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(54) **THERMISTOR ELEMENT AND ELECTROMAGNETIC WAVE SENSOR**

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(57) **ABSTRACT**

A thermistor element includes: a thermistor film formed of an oxide having a spinel crystal structure; a first surface-side electrode provided in contact with a first surface of the thermistor film; and a second surface-side electrode provided in contact with a second surface of the thermistor film, wherein the first surface-side electrode includes a first electrode and a second electrode, and at least a part of the first electrode and at least a part of the second electrode are disposed to overlap the second surface-side electrode, and in the thermistor film, an oxygen concentration of a second region between the first electrode and the second electrode in a plan view is higher than that of a first region consisting of a region that overlaps the first electrode and the second surface-side electrode and a region that overlaps the second electrode and the second surface-side electrode.

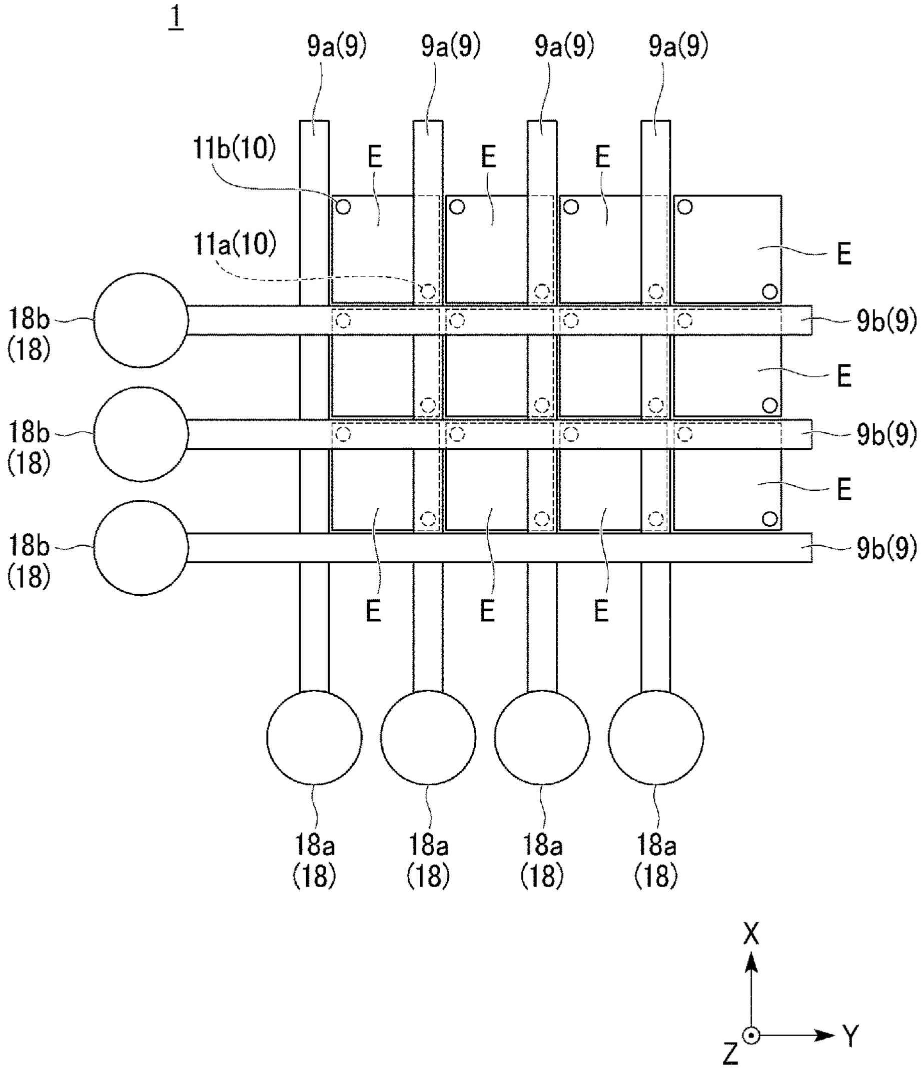
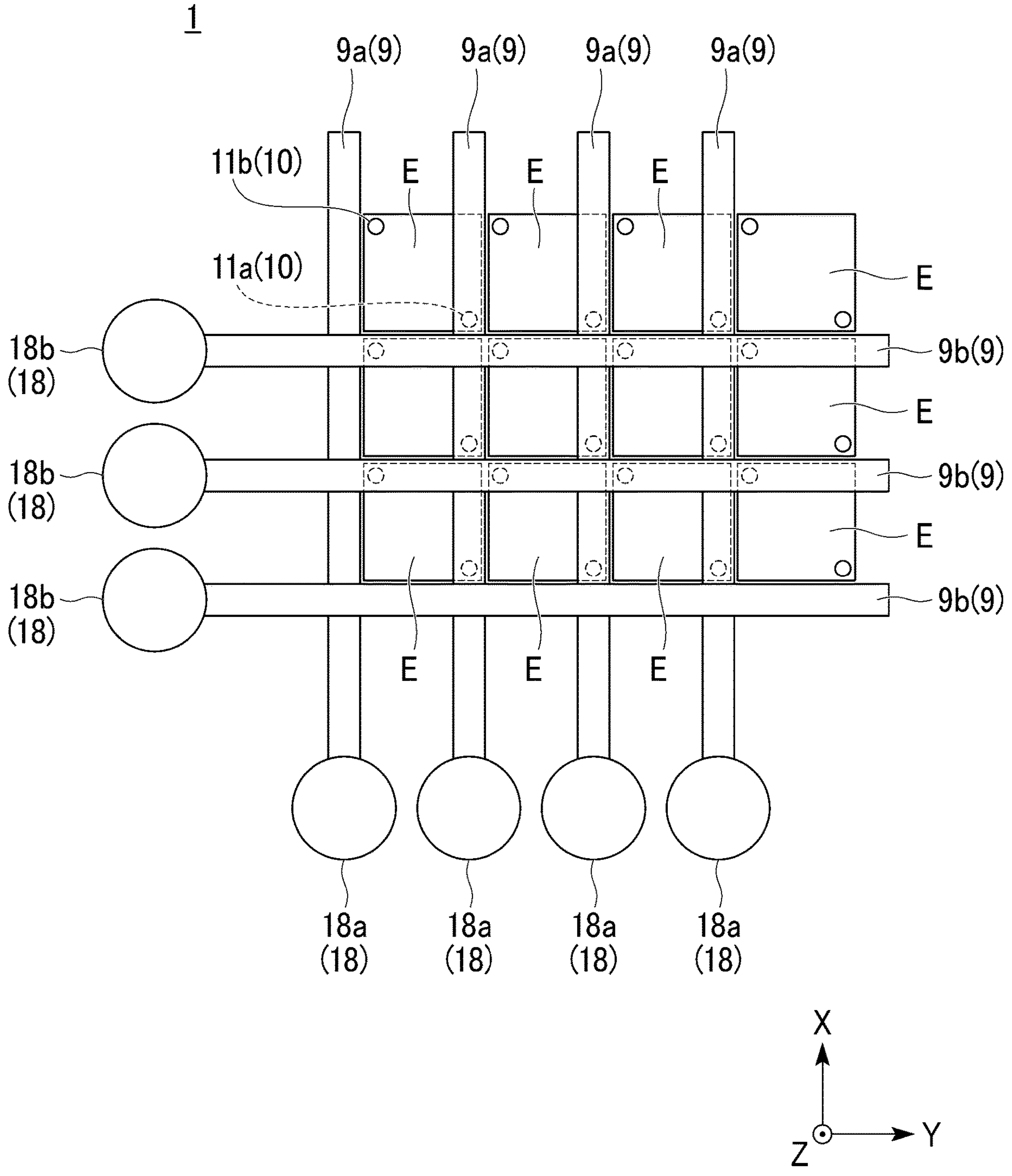


FIG. 1


1
9a(9)
9a(9)
9a(9)
9a(9)
11b(10)
E
E
E
11a(10)
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(18)
9b(9)
E
18b
(18)
9b(9)
E
18b
(18)
9b(9)
E
E
E
18a
(18)
18a
(18)
18a
(18)
18a
(18)
X
Z
Y

FIG. 2

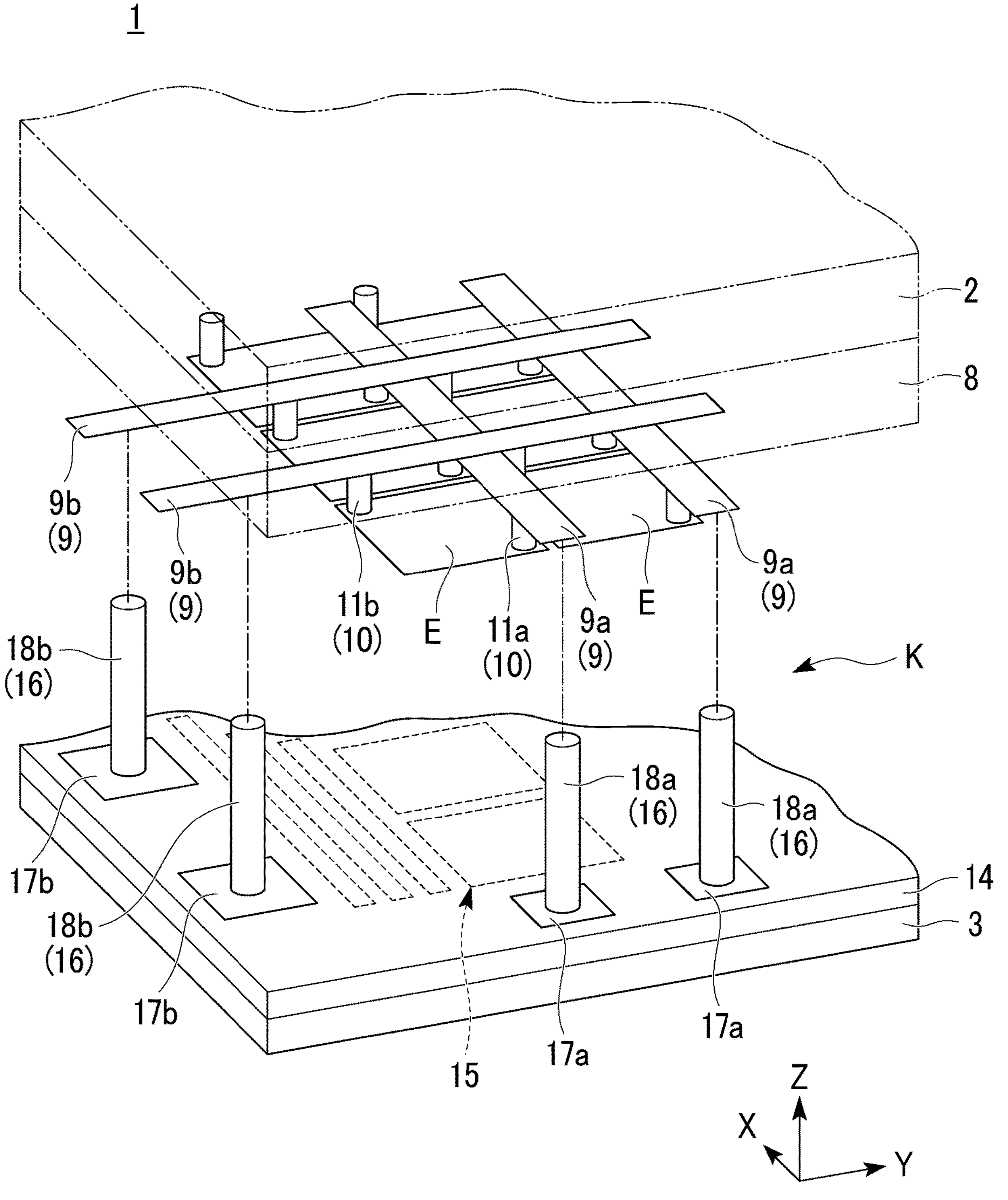

1
2
8
9b
(9)
9b
(9)
11b
(10)
E
11a
(10)
9a
(9)
E
9a
(9)
K
18b
(16)
18a
(16)
18a
(16)
17b
18b
(16)
14
3
17b
15
17a
17a
Z
X
Y

