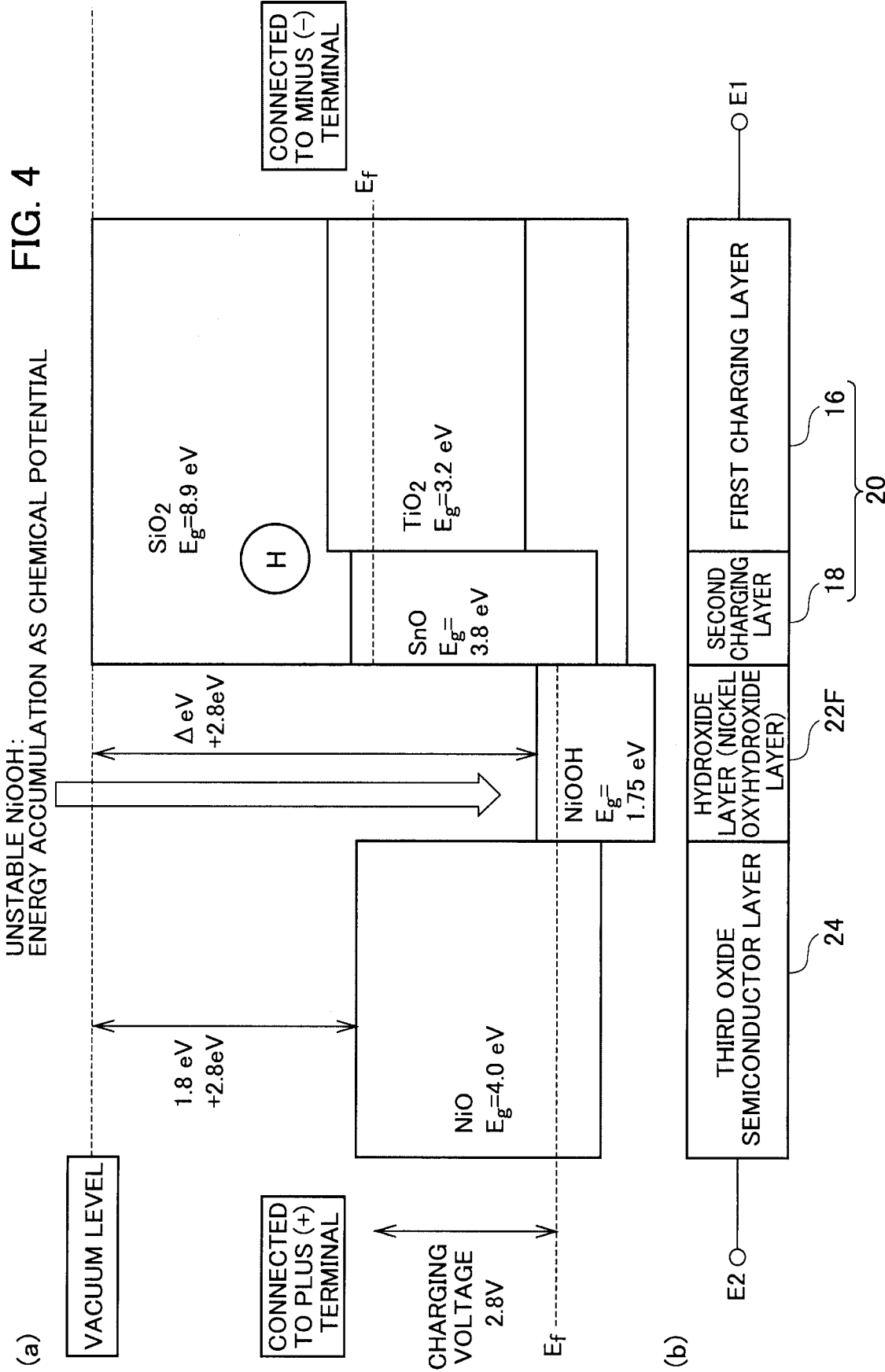
1/11

FIG. 1