FIG. 3

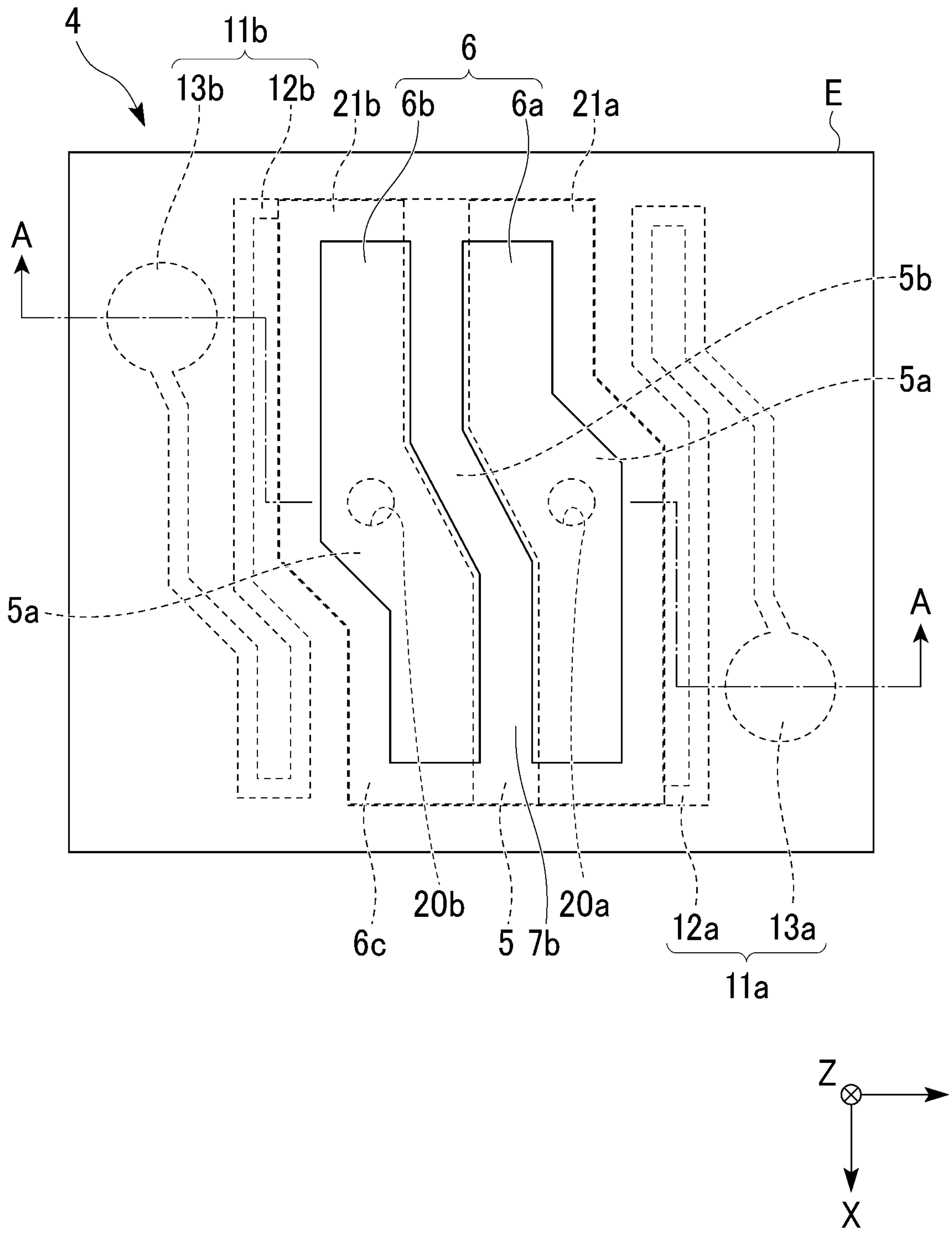

4
11b
13b
12b
6
21b
6b
6a
21a
E
A
5b
5a
5a
A
6c
20b
5
7b
20a
12a
13a
11a
Z
Y
X

FIG. 4

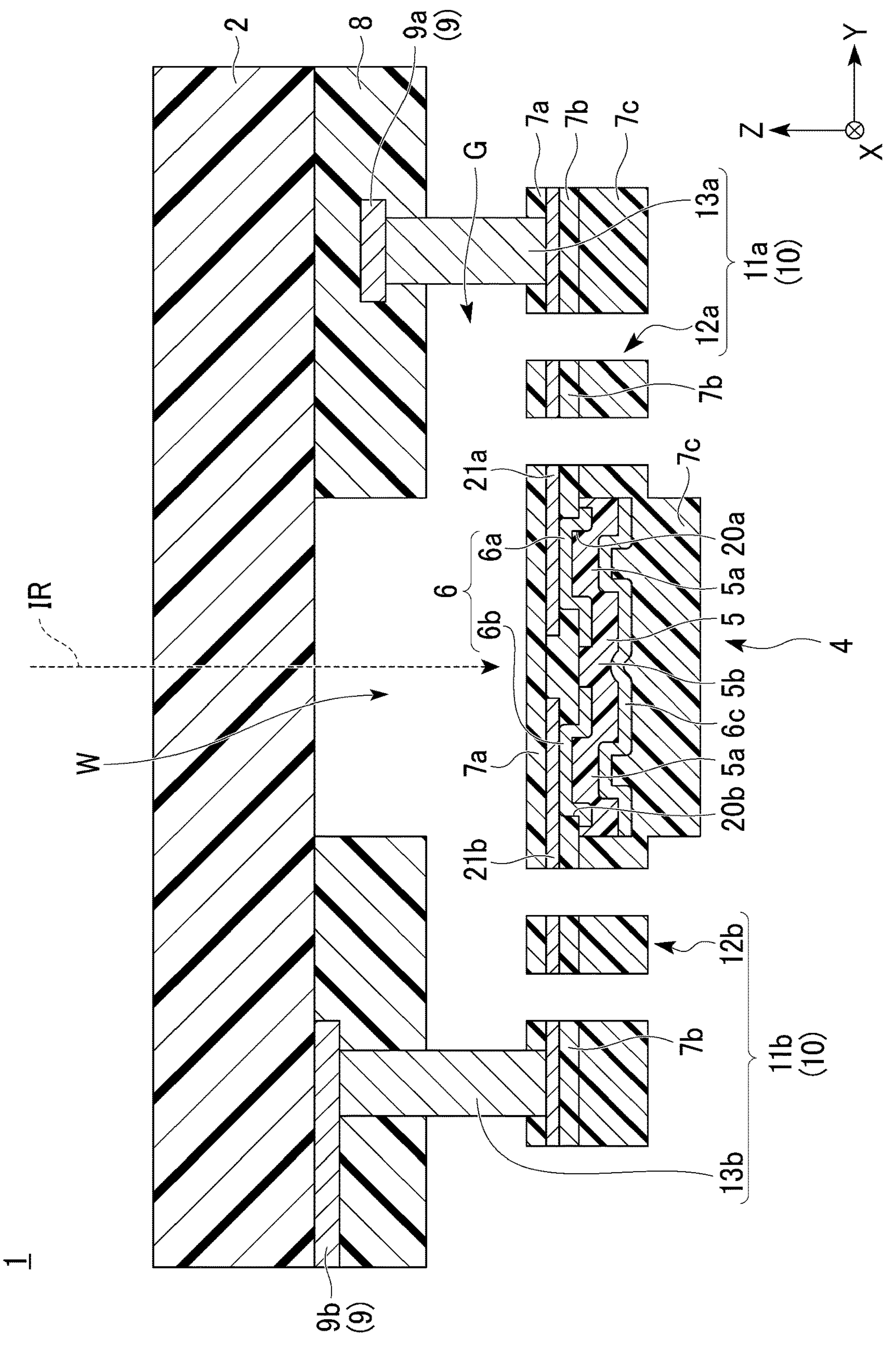

1
2
8
9a
(9)
9b
(9)
G
IR
W
7a
7b
7c
13a
11a
(10)
12a
7b
21a
7c
6a
20a
6
5a
5
4
6b
5b
6c
7a
5a
20b
21b
12b
7b
11b
(10)
13b
Y
Z
X

FIG. 5

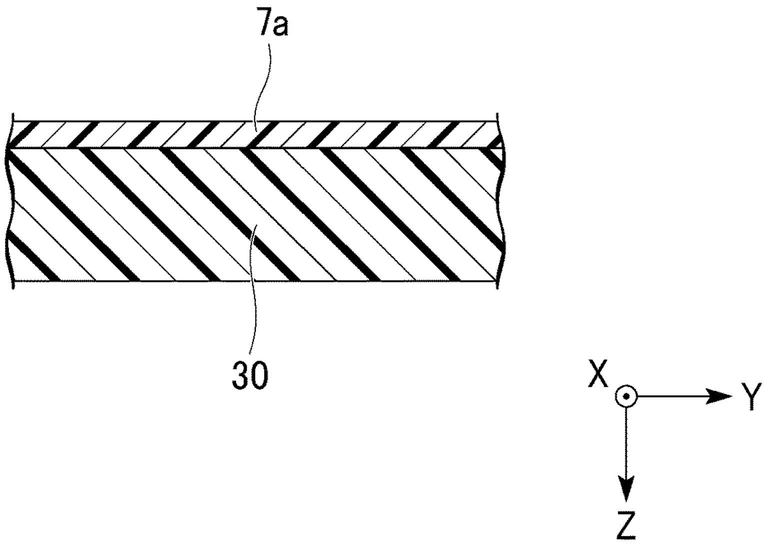


FIG. 6

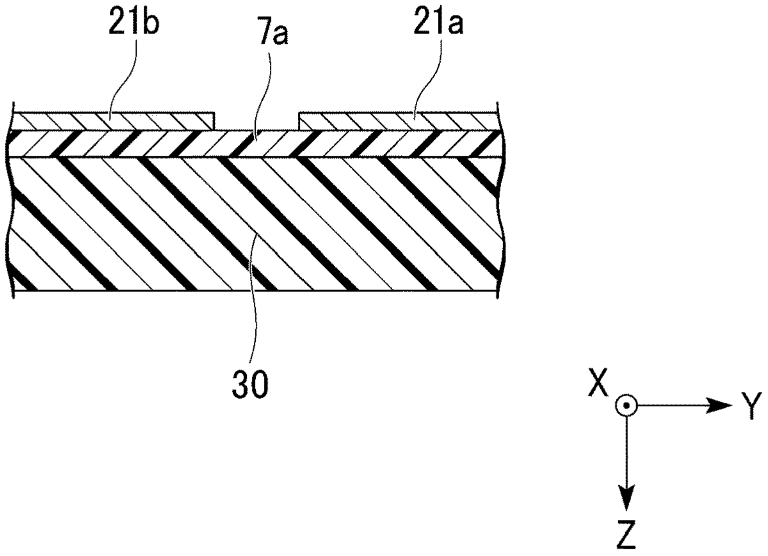


FIG. 7

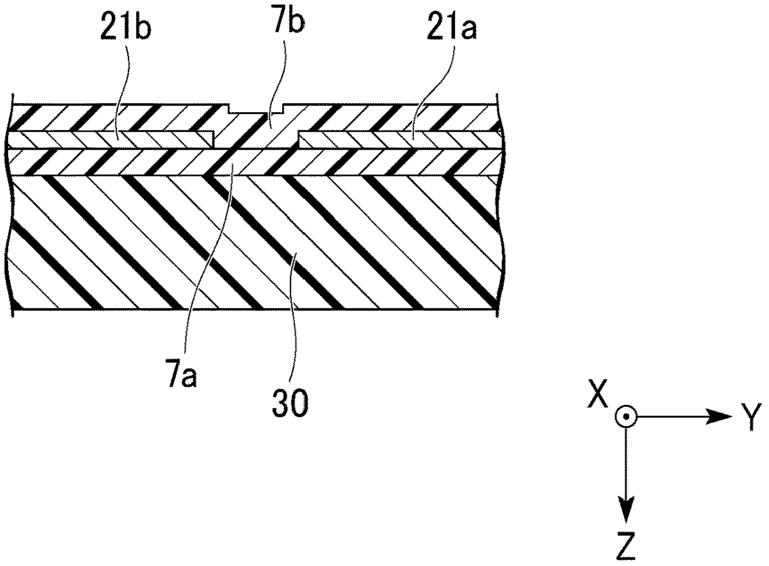


FIG. 8

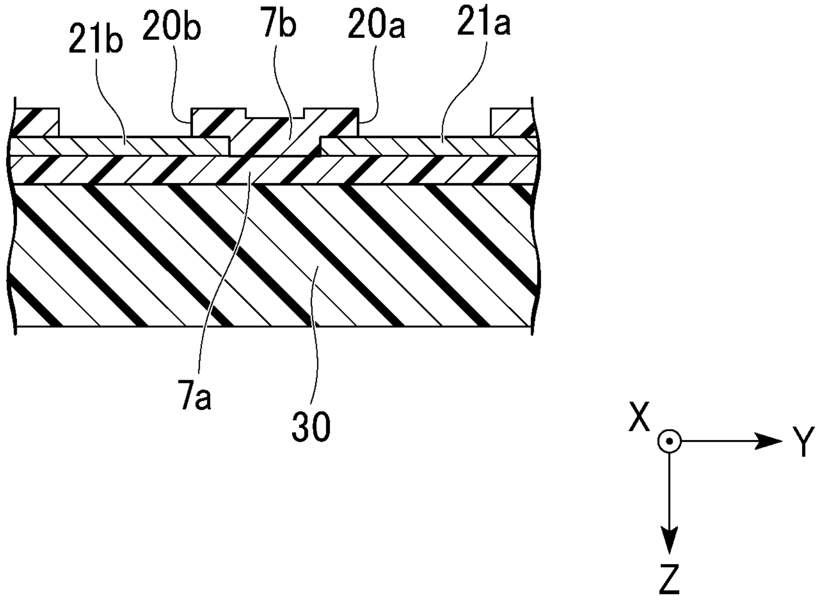

21b
20b
7b
20a
21a
7a
30
X
Y
Z

FIG. 9

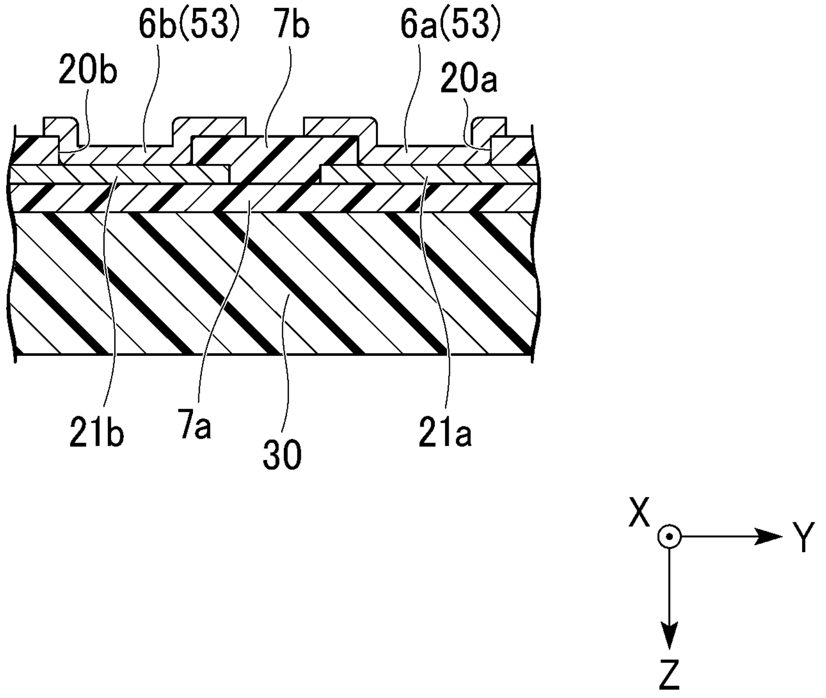

6b(53)
7b
6a(53)
20b
20a
21b
7a
30
21a
X
Y
Z

FIG. 10

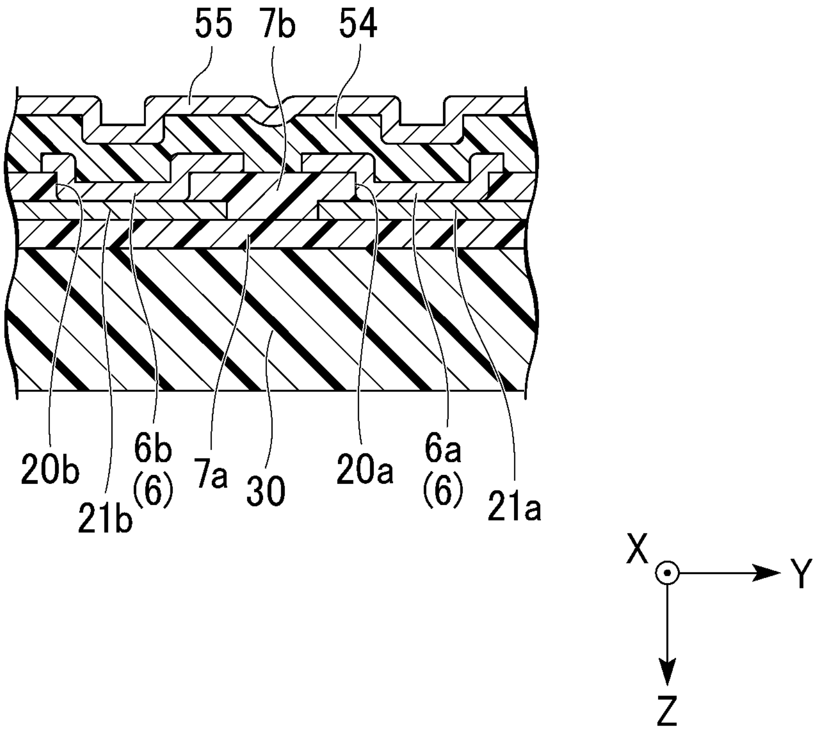

55
7b
54
20b
21b
6b
(6)
7a
30
20a
6a
(6)
21a
X
Y
Z

FIG. 11

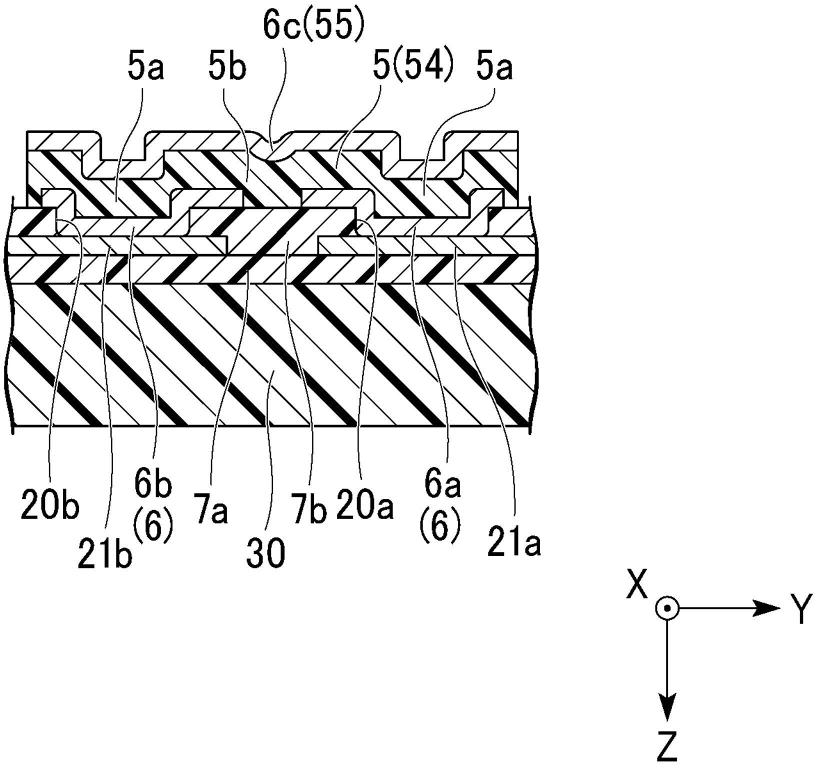

6c(55)
5a
5b
5(54)
5a
20b
21b
6b
(6)
7a
30
7b
20a
6a
(6)
21a
X
Y
Z

FIG. 12

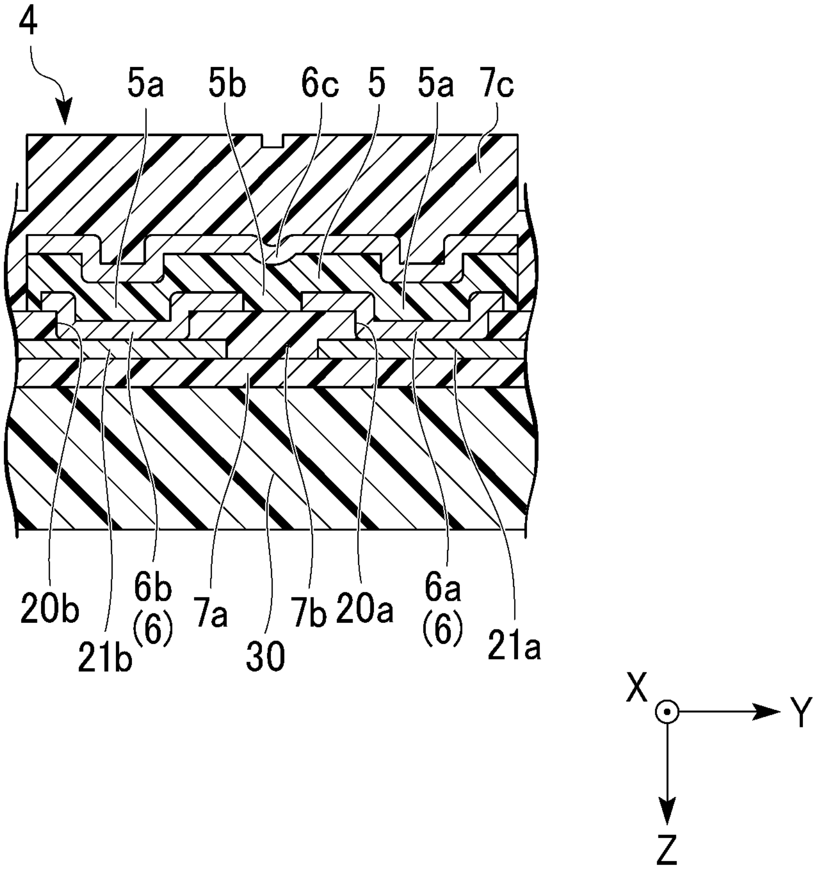


FIG. 13

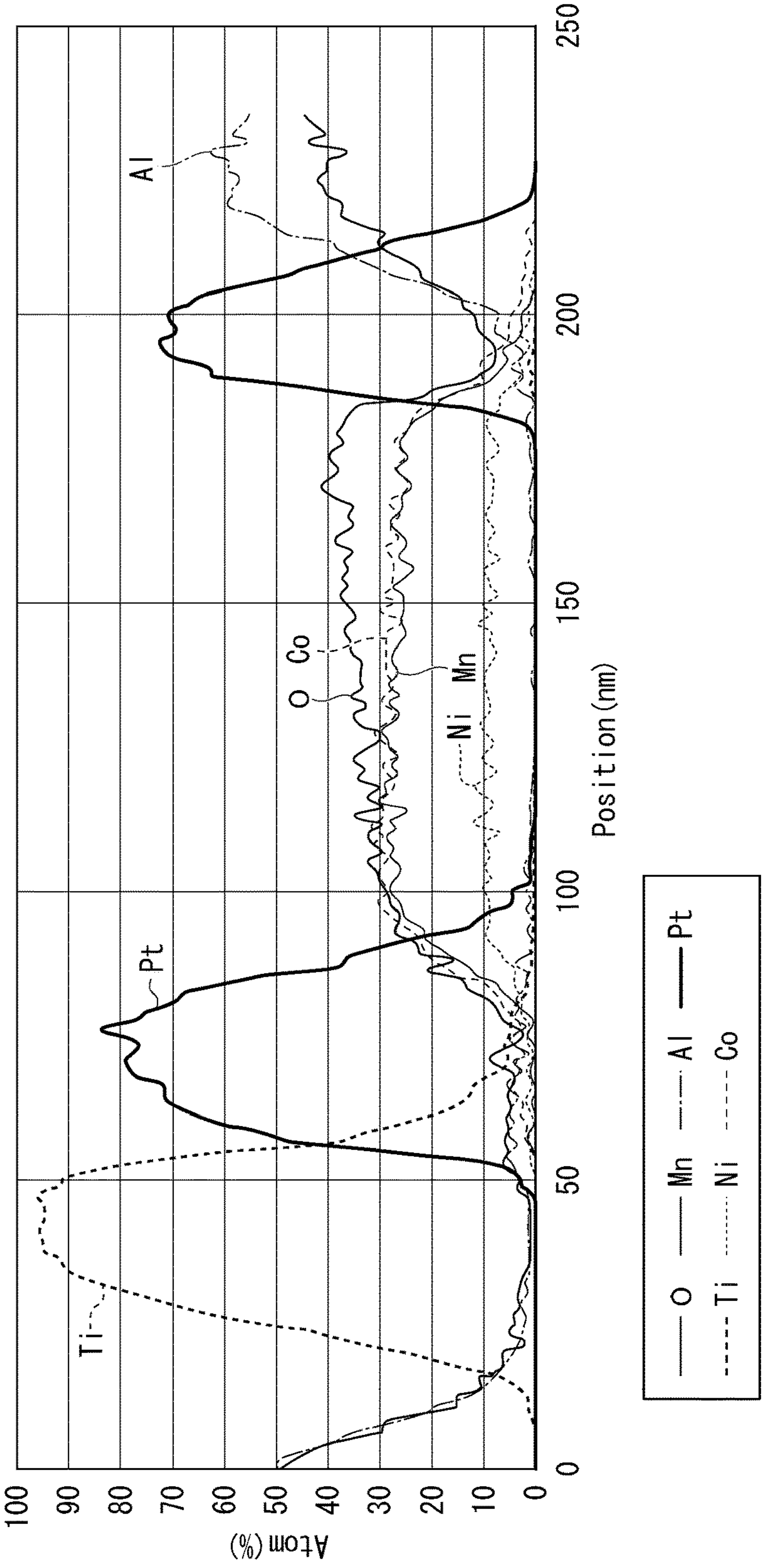
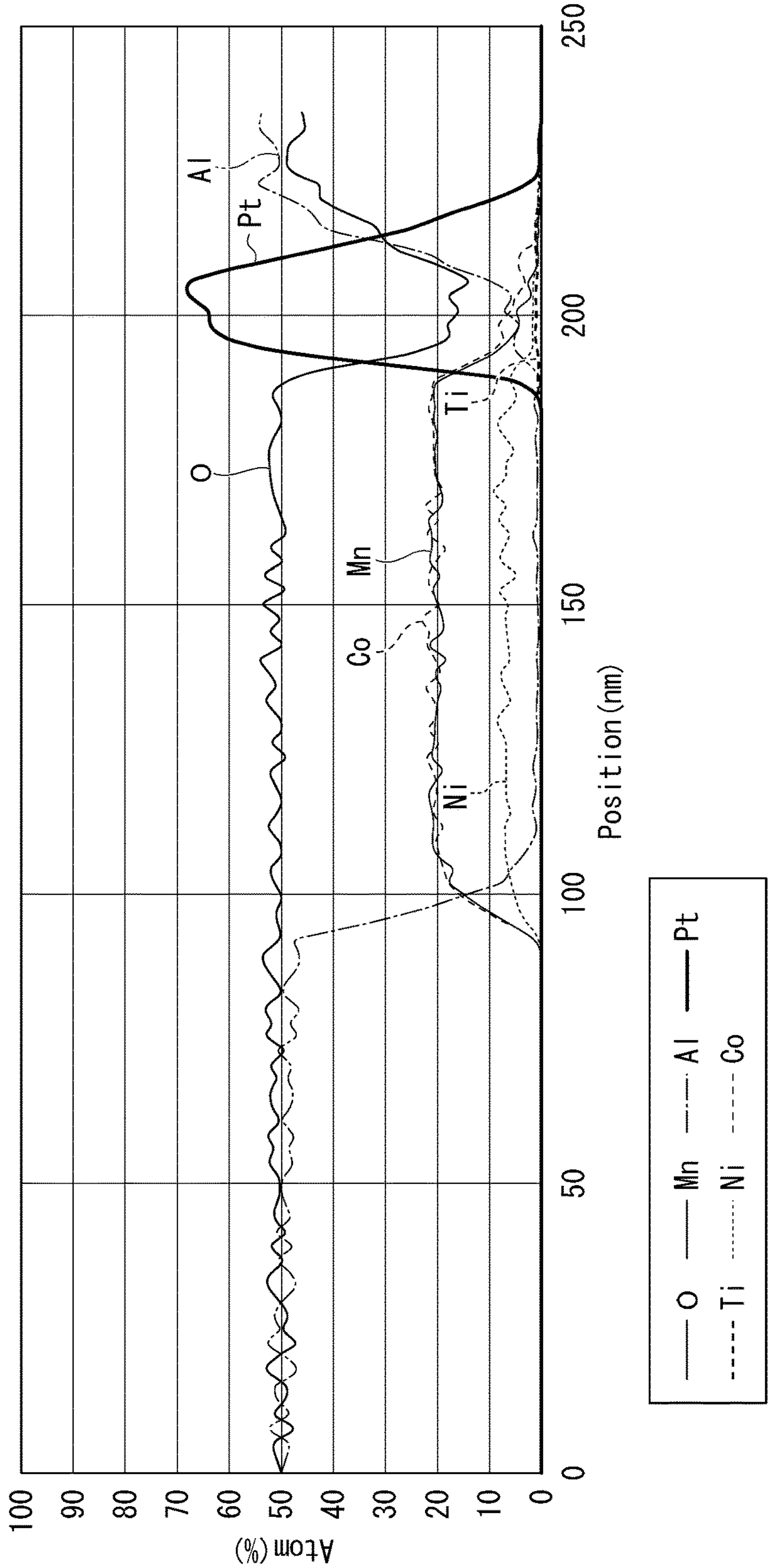

Atom (%)
100
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
250
Position (nm)
Ti
Pt
O
Co
Ni
Mn
Al
O
Mn
Al
Pt
Ti
Ni
Co

FIG. 14


Atom (%)
100
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
250
Position (nm)
O
Mn
Co
Ni
Ti
Pt
Al
O
Mn
Al
Pt
Ti
Ni
Co

THERMISTOR ELEMENT AND ELECTROMAGNETIC WAVE SENSOR

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application relies for priority upon Japanese Patent Application No. 2023-037506 filed on Mar. 10, 2023, the entire contents of which are hereby incorporated herein by reference for all purposes as if fully set forth herein.

BACKGROUND

[0002] The present disclosure relates to a thermistor element and an electromagnetic wave sensor.

[0003] In the related art, there is an electromagnetic wave sensor including electromagnetic wave detection elements such as thermistor elements. In a thermistor element provided in such an electromagnetic wave sensor, since infrared rays incident on the thermistor element are absorbed by a thermistor film or a material near the thermistor film, the temperature of the thermistor film may change and thus electrical resistance of the thermistor film may change.

[0004] An example of such an electromagnetic wave sensor using thermistor elements is described in Patent Document 1. An electromagnetic wave sensor including thermistor elements which are arranged in an array is described in Patent Document 1. In Patent Document 1, a thermistor element including a thermistor film, a pair of first electrodes provided in contact with one surface of the thermistor film, and a second electrode provided in contact with the other surface of the thermistor film is described.

[0005] The thermistor element described in Patent Document 1 has a current-perpendicular-to-plane (CPP) structure in which a current flows in a direction perpendicular to the surface of the thermistor film.

PATENT DOCUMENTS

[0006] [Patent Document 1] Japanese Unexamined Patent Application, First Publication No. 2022-126582

SUMMARY

[0007] However, in the electromagnetic wave sensor according to the related art using thermistor elements having a CPP structure in which a current flows in the direction perpendicular to the surface of the thermistor film, there is need for further improvement in measurement accuracy.

[0008] It is desirable to provide a thermistor element that can provide an electromagnetic wave sensor with high measurement accuracy and an electromagnetic wave sensor including the thermistor element.

[0009] The following means are provided.

[0010] According to an aspect of the present disclosure, there is provided a thermistor element including: a thermistor film formed of an oxide having a spinel crystal structure; a first surface-side electrode provided in contact with a first surface of the thermistor film; and a second surface-side electrode provided in contact with a second surface of the thermistor film, wherein the first surface-side electrode includes a first electrode and a second electrode that is disposed to be separated from the first electrode in a plan view, and at least a part of the first electrode and at least a part of the second electrode are disposed to overlap the second surface-side electrode in a plan view, and an oxygen concentration of a second region located between the first electrode and the second electrode in the thermistor film is higher than an oxygen concentration of a first region consisting of a region that overlaps the first electrode and the second surface-side electrode in a plan view and a region that overlaps the second electrode and the second surface-side electrode in a plan view.