5/11

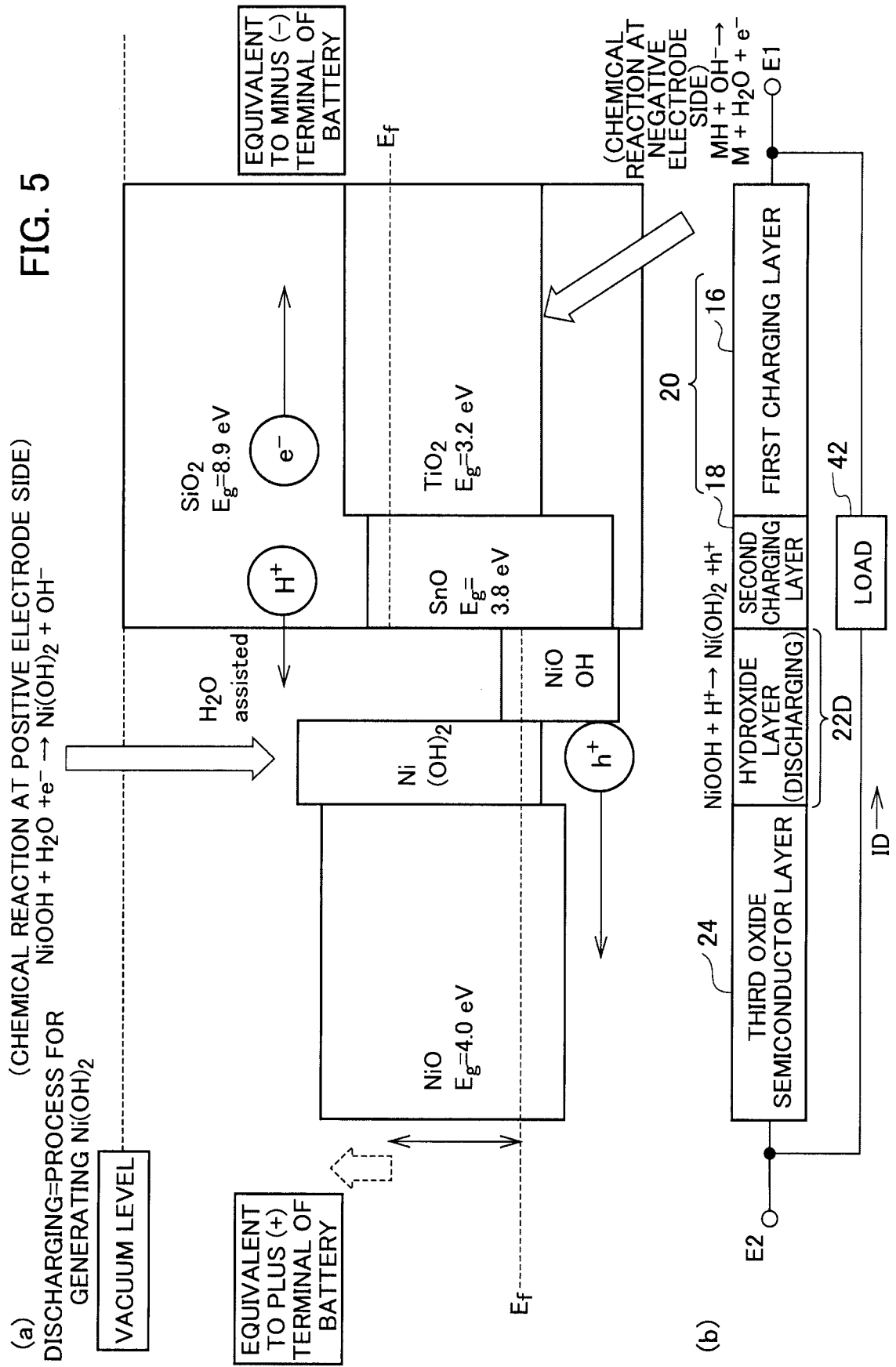
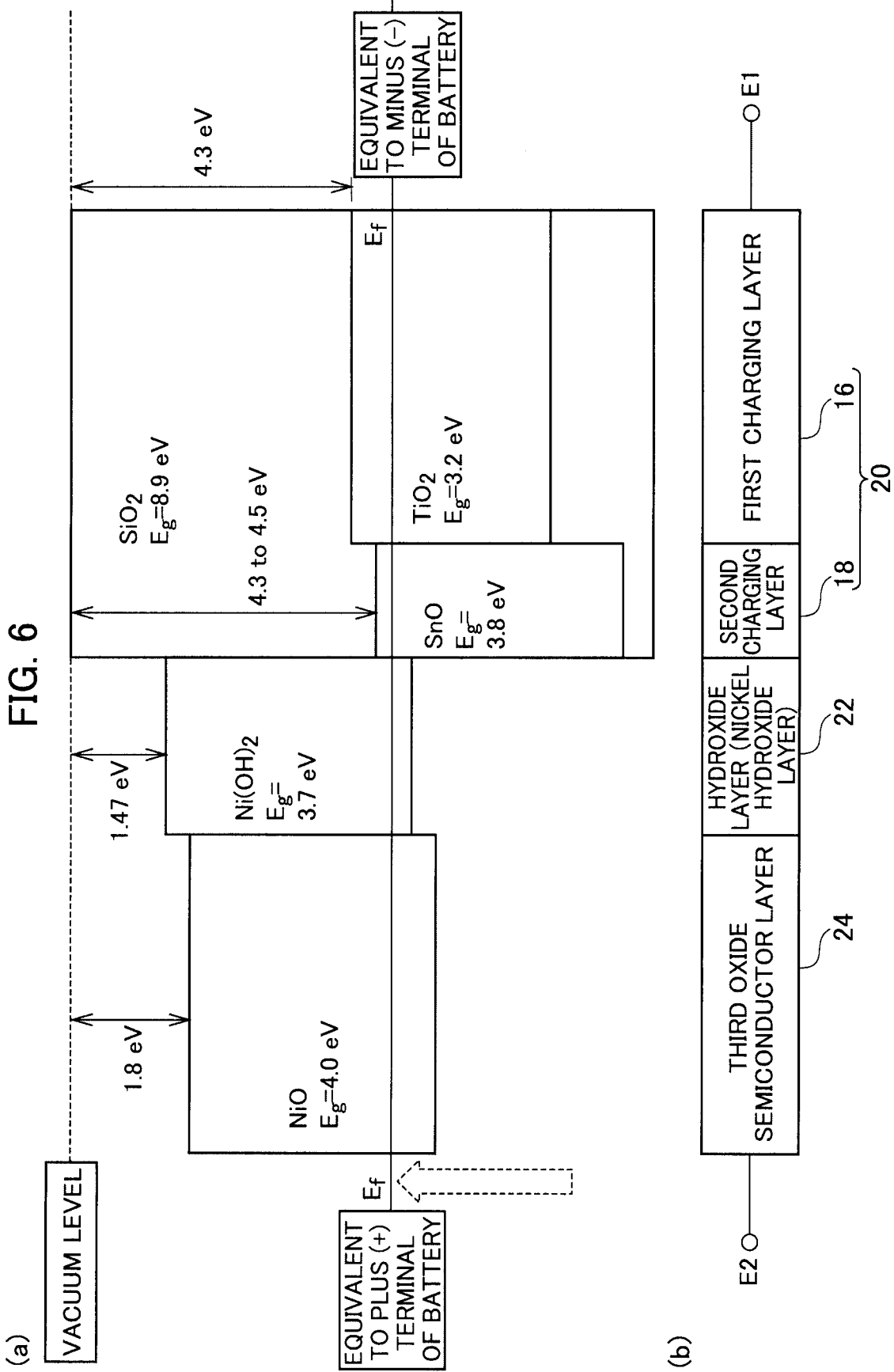
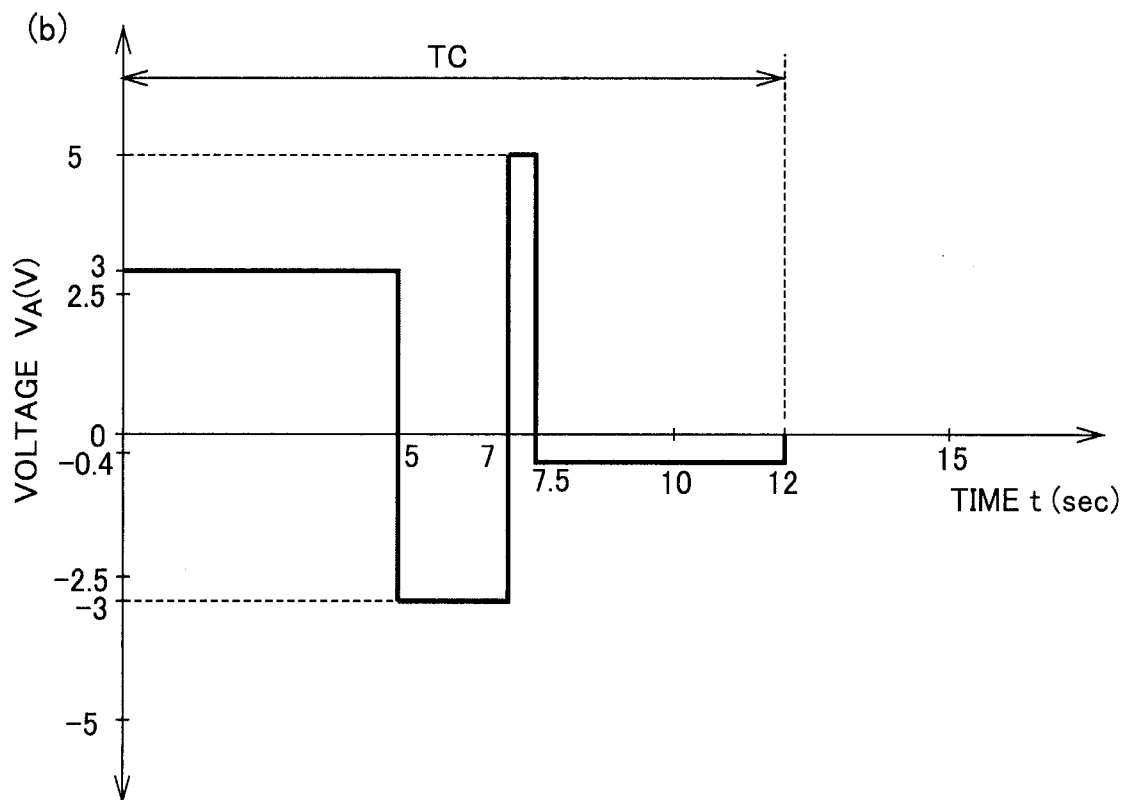