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG. **1** is a plan view illustrating a configuration of an electromagnetic wave sensor according to an embodiment of the present disclosure.

[0012] FIG. **2** is an exploded perspective view illustrating the configuration of the electromagnetic wave sensor illustrated in FIG. **1**.

[0013] FIG. **3** is a partially enlarged plan view of the electromagnetic wave sensor illustrated in FIG. **1** and a plan view of a layer in which a first surface-side electrode of a thermistor element is provided.

[0014] FIG. **4** is a partially enlarged sectional view of the electromagnetic wave sensor illustrated in FIG. **1** and a sectional view along line A-A in FIG. **3**.

[0015] FIG. **5** is a sectional view sequentially illustrating a process of manufacturing a thermistor element provided in the electromagnetic wave sensor illustrated in FIG. **1**.

[0016] FIG. **6** is a sectional view sequentially illustrating a process of manufacturing the thermistor element provided in the electromagnetic wave sensor illustrated in FIG. **1**.

[0017] FIG. **7** is a sectional view sequentially illustrating a process of manufacturing the thermistor element provided in the electromagnetic wave sensor illustrated in FIG. **1**.

[0018] FIG. **8** is a sectional view sequentially illustrating a process of manufacturing the thermistor element provided in the electromagnetic wave sensor illustrated in FIG. **1**.

[0019] FIG. **9** is a sectional view sequentially illustrating a process of manufacturing the thermistor element provided in the electromagnetic wave sensor illustrated in FIG. **1**.

[0020] FIG. **10** is a sectional view sequentially illustrating a process of manufacturing the thermistor element provided in the electromagnetic wave sensor illustrated in FIG. **1**.

[0021] FIG. **11** is a sectional view sequentially illustrating a process of manufacturing the thermistor element provided in the electromagnetic wave sensor illustrated in FIG. **1**.

[0022] FIG. **12** is a sectional view sequentially illustrating a process of manufacturing the thermistor element provided in the electromagnetic wave sensor illustrated in FIG. **1**.

[0023] FIG. **13** is a graph illustrating a relationship between a position in a thickness direction of a cross-section including a first region **5***a* of a thermistor element **4** according to Example 1 and element concentrations.

[0024] FIG. **14** is a graph illustrating a relationship between a position in the thickness direction of a cross-section including a second region **5***b* of the thermistor element **4** according to Example 1 and element concentrations.

DETAILED DESCRIPTION

[0025] In order to achieve the aforementioned objective, the inventor earnestly studied a thermistor element including a first electrode and a second electrode provided in contact with a first surface of a thermistor film and provided to be apart from each other and a second surface-side electrode provided in contact with a second surface of the thermistor film such that measurement accuracy of an electromagnetic wave sensor including the thermistor element is improved.

[0026] As a result, the inventor found that a current component flowing in an in-plane direction of the thermistor film between the first electrode and the second electrode via the thermistor film is one factor that decreases measurement accuracy of the electromagnetic wave sensor including the thermistor element.