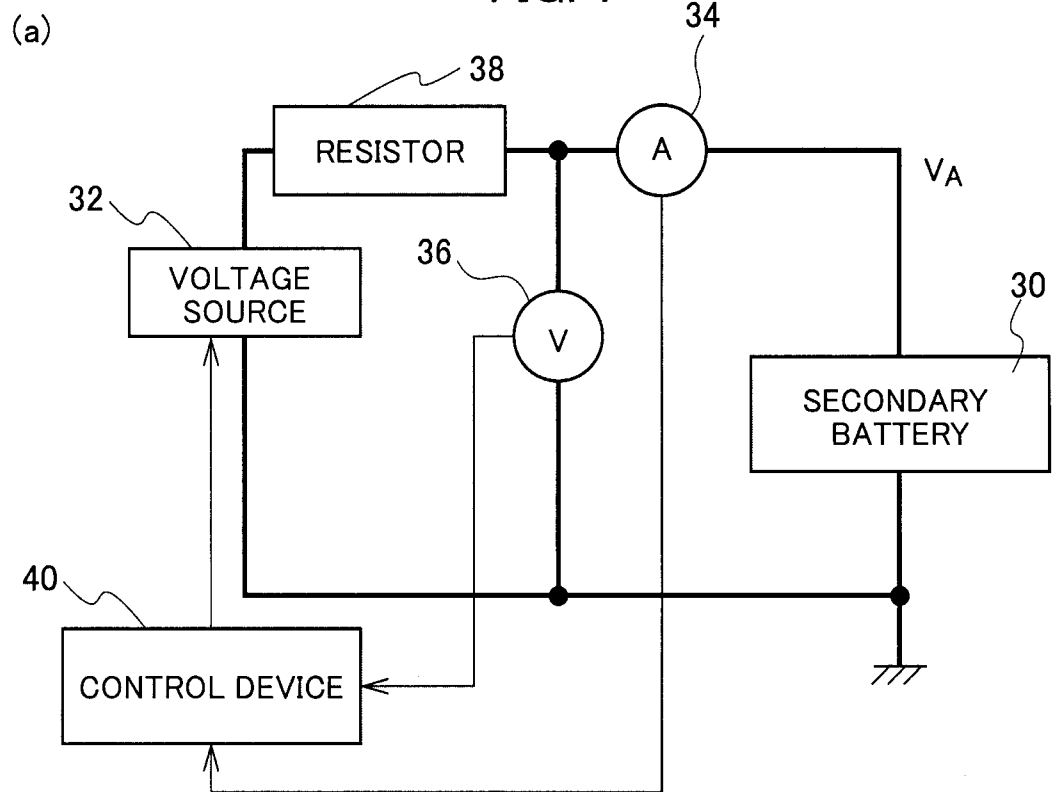


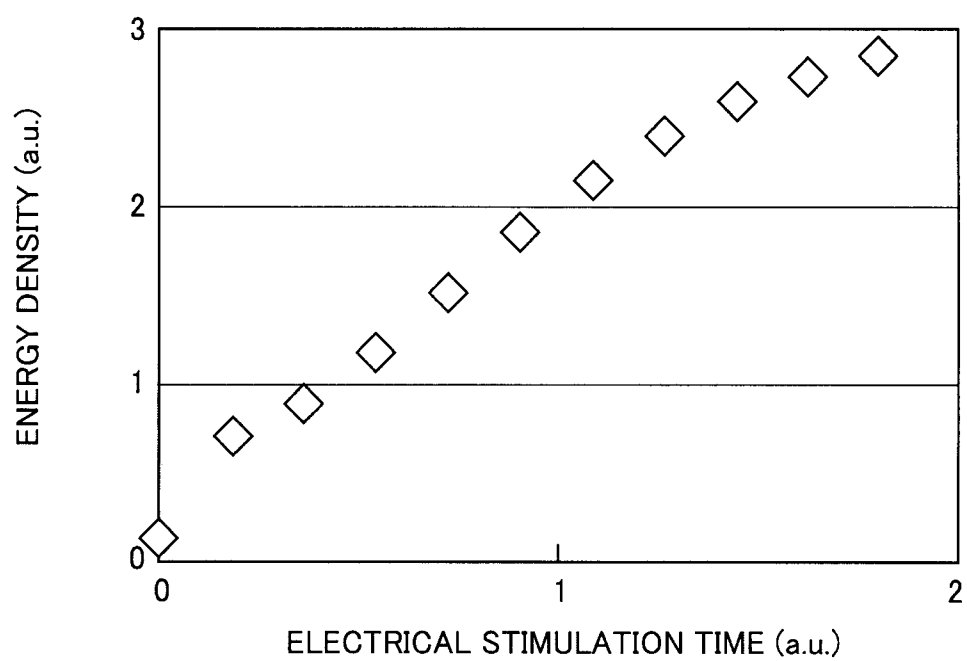
FIG. 6



7/11
FIG. 7

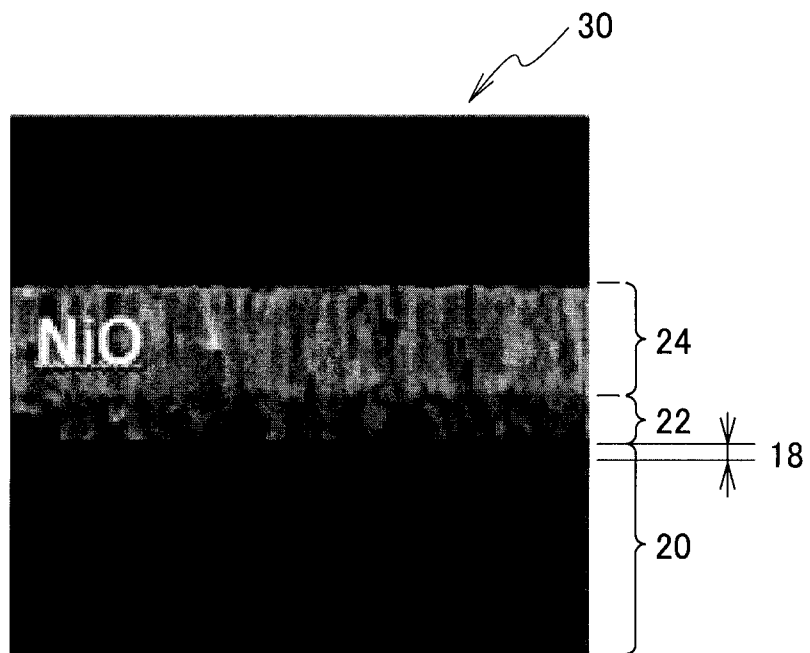