[0027] Therefore, the inventor studied with a focus on electrical resistance and materials of the thermistor film. As a result, the inventor found that a thermistor film of a thermistor element should be formed of an oxide having a spinel crystal structure and an oxygen concentration in a second region located between the first electrode and the second electrode in a plan view should be higher than in a first region consisting of a region that overlaps the first electrode and the second surface-side electrode in a plan view and a region that overlaps the second electrode and the second surface-side electrode in a plan view, and made the present disclosure.

[0028] In such a thermistor element, it is estimated that electric resistivity of the thermistor film is higher in the second region than in the first region and a current does not easily flow in an in-plane direction of the thermistor film between the first electrode and the second electrode. As a result, with an electromagnetic wave sensor including such thermistor elements, it is estimated that a decrease in measurement accuracy due to a current component flowing in the in-plane direction of the thermistor film between the first electrode and the second electrode is curbed and measurement accuracy is high.

[0029] The present disclosure includes the following configurations.

[0030] [1] A thermistor element including:

- **[0031]** a thermistor film formed of an oxide having a spinel crystal structure;
- **[0032]** a first surface-side electrode provided in contact with a first surface of the thermistor film; and
- **[0033]** a second surface-side electrode provided in contact with a second surface of the thermistor film,
- **[0034]** wherein the first surface-side electrode includes a first electrode and a second electrode that is disposed to be separated from the first electrode in a plan view, and at least a part of the first electrode and at least a part of the second electrode are disposed to overlap the second surface-side electrode in a plan view, and
- **[0035]** wherein an oxygen concentration of a second region located between the first electrode and the second electrode in a plan view in the thermistor film is higher than an oxygen concentration of a first region consisting of a region that overlaps the first electrode and the second surface-side electrode in a plan view and a region that overlaps the second electrode and the second surface-side electrode in a plan view.

[0036] [2] An electromagnetic wave sensor including the thermistor element according to [1].

[0037] The thermistor element according to the present disclosure is formed of an oxide having a spinel crystal structure and includes a thermistor film in which the oxygen concentration in the second region located between the first electrode and the second electrode in a plan view is higher than the oxygen concentration of the first region consisting of a region that overlaps the first electrode and the second surface-side electrode in a plan view and a region that overlaps the second electrode and the second surface-side electrode in a plan view. Accordingly, in the thermistor element according to the present disclosure, a current does not easily flow in an in-plane direction in the second region of the thermistor film. As a result, in the electromagnetic wave sensor including the thermistor element according to the present disclosure, a decrease in measurement accuracy due to a current component flowing in the in-plane direction in the thermistor film of the thermistor element is curbed, and measurement accuracy is enhanced.

[0038] Hereinafter a thermistor element and an electromagnetic wave sensor according to an embodiment will be described in detail with reference to the accompanying drawings. In the drawings mentioned in the following description, for the purpose of convenience, feature parts may be enlarged so that features of the present disclosure can be easily understood. Accordingly, dimensions, ratios, and the like of constituents may be different from real ones. Materials, dimensions, and the like described in the following description are merely examples, and the present disclosure is not limited thereto but can be appropriately modified without departing from the gist thereof.

[Electromagnetic Wave Sensor]

[0039] An electromagnetic wave sensor according to this embodiment detects electromagnetic waves which are radiated from a measurement target. Examples of electromagnetic waves detected by the electromagnetic wave sensor according to this embodiment include infrared rays and terahertz waves. Specifically, the electromagnetic wave sensor according to this embodiment may detect, for example, infrared rays of which a wavelength is equal to or greater than 0.75 μm and equal to or less than 1000 μm (hereinafter also referred to as "infrared rays IR"). The infrared rays IR may be far-infrared rays, mid-infrared rays, or near-infrared rays. The infrared rays IR may be long-wavelength infrared rays of which a wavelength ranges from 8 μm to 14 μm. The electromagnetic wave sensor according to this embodiment may detect, for example, terahertz waves of which a wavelength is equal to or greater than 30 μm and equal to or less than 3 mm.

[0040] Hereinafter, an electromagnetic wave sensor detecting infrared rays IR radiated from a measurement target will be described as an example of the electromagnetic wave sensor according to this embodiment. The electromagnetic wave sensor according to this embodiment may be an infrared imaging device (an infrared image sensor) that detects infrared rays IR radiated from a measurement target and two-dimensionally detects (images) a temperature distribution of the measurement target. The infrared image sensor may be used for an infrared camera for indoor and/or outdoor dark vision or the like. The infrared image sensor may be used as a non-contact type temperature sensor for measuring the temperature of a person or an object, or the like.

[0041] FIG. **1** is a plan view illustrating a configuration of an electromagnetic wave sensor according to an embodiment of the present disclosure. FIG. **2** is an exploded perspective view illustrating the configuration of the electromagnetic wave sensor illustrated in FIG. **1**. FIG. **3** is a partially enlarged plan view of the electromagnetic wave sensor illustrated in FIG. **1** and a plan view of a layer in which a first surface-side electrode of a thermistor element is provided. FIG. **4** is a partially enlarged sectional view of the electromagnetic wave sensor illustrated in FIG. **1** and a sectional view along line A-A in FIG. **3**. FIGS. **5** to **12** are sectional views sequentially illustrating processes of manufacturing a thermistor element provided in the electromagnetic wave sensor illustrated in FIG. **1**.

[0042] In FIGS. **1** to **12**, an XYZ orthogonal coordinate system is set. In FIGS. **1** to **12**, an X-axis direction is defined as a first direction X in a specific plane of the electromagnetic wave sensor, a Y-axis direction is defined as a second direction Y perpendicular to the first direction X in the specific plane of the electromagnetic wave sensor, and a Z-axis direction is defined as a third direction Z perpendicular to the specific plane of the electromagnetic wave sensor.

[0043] As illustrated in FIG. **2**, the electromagnetic wave sensor **1** according to this embodiment includes a first substrate **2** and a second substrate **3** that are disposed to face each other and the thermistor elements **4** that are disposed between the first substrate **2** and the second substrate **3**. A single thermistor element **4** is provided for each region E. The regions E are regions which are defined by the first lead wires **9***a* and the second lead wires **9***b* in a plan view as illustrated in FIGS. **1** and **2**.

[0044] As illustrated in FIG. **2**, the first substrate **2** and the second substrate **3** form a closed internal space K therebetween by sealing the surroundings of the opposite surfaces with a sealing material (not illustrated). The internal space K is decompressed in a high vacuum. Accordingly, in the electromagnetic wave sensor **1** according to this embodiment, an influence of heat due to convection in the internal space K is curbed, and an influence of heat other than infrared rays IR radiated from a measurement target to the thermistor element **4** is excluded.

[0045] The electromagnetic wave sensor **1** according to this embodiment is not limited to the configuration including the closed and decompressed internal space K. The electromagnetic wave sensor **1** according to this embodiment may have a configuration including a closed internal space K with atmospheric pressure or may have a configuration including an open internal space K.

[0046] The first substrate **2** and the second substrate **3** are formed of substrates which are transparent to electromagnetic waves of a specific wavelength. For example, when the electromagnetic waves of a specific wavelength are infrared rays IR, for example, silicon substrates can be used as the first substrate **2** and the second substrate **3**, or germanium substrates or the like may be used.

[0047] The thermistor elements **4** provided in the electromagnetic wave sensor **1** have the same size. As illustrated in FIGS. **1** and **2**, the thermistor elements **4** are arranged in an array in a plane parallel to the first substrate **2** and the second substrate **3** (hereinafter referred to as a "specific plane").

[0048] The thermistor elements **4** are provided for the regions E illustrated in FIGS. **1** and **2**, and thus the thermistor elements **4** are arranged in a matrix shape in the first direction X and the second direction Y crossing each other (perpendicular to each other in this embodiment) in the specific plane. The thermistor elements **4** are arranged at constant intervals in the first direction X and are arranged at constant intervals in the second direction Y, where the first direction X is a row direction and the second direction Y is a column direction.

[0049] The numbers of rows and columns of the thermistor elements **4** (that is, the numbers of rows and columns of the regions E) may be, for example, 640 rows×480 columns or 1024 rows×768 columns. The numbers of rows and columns of the thermistor elements **4** are not limited thereto and can be appropriately changed.

[Thermistor Element]

[0050] As illustrated in FIG. **4**, each thermistor element **4** includes a thermistor film **5** serving as a temperature detecting element, a first surface-side electrode **6** provided in contact with one surface (a first surface) of the thermistor film **5**, and a second surface-side electrode **6***c* provided in contact with the other surface (a second surface) of the thermistor film **5**.

[0051] The first surface-side electrode **6** is a pair of electrodes including a first electrode **6***a* and a second electrode **6***b*. As illustrated in FIGS. **3** and **4**, the first electrode **6***a* and the second electrode **6***b* are separated from each other in a plan view. As illustrated in FIGS. **3** and **4**, at least a part (the whole part in this embodiment) of the first electrode **6***a* and at least part (the whole part in this embodiment) of the second electrode **6***b* are disposed to overlap the second surface-side electrode **6***c* and the thermistor film **5** in a plan view. The first electrode **6***a* and the second electrode **6***b* in this embodiment have the substantially same shape.

[0052] The second surface-side electrode **6***c* in this embodiment can be formed, for example, in the same shape as the thermistor film **5** in a plan view as illustrated in FIGS. **3** and **4**.

[0053] As illustrated in FIG. **4**, each thermistor element **4** provided in the electromagnetic wave sensor **1** according to this embodiment has a current-perpendicular-to-plane (CPP) structure in which the first surface-side electrode **6** (the first electrode **6***a* and the second electrode **6***b*) and the second surface-side electrode **6***c* are provided with the thermistor film **5** interposed therebetween and a current flows in a direction perpendicular to the surface of the thermistor film **5**. The thermistor element **4** can cause a current to flow in the direction perpendicular to the surface of the thermistor film **5** from the first electrode **6***a* of the first surface-side electrode **6** to the second surface-side electrode **6***c* and cause a current to flow in the direction perpendicular to the surface of the thermistor film **5** from the second surface-side electrode **6***c* to the second electrode **6***b*.

[0054] As illustrated in FIG. **4**, wiring layers **21***a* and **21***b* are in contact with the sides of the first electrode **6***a* and the second electrode **6***b* of the first surface-side electrode **6** opposite to the thermistor film **5**. In this embodiment, parts of the first electrode **6***a* and the second electrode **6***b* not in contact with the thermistor film **5** and the wiring layers **21***a* and **21***b* are covered by a second insulating film **7***b* (an insulating film). The second insulating film **7***b* is also provided between the first electrode **6***a* and the second electrode **6***b* of the first surface-side electrode **6** in a plan view as illustrated in FIGS. **3** and **4**. Accordingly, the second insulating film **7***b* is in contact with a part of one surface (the first surface) of the thermistor film **5** not in contact with the first surface-side electrode **6** (the first electrode **6***a* and the second electrode **6***b*).

[0055] In the second insulating film **7***b* according to this embodiment, as illustrated in FIGS. **3** and **4**, circular openings **20***a* and **20***b* penetrating the second insulating film **7***b* are provided at positions overlapping a substantially central part of the first electrode **6***a* and a substantially central part of the second electrode **6***b* in a plan view. As illustrated in FIGS. **3** and **4**, the first electrode **6***a* and the second electrode

6*b* are continuously formed in parts located in regions overlapping the openings **20***a* and **20***b* in a plan view and parts located in a region other than the regions overlapping the openings **20***a* and **20***b* in a plan view. Accordingly, each of the first electrode **6***a* and the second electrode **6***b* has a shape including a protruded/recessed portion in which the thermistor film **5** side is recessed and the wiring layers **21***a* and **21***b* side is protruded. As a result, in comparison with a case in which the protruded/recessed portion is not provided, a contact area of the first electrode **6***a* and the second electrode **6***b* with the thermistor film **5** is larger.

[0056] In this embodiment, as illustrated in FIGS. **3** and **4**, the whole surfaces of the first electrode **6***a* and the second electrode **6***b* on the thermistor film **5** side are in contact with one surface of the thermistor film **5**, and the whole surface of the second surface-side electrode **6***c* on the thermistor film **5** side is in contact with the other surface of the thermistor film **5**. Accordingly, the thermistor film **5** and the second surface-side electrode **6***c* include two protruded/recessed portions corresponding to the shape inside of the protruded/recessed portions of the first electrode **6***a* and the second electrode **6***b* as illustrated in FIG. **4**.

[0057] As illustrated in FIG. **4**, an insulating film **7***a* is disposed on the side of the wiring layers **21***a* and **21***b* and the second insulating film **7***b* opposite to the thermistor film **5** to cover the wiring layers **21***a* and **21***b* and the second insulating film **7***b*.

[0058] On the side of the second surface-side electrode **6***c* opposite to the thermistor film **5**, a third insulating film **7***c* is provided in contact with the second surface-side electrode **6***c*. In this embodiment, as illustrated in FIG. **4**, the third insulating film **7***c* covers the side surfaces of the second surface-side electrode **6***c* and the thermistor film **5** and is in contact with the surface of the second insulating film **7***b* on the thermistor film **5** side.

[0059] The thermistor film **5** is formed of an oxide having a spinel crystal structure, and an oxygen concentration of a second region **5***b* located between the first electrode **6***a* and the second electrode **6***b* in a plan view is higher than the oxygen concentration of a first region **5***a* consisting of a region that overlaps the first electrode **6***a* and the second surface-side electrode **6***c* in a plan view and a region that overlaps the second electrode **6***b* and the second surface-side electrode **6***c* in a plan view.

[0060] The oxygen concentration of the second region **5***b* is higher than one time the oxygen concentration of the first region **5***a*, may be equal to or higher than 1.2 times, and may be equal to or higher than 1.5 times. As an oxygen concentration ratio between the second region **5***b* and the first region **5***a* of the thermistor film **5** increases, a difference in electric resistivity between the first region **5***a* and the second region **5***b* increases, a current flows more easily in the direction perpendicular to the surface in the first region **5***a*, and a current flows less easily in the in-plane direction in the second region **5***b*. As a result, a decrease in measurement accuracy due to a current component flowing in the in-plane direction in the thermistor film **5** is curbed, and the measurement accuracy is enhanced.

[0061] Since the thermistor element can be efficiently manufactured using a manufacturing method which will be described later, the oxygen concentration of the second region **5***b* may be equal to or lower than two times the oxygen concentration of the first region **5***a* and may be equal to or lower than 1.8 times.

[0062] The oxygen concentration of the first region **5***a* may be substantially uniform in the thickness direction. In this embodiment, when the thermistor film **5** is divided into three regions including a region close to one surface (the first surface), a region close to the other surface (the second surface), and a region including a central part in the thickness direction in the thickness direction, the oxygen concentration of the second region **5***b* is higher than the oxygen concentration of the first region **5***a* in any of the three regions. Accordingly, a current flows more easily in the direction perpendicular to the surface in the first region **5***a* and a current flows less easily in the in-plane direction in the second region **5***b*.

[0063] The thermistor film **5** is formed of an oxide having a spinel crystal structure. When heat treatment at 250° C. or higher in the atmospheric air is performed on a film formed of an oxide having a spinel crystal structure after an insulating film formed of an oxide has been disposed in contact therewith, oxygen can diffuse from the insulating film to increase the oxygen concentration in the oxide having a spinel crystal structure.

[0064] In the oxide having a spinel crystal structure, for example, a base metal element including cobalt (Co) and manganese (Mn) or a base metal element including nickel (Ni) and manganese (Mn) may be located in at least a part of one or both of site A and site B of the spinel crystal structure. Such a base metal element can be located in any of site A and site B of the spinel crystal structure expressed by Formula AB_2O_4.

[0065] The oxide having a spinel crystal structure may include, for example, at least one additive element selected from transition metal elements such as cobalt (Co), nickel (Ni), copper (Cu), iron (Fe), zirconium (Zr)m, titanium (Ti), vanadium (V), chromium (Cr), scandium (Sc), Yttrium (Y), niobium (Nb), and molybdenum (Mo), aluminum (Al), and zinc (Zn) in addition to the base metal element. The additive element may include at least one selected from aluminum (Al), cobalt (Co), nickel (Ni), copper (Cu), iron (Fe), and zirconium (Zr). The additive element can be positioned in any of site A and site B of the spinel crystal structure expressed by formula AB_2O_4. The additive element may be substitutionally dissolved in one or both of site A and site B of the spinel crystal structure or may be positioned in a site other than site A and site B without being substitutionally dissolved in site A and site B.

[0066] In this embodiment, the thickness of the thermistor film **5** may range from 80 nm to 300 nm and may range from 100 nm to 200 nm.

[0067] The first electrode **6***a* and the second electrode **6***b* of the first surface-side electrode **6** and the second surface-side electrode **6***c* are both formed of a conductive film. When the thermistor element **4** is manufactured using a manufacturing method which will be described later, the first electrode **6***a* and the second electrode **6***b* also serve as an oxygen diffusion suppressing layer for suppressing diffusion of oxygen from the second insulating film **7***b* to the thermistor film **5**. When the thermistor element **4** is manufactured using a manufacturing method which will be described later, the second surface-side electrode **6***c* also serves as an oxygen diffusion suppressing layer for suppressing diffusion of oxygen from the heat treatment atmosphere (for example, the atmospheric air) to the thermistor film **5**. The conductive films forming the first electrode **6***a*, the second electrode **6***b*, and the second surface-side electrode **6***c* may be different or some or all thereof may be the same.

[0068] In this embodiment, as the conductive films forming the first electrode **6***a* and the second electrode **6***b* of the first surface-side electrode **6** and the second surface-side electrode **6***c*, for example, films including at least one selected from platinum (Pt), gold (Au), palladium (Pd), silver (Ag), ruthenium (Ru), iridium (Ir), rhodium (Rh), osmium (Os), titanium (Ti), rhenium (Re), copper (Cu), nickel (Ni), tantalum (Ta), chromium (Cr), and nickel-chromium (NiCr) alloys can be used. Each of the first electrode **6***a*, the second electrode **6***b*, and the second surface-side electrode **6***c* may be a stacked film in which the conductive films are stacked. For example, a stacked film in which two conductive films including a nickel-chromium (NiCr) alloy film and a platinum (Pt) film are stacked can be used as each of the first electrode **6***a* and the second electrode **6***b*.

[0069] In this embodiment, all of the first electrode **6***a*, the second electrode **6***b*, and the second surface-side electrode **6***c* may be be conductive films formed of a precious metal (a simple precious metal or an alloy including precious metal elements) selected from platinum (Pt), gold (Au), palladium (Pd), silver (Ag), ruthenium (Ru), iridium (Ir), rhodium (Rh), osmium (Os), and rhenium (Re). This is because it is less easily degenerated and a degenerated layer is less easily formed between the electrodes and the thermistor film **5** at the time of heat treatment in the method of manufacturing the thermistor element **4** which will be described later. All of the first electrode **6***a*, the second electrode **6***b*, and the second surface-side electrode **6***c* may be conductive films formed of precious metal, since they have excellent conductivity. When each of the first electrode **6***a*, the second electrode **6***b*, and the second surface-side electrode **6***c* is a stacked film in which the conductive films are stacked, the conductive film in contact with the thermistor film **5** may be formed of precious metal.

[0070] In this embodiment, the thicknesses of the first electrode **6***a*, the second electrode **6***b*, and the second surface-side electrode **6***c* range, for example, from 7 nm to 100 nm. The thicknesses of the first electrode **6***a* and the second electrode **6***b* may be thicknesses with which they serve as oxygen diffusion suppressing layers for suppressing diffusion of oxygen from the second insulating film **7***b* to the thermistor film **5** at the time of heat treatment. The thicknesses of the first electrode **6***a* and the second electrode **6***b* are appropriately determined according to the material of the first electrode **6***a* and the second electrode **6***b* and the material of the second insulating film **7***b*. The thickness of the second surface-side electrode **6***c* may be a thickness with which it can serve as an oxygen diffusion suppressing layer for suppressing diffusion of oxygen from the heat treatment atmosphere (for example, the atmospheric air) to the thermistor film **5** at the time of heat treatment. The thickness of the second surface-side electrode **6***c* is appropriately determined according to the material of the second surface-side electrode **6***c*.

[0071] The materials of the first insulating film **7***a*, the second insulating film **7***b*, and the third insulating film **7***c* may be different or some or all thereof may be the same. As each of the first insulating film **7***a*, the second insulating film **7***b*, and the third insulating film **7***c*, for example, a film formed of aluminum nitride, silicon nitride, aluminum oxide, silicon oxide, magnesium oxide, tantalum oxide, niobium oxide, hafnium oxide, zirconium oxide, germanium oxide, yttrium oxide, tungsten oxide, bismuth oxide, calcium oxide, aluminum oxynitride, silicon oxynitride, aluminum magnesium oxide, silicon boride, boron nitride, or sialon (oxynitride of silicon and aluminum) can be used.

[0072] In this embodiment, for the following reasons, at least the second insulating film **7***b* of the first insulating film **7***a*, the second insulating film **7***b*, and the third insulating film **7***c* may be formed of an oxide. As illustrated in FIGS. **3** and **4**, a part of the second insulating film **7***b* is located between the first electrode **6***a* and the second electrode **6***b* of the first surface-side electrode **6** and is in contact with a part of one surface (the first surface) of the thermistor film **5** located between the first electrode **6***a* and the second electrode **6***b* in a plan view. Accordingly, when the second insulating film **7***b* is formed of an oxide, oxygen can be diffused from the second insulating film **7***b* to the thermistor film **5** by manufacturing the thermistor element **4** using a manufacturing method which will be described later. As a result, it is possible to easily manufacture the thermistor element **4** including thermistor film **5** in which the oxygen concentration in the second region **5***b* is higher than that in the first region **5***a*.

[Element Periphery Structure]

[0073] As illustrated in FIG. **2**, a first insulator layer **8**, a wiring part **9** that is electrically connected to a circuit part **15** which will be described later, and a first connection part **10** that electrically connects each thermistor element **4** and the wiring part **9** are provided on one surface of the first substrate **2** (a surface facing the second substrate **3**) in the electromagnetic wave sensor **1** according to this embodiment.

[0074] The first insulator layer **8** is an insulating film stacked on one surface of the first substrate **2** (the surface facing the second substrate **3**). For example, one or two or more kinds of insulating films formed of aluminum nitride, silicon nitride, aluminum oxide, silicon oxide, magnesium oxide, tantalum oxide, niobium oxide, hafnium oxide, zirconium oxide, germanium oxide, yttrium oxide, tungsten oxide, bismuth oxide, calcium oxide, aluminum oxinitride, silicon oxynitride, aluminum magnesium oxide, silicon boride, boron nitride, or sialon (oxynitride of silicon and aluminum) can be used as the first insulator layer **8**.

[0075] As illustrated in FIGS. **1** and **2**, the wiring part **9** includes the first lead wires **9***a* and the second lead wires **9***b*. The first lead wires **9***a* extend in the first direction X and are arranged at constant intervals in the second direction Y. On the other hand, the second lead wires **9***b* extend in the second direction Y and are arranged at constant intervals in the first direction X. As illustrated in FIG. **4**, the first lead wires **9***a* and the second lead wires **9***b* are disposed at different positions in the thickness direction (the third direction Z) of the first insulator layer **8** and are provided to three-dimensionally cross each other as illustrated in FIG. **2**.

[0076] Each first lead wire **9***a* and each second lead wire **9***b* are formed of, for example, a conductive film of copper or gold.

[0077] A first connection part **10** includes a pair of first connection members **11***a* and **11***b*. As illustrated in FIGS. **3** and **4**, the pair of first connection members **11***a* and **11***b* include a pair of arm parts **12***a* and **12***b* and a pair of leg parts **13***a* and **13***b*. The leg parts **13***a* and **13***b* of the pair of first connection members **11***a* and **11***b* are disposed at ends in a diagonal direction of each region E having a substantially rectangular shape in a plan view (see FIGS. **1** to **4**).

[0078] As illustrated in FIG. **4**, each of the arm parts **12***a* and **12***b* includes a part of each of the wiring layers **21***a* and **21***b* (a conductor pattern part which will be described later), the first insulating film **7***a* covering one surface of the wiring layers **21***a* and **21***b*, the second insulating film **7***b* covering the other surface of the wiring layers **21***a* and **21***b*, and the third insulating film **7***c* covering the surface of the second insulating film **7***b* opposite to the wiring layers **21***a* and **21***b*.