8/11

FIG. 8



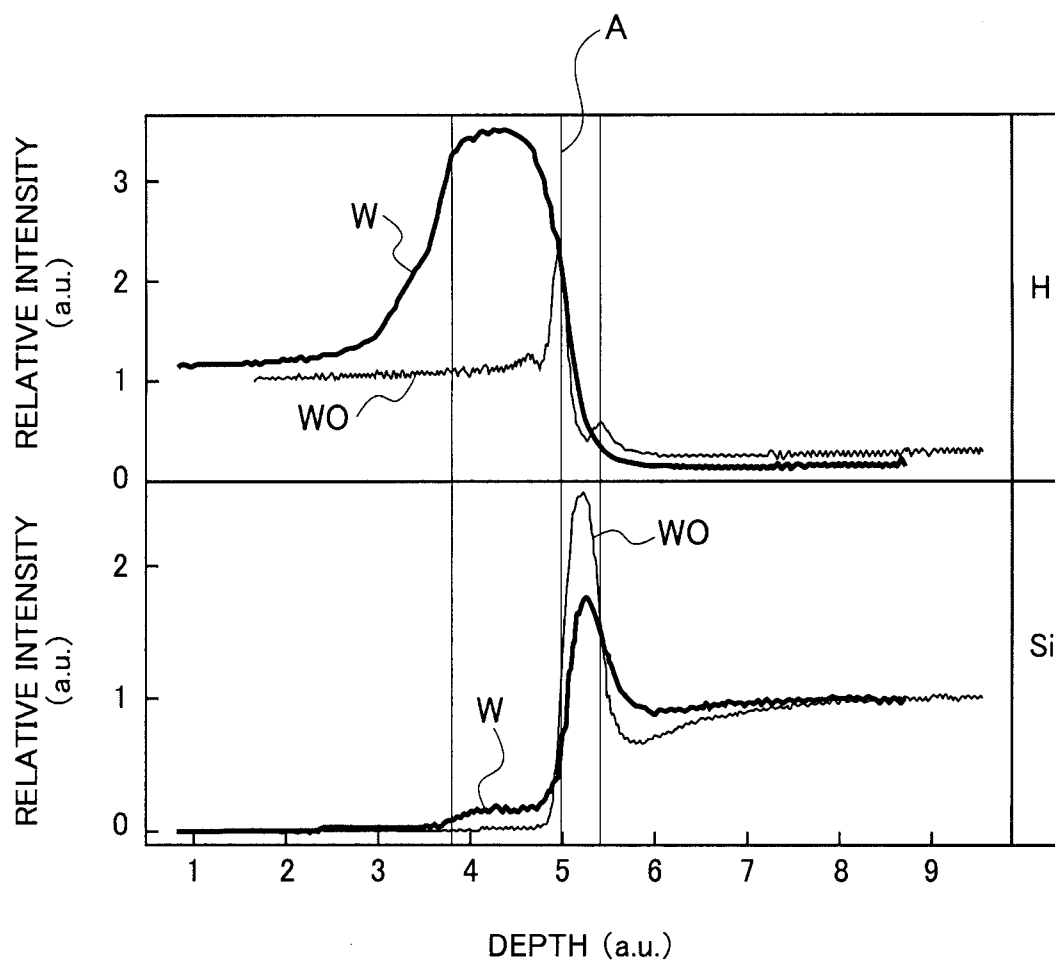
9/11

FIG. 9



10/11

FIG. 10



11/11

FIG. 11