[0079] As illustrated in FIGS. **3** and **4**, each of the wiring layers **21***a* and **21***b* includes a conductor pattern part of a bent line shape that is formed along the perimeter of the thermistor film **5** in a plan view and a conductor part that is formed at a position overlapping the thermistor film **5** in a plan view and connected to the first electrode **6***a* or the second electrode **6***b*.

[0080] All the first insulating film **7***a*, the second insulating film **7***b*, and the third insulating film **7***c* covering the wiring layers **21***a* and **21***b* forming the conductor pattern part are formed in the substantially same shape as the shapes of the wiring layers **21***a* and **21***b* forming the conductor pattern part in a plan view.

[0081] The wiring layers **21***a* and **21***b* are formed of, for example, at least one kind selected from aluminum, tungsten, titanium, tantalum, titanium nitride, tantalum nitride, chromium nitride, and zirconium nitride.

[0082] The leg part **13***a* serves as a contact plug that electrically connects the first lead wire **9***a* and the wiring layer **21***a* of the arm part **12***a*. The leg part **13***b* serves as a contact plug that electrically connects the second lead wire **9***b* and the wiring layer **21***b* of the arm part **12***b*. As illustrated in FIGS. **3** and **4**, each of the leg parts **13***a* and **13***b* is formed of a conductor pillar with a circular section formed to extend in the third direction Z.

[0083] Each of the leg parts **13***a* and **13***b* is formed of, for example, copper, gold, FeCoNi alloy, or NiFe alloy (permalloy).

[0084] As illustrated in FIGS. **3** and **4**, the first connection member **11***a* includes the wiring layer **21***a* electrically connected to the first electrode **6***a* of the first surface-side electrode **6** and the leg part **13***a* electrically connecting the wiring layer **21***a* and the first lead wire **9***a* and electrically connects the first electrode **6***a* and the first lead wire **9***a*.

[0085] The first connection member **11***b* includes the wiring layer **21***b* electrically connected to the second electrode **6***b* and the leg part **13***b* electrically connecting the wiring layer **21***b* and the second lead wire **9***b* and electrically connects the second electrode **6***b* and the second lead wire **9***b*.

[0086] As illustrated in FIG. **2**, a second insulator layer **14**, a circuit part **15**, a second connection part **16**, and connection terminals **17***a* and **17***b* are provided on one surface of the second substrate **3** (a surface facing the first substrate **2**) in the electromagnetic wave sensor **1** according to this embodiment.

[0087] The second insulator layer **14** is an insulating film stacked on one surface (the surface facing the first substrate **2**) of the second substrate **3**. The same as the insulating film used for the first insulator layer **8** can be used as the second insulator layer **14**. The insulating film forming the second insulator layer **14** may be the same as the insulating film forming the first insulator layer **8** or may be different therefrom.

[0088] The circuit part **15** detects a change in voltage output from the thermistor element **4** and converts the detected change in voltage to a luminance temperature. The circuit part **15** is provided in the layer of the second insulator layer **14**. The circuit part is formed of a readout integrated circuit (ROIC), a regulator, an analog-to-digital (A/D) converter, a multiplexer, or the like.

[0089] As illustrated in FIG. **2**, the circuit part **15** is electrically connected to the first lead wires **9***a* via a second connection member **18***a* and the connection terminal **17***a*. The circuit part **15** is electrically connected to the second lead wires **9***b* via a second connection member **18***b* and the connection terminal **17***b*.

[0090] As illustrated in FIG. **2**, the second connection part **16** includes a plurality of second connection members **18***a* and **18***b*. Each of the second connection members **18***a* and **18***b* is formed of a conductor pillar having a circular section formed to extend in the third direction Z. The second connection members **18***a* and **18***b* are provided to correspond to the first lead wires **9***a* and the second lead wires **9***b*. The second connection member **18***a* electrically connects one end of the first lead wire **9***a* and the connection terminal **17***a*. The second connection member **18***b* electrically connects one end of the second lead wire **9***b* and the connection terminal **17***b*.

[0091] The second connection members **18***a* and **18***b* are formed of, for example, a conductive material such as copper and/or gold.

[0092] As illustrated in FIG. **2**, the connection terminals **17***a* and **17***b* are provided on the surface of the second insulator layer **14**. The connection terminals **17***a* and **17***b* correspond to the first lead wires **9***a* and the second lead wires **9***b*. The connection terminal **17***a* is located in a region on one side in the first direction X surrounding the circuit part **15** and is arranged at constant intervals in the second direction Y. The connection terminal **17***b* is located in a region on one side in the second direction Y surrounding the circuit part **15** and is arranged at constant intervals in the first direction X. The connection terminals **17***a* and **17***b* are formed of, for example, a conductive material such as copper and/or gold.

[0093] As illustrated in FIGS. **1** and **2**, the thermistor element **4** in the electromagnetic wave sensor **1** according to this embodiment is provided for each region defined by the first lead wires **9***a* and the second lead wires **9***b* in a plan view.

[0094] As illustrated in FIGS. **2** and **4**, the thermistor elements **4** are supported by a pair of first connection members **11***a* and **11***b* in a state in which they are suspended in the third direction Z. Accordingly, as illustrated in FIG. **4**, a space G is provided between the thermistor element **4** and the first insulator layer **8**. As illustrated in FIG. **4**, a window part W transmitting infrared rays IR between the first substrate **2** and the thermistor film **5** is present in a region facing the thermistor film **5** of each thermistor element **4** in the thickness direction of the first substrate **2** (an overlapping region in a plan view).

[0095] In the electromagnetic wave sensor **1** according to this embodiment, infrared rays IR radiated from a measurement target is input from the first substrate **2** side to the thermistor element **4** via the window part W. The infrared rays IR input to the thermistor element **4** are absorbed by the first insulating film **7***a*, the second insulating film **7***b*, and the third insulating film **7***c* which are formed in the vicinity of the thermistor film **5** and the thermistor film **5**. Accordingly, the temperature of the thermistor film **5** changes, electrical resistance thereof changes, and an output voltage between the first electrode **6***a* and the second electrode **6***b* of the first surface-side electrode **6** changes. Accordingly, in the electromagnetic wave sensor **1** according to this embodiment, the thermistor element **4** serves as a bolometer element.

[0096] The electromagnetic wave sensor **1** according to this embodiment two-dimensionally detects infrared rays IR radiated from a measurement target using the thermistor elements **4**. In the electromagnetic wave sensor **1** according to this embodiment, it is possible to two-dimensionally detect (image) a temperature distribution (a temperature image) of a measurement target by converting electrical signals (voltage signals) output from the thermistor elements **4** to luminance temperatures. When a positive voltage is applied to the thermistor film **5** of each thermistor element **4**, a change in current flowing in the thermistor film **5** with a change in temperature of the thermistor film **5** can be detected and converted to a luminance temperature.

[Method of Manufacturing Electromagnetic Wave Sensor]

[0097] A method of manufacturing the electromagnetic wave sensor **1** according to this embodiment will be described below. The electromagnetic wave sensor **1** according to this embodiment can be manufactured, for example, using the following manufacturing method.

[0098] First, the aforementioned members such as the first insulator layer **8**, the wiring part **9**, and the leg parts **13***a* and **13***b* are formed on the first substrate **2** using known methods. Thereafter, a thermistor element **4** is formed on the surface of the first substrate **2** on the first insulator layer **8** side using the following method.

[0099] FIGS. **5** to **12** are sectional views sequentially illustrating processes of manufacturing a thermistor element provided in the electromagnetic wave sensor illustrated in FIG. **1**. In this embodiment, for example, the constituent members of the thermistor element **4** are sequentially formed from a member disposed on the first insulating film **7***a* side to the third insulating film **7***c*.

[0100] First, a known organic material layer **30** formed of a resistor or the like is formed on the surface of the first substrate **2** in which the aforementioned members are formed on the first insulator layer **8** side. Then, as illustrated in FIG. **5**, for example, the first insulating film **7***a* formed of aluminum oxide (Al_2O_3) is formed on the whole surface of the organic material layer **30**.

[0101] Then, for example, a conductive film formed of titanium (Ti) is formed on the whole surface of the first insulating film **7***a* illustrated in FIG. **5**. Thereafter, the conductive film is patterned using photolithography technology. Accordingly, wiring layers **21***a* and **21***b* having a predetermined patterned shape are formed as illustrated in FIG. **6**.

[0102] Then, as illustrated in FIG. **7**, the second insulating film **7***b* formed of aluminum oxide (Al_2O_3) is formed on the whole surface of the wiring layers **21***a* and **21***b*.

[0103] Then, the second insulating film **7***b* is patterned using photolithography technology. Accordingly, as illustrated in FIG. **8**, the openings **20***a* and **20***b* penetrating the second insulating film **7***b* are formed on the wiring layers **21***a* and **21***b*.

[0104] Then, for example, a conductive film **53** formed of platinum (Pt) is formed on the whole surface of the second insulating film **7***b* including the openings **20***a* and **20***b*, and the conductive film **53** is embedded in the openings **20***a* and **20***b*. Thereafter, the conductive film **53** is patterned using photolithography technology. Accordingly, the first surface-side electrode **6** including the first electrode **6***a* and the second electrode **6***b* is formed as illustrated in FIG. **9**.

[0105] In this embodiment, when the first surface-side electrode **6** is formed of platinum (Pt), the thickness of the first surface-side electrode **6** may range from 20 nm to 60 nm. When the thickness of the first surface-side electrode **6** formed of platinum (Pt) is equal to or greater than 20 nm, the first surface-side electrode **6** effectively serves as an oxygen diffusion suppressing layer for suppressing diffusion of oxygen from the second insulating film **7***b* to the thermistor film **5**. The thickness of the first surface-side electrode **6** formed of platinum (Pt) may be equal to or less than 60 nm, since a process of patterning the conductive film **53** to form the first surface-side electrode **6** is facilitated.

[0106] Then, as illustrated in FIG. **10**, for example, a thermistor material film **54** formed of an oxide having a spinel crystal structure and a conductive film **55** formed of platinum (Pt) are sequentially formed on the whole surface of the second insulating film **7***b* in which the first surface-side electrode **6** is provided.

[0107] Then, the second surface-side electrode **6***c* and the thermistor film **5** patterned in the same shape are formed as illustrated in FIG. **11** by patterning the thermistor material film **54** and the conductive film **55** using photolithography technology.

[0108] In this embodiment, when the second surface-side electrode **6***c* is formed of platinum (Pt), the thickness of the second surface-side electrode **6***c* may range from 20 nm to 60 nm. When the thickness of the second surface-side electrode **6***c* formed of platinum (Pt) is equal to or greater than 20 nm, the second surface-side electrode **6***c* effectively serves as an oxygen diffusion suppressing layer for suppressing diffusion of oxygen from the heat treatment atmosphere (for example, the atmospheric air) to the thermistor film **5** at the time of heat treatment. The thickness of the second surface-side electrode **6***c* formed of platinum (Pt) may be equal to or less than 60 nm, since a process of patterning the conductive film **55** to form the second surface-side electrode **6***c* is facilitated.

[0109] Then, in this embodiment, heat treatment (annealing) is performed on the thermistor element in which layers up to the second surface-side electrode **6***c* are formed and of which manufacturing is being performed in the atmospheric air at 250° C. or higher. Accordingly, oxygen diffuses from the second insulating film **7***b* to the thermistor film **5** disposed in contact with the second insulating film **7***b*. At this time, diffusion of oxygen from the second insulating film **7***b* to the thermistor film **5** disposed in contact with the first surface-side electrode **6** (the first electrode **6***a* and the second electrode **6***b*) is suppressed by the first electrode **6***a* and the second electrode **6***b*. Diffusion of oxygen from the atmospheric air to the thermistor film **5** disposed in contact with the second surface-side electrode **6***c* is suppressed by the second surface-side electrode **6***c*. As a result, the thermistor film **5** in which the oxygen concentration in the second region **5***b* is higher than the oxygen concentration in the first region **5***a* is obtained.

[0110] The heat treatment temperature in the heat treatment is, for example, equal to or higher than 250° C. and may range from 250° C. to 325° C., for example, when the material of the second insulating film **7***b* is aluminum oxide (Al_2O_3). Since the heat treatment temperature is equal to or higher than 250° C., oxygen can be diffused from the second insulating film **7***b* to the thermistor film **5** disposed in contact with the second insulating film **7***b*. The heat treatment temperature may be equal to or lower than 325° C., since interlayer peeling due to a decrease in film thickness of the organic material layer **30** is less likely to occur.

[0111] For example, the heat treatment time in the heat treatment is set to a range of from 0.5 hours to 5 hours and may be set to a range of from 1 hour to 3 hours. The heat treatment time in the heat treatment can be appropriately determined according to the materials of the constituent members of the thermistor element **4**, the material of the second insulating film **7***b*, and the material and the thickness of the thermistor film **5**.

[0112] In this embodiment, since the atmosphere of the heat treatment is the atmospheric air, it is possible to suppress diffusion of oxygen from the atmospheric air to the thermistor film **5** using the second surface-side electrode **6***c*. On the other hand, for example, when the heat treatment is performed in the atmosphere of oxygen, an effect of preventing diffusion of oxygen from the atmosphere of oxygen to the thermistor film **5** using the second surface-side electrode **6***c* is not satisfactorily obtained, and there is a likelihood that the oxygen concentration of the thermistor film **5** as a whole increases.

[0113] Then, as illustrated in FIG. **12**, for example, an insulating film formed of silicon dioxide (SiO_2) is formed on the whole surface of the second surface-side electrode **6***c* to form the third insulating film **7***c* covering the top surface of the second surface-side electrode **6***c* and the side surfaces of the second surface-side electrode **6***c* and the thermistor film **5**. Thereafter, the thermistor element **4** and the arm parts **12***a* and **12***b* are formed in a predetermined shape as illustrated in FIG. **4** by performing patterning thereon.

[0114] Thereafter, a space G is formed by removing the organic material layer **30** through ashing. Through these processes, the thermistor element **4** is obtained.

[0115] A second substrate **3** including the aforementioned constituent members is manufactured using known methods.

[0116] Then, the second substrate **3** is disposed on one surface (a surface on the thermistor element **4** side) of the first substrate **2** including the thermistor element **4**. Thereafter, the first substrate **2** and the second substrate **3** are electrically connected using the aforementioned members using a known method, and the surroundings of the opposite surfaces of the first substrate **2** and the second substrate **3** are sealed with a sealing member (not illustrated) to form a closed internal space K (see FIG. **2**) therebetween.

[0117] Through these processes, the electromagnetic wave sensor **1** according to this embodiment is obtained.

[0118] The thermistor element **4** according to this embodiment includes a thermistor film **5** which is formed of an oxide having a spinel crystal structure and in which the oxygen concentration of the second region **5***b* located between the first electrode **6***a* and the second electrode **6***b* in a plan view is higher than the oxygen concentration of the first region **5***a* consisting of a region that overlaps the first electrode **6***a* and the second surface-side electrode **6***c* in a plan view and a region that overlaps the second electrode **6***b* and the second surface-side electrode **6***c* in a plan view. Accordingly, in the thermistor element **4** according to this embodiment, a current flows less easily in the in-plane direction in the second surface-side electrode **6***c* of the thermistor film **5**.

[0119] Accordingly, in the electromagnetic wave sensor **1** including the thermistor element **4** according to this embodiment, a decrease in measurement accuracy due to a current component flowing in the in-plane direction in the thermistor film **5** of the thermistor element **4** is curbed, and the measurement accuracy is enhanced.

[0120] While an embodiment of the present disclosure has been described above in detail with reference to the drawings, the configurations in the embodiment, combinations thereof, and the like are merely examples, and the embodiment can be subjected to addition, omission, replacement, and other modification of an element without departing from the gist of the present disclosure.

[0121] For example, the thermistor element according to the present disclosure is not limited to application to an infrared image sensor in which the thermistor elements **4** are arranged in an array. The thermistor element according to the present disclosure may be applied to an electromagnetic wave sensor including only a single thermistor element **4** or may be applied to an electromagnetic wave sensor in which the thermistor elements **4** are arranged linearly.

[0122] The thermistor element according to the present disclosure may also be used as a temperature sensor that measures the temperature.

[0123] In the aforementioned embodiment, an example in which the oxygen concentration of the second region **5***b* is set to be higher than the oxygen concentration of the first region **5***a* of the thermistor film **5** formed of an oxide having a spinel crystal structure by performing heat treatment (annealing) at 250° C. or higher in the atmospheric air on a thermistor element in which constituent layers up to the second surface-side electrode **6***c* are provided and of which manufacturing is being performed has been described, but the method of manufacturing the thermistor element according to the present disclosure is not limited to the aforementioned method as long as the thermistor film **5** formed of an oxide having a spinel crystal structure in which the oxygen concentration of the second region **5***b* is higher than that of the first region **5***a* can be formed.

[0124] The planar shapes of the thermistor film **5**, the first electrode **6***a*, the second surface-side electrode **6***c*, and the second electrode **6***b* included in the thermistor element **4** can be appropriately modified.

[0125] In the thermistor element **4** according to the embodiment, the shape and arrangement and the number of the openings **20***a* and **20***b* are not limited to the aforementioned configuration, but can be appropriately modified.

EXAMPLES

Example 1

[Method of Manufacturing Electromagnetic Wave Sensor]

[0126] A thermistor element **4** illustrated in FIG. **12** was manufactured using the following manufacturing method.

[0127] The constituent members illustrated in FIG. **4** such as the first insulator layer **8**, the wiring part **9**, and the leg parts **13***a* and **13***b* were formed on a first substrate **2** formed of a silicon substrate, and then an organic material layer **30** formed of a resist was provided on the surface thereof on the first insulator layer **8** side. Then, as illustrated in FIG. **5**, a first insulating film **7***a* with a thickness of 200 nm formed of aluminum oxide (Al_2O_3) was formed on the whole surface of the organic material layer **30** using a sputtering method.

[0128] Then, a conductive film with a thickness of 60 nm formed of titanium (Ti) was formed on the whole surface of the first insulating film **7***a* illustrated in FIG. **5** using a sputtering method. Thereafter, the conductive film was patterned using photolithography technology. Accordingly, wiring layers **21***a* and **21***b* having a predetermined pattern shape were formed as illustrated in FIG. **6**.

[0129] Then, as illustrated in FIG. **7**, a second insulating film **7***b* with a thickness of 70 nm formed of aluminum oxide (Al_2O_3) was formed on the whole surface of the wiring layers **21***a* and **21***b* using a sputtering method.

[0130] Then, the second insulating film **7***b* was patterned using photolithography technology. Accordingly, as illustrated in FIG. **8**, openings **20***a* and **20***b* with a circular shape with a diameter of 1.2 μm penetrating the second insulating film **7***b* were formed on the wiring layers **21***a* and **21***b*.

[0131] Then, a conductive film **53** with a thickness of 30 nm formed of platinum (Pt) was formed on the whole surface of the second insulating film **7***b* including the openings **20***a* and **20***b* using a sputtering method, and the conductive film **53** was embedded in the openings **20***a* and **20***b*. Thereafter, the conductive film **53** was patterned using photolithography technology. Accordingly, as illustrated in FIG. **9**, a first surface-side electrode **6** including the first electrode **6***a* and the second electrode **6***b* was formed.

[0132] Then, as illustrated in FIG. **10**, a thermistor material film **54** with a thickness of 100 nm formed of an oxide having a spinel crystal structure and a conductive film **55** with a thickness of 20 nm formed of platinum (Pt) were sequentially formed on the whole surface of the second insulating film **7***b* in which the first surface-side electrode **6** was formed using a sputtering method.

[0133] An oxide having a spinel crystal structure (Co:Mn:Ni=43.7 at %:42.3 at %:14.0 at %) including Co and Mn as base metal elements and Ni as an additive element was used as the material of the thermistor material film **54**.

[0134] Then, as illustrated in FIG. **11**, a second surface-side electrode **6***c* and a thermistor film **5** which were patterned in the same shape were formed by patterning the thermistor material film **54** and the conductive film **55** using photolithography technology.

[0135] Then, heat treatment (annealing) was performed on the thermistor element in which layers up to the second surface-side electrode **6***c* were formed and of which manufacturing is being performed in the atmospheric air at 250° C. for 1 hour. Then, as illustrated in FIG. **12**, a third insulating film **7***c* formed of aluminum oxide (Al_2O_3) was formed on the whole surface of the second surface-side electrode **6***c* using a sputtering method. Accordingly, the third insulating film **7***c* covering the top surface of the second surface-side electrode **6***c* and the side surfaces of the second surface-side electrode **6***c* and the thermistor film **5** was formed.

[0136] Thereafter, the organic material layer **30** was removed by ashing.

[0137] Through these processes, a thermistor element **4** according to Example 1 was obtained.

[0138] An oxygen concentration in the thickness direction in the thermistor film **5** of the obtained thermistor element **4** was measured using the following method.

<<Measurement of Oxygen Concentration>>

[0139] A test sample was manufactured by film-processing the thermistor element **4** using a dual beam FIB (focus ion beam) processing and observation device (product name: Helios450F1; manufactured by Thermo Fisher Inc.). The test sample was manufactured such that a cross-section of the first region **5***a* consisting of a region that overlaps the first electrode **6***a* and the second surface-side electrode **6***c* in a plan view and a region that overlaps the second electrode **6***b* and the second surface-side electrode **6***c* in a plan view and a cross-section of the second region **5***b* located between the first electrode **6***a* and the second electrode **6***b* in a plan view in the thermistor film **5** can be observed.

[0140] On the obtained test sample, energy distributed X-ray analysis (EDS) (product name: NSS (NORAN SYSTEM SEVEN); manufactured by Thermo Fisher Inc.) was performed while scanning the test sample from the first surface-side electrode **6** side to the second surface-side electrode **6***c* side using a scanning transmission electron microscope (STEM) (product name: ARM200F; manufactured by JEOL LTD.). Accordingly, element concentrations of oxygen (O), titanium (Ti), manganese (Mn), nickel (Ni), aluminum (Al), cobalt (Co), and platinum (Pt) in the thickness direction in the cross-section of the first region **5***a* and the cross-section of the second region **5***b* were measured. Results thereof are illustrated in FIGS. **13** and **14**.

[0141] FIG. **13** is a graph illustrating a relationship between a position in the thickness direction of the cross-section including the first region **5***a* of the thermistor element **4** according to Example 1 and element concentrations. FIG. **14** is a graph illustrating a relationship between a position in the thickness direction of the cross-section including the second region **5***b* of the thermistor element **4** according to Example 1 and element concentrations. In FIGS. **13** and **14**, the horizontal axis represents a position (nm) in the thickness between the first insulating film **7***a* and the third insulating film **7***c* when an arbitrary position in the first insulating film **7***a* is set to 0. The vertical axis in FIGS. **13** and **14** represents an element concentration (at %).

[0142] The peak of platinum (Pt) in FIGS. **13** and **14** indicates a position in the thickness direction of the first surface-side electrode **6** and the second surface-side electrode **6***c* in the test sample. The peak of titanium (Ti) indicates a position in the thickness direction of the wiring layers **21***a* and **21***b* in the test sample. The peaks of manganese (Mn), nickel (Ni), and cobalt (Co) indicate positions in the thickness direction of the thermistor film **5** in the test sample. The peak of aluminum (Al) indicates a position in the thickness direction of the first insulating film **7***a*, the second insulating film **7***b*, and the third insulating film **7***c* in the test sample.

[0143] The peak of oxygen (O) in the region in which manganese (Mn), nickel (Ni), and cobalt (Co) are detected in FIG. **13** indicates an oxygen concentration in the thermistor film **5** in the first region **5***a*.

[0144] The peak of oxygen (O) in the region in which manganese (Mn), nickel (Ni), and cobalt (Co) are detected in FIG. **14** indicates an oxygen concentration in the thermistor film **5** in the second region **5***b*.

[0145] As illustrated in FIG. **13**, the oxygen concentration of the first region **5***a* in the thermistor film **5** ranges from 30 at % to 40 at %. As illustrated in FIG. **14**, the oxygen concentration of the second region **5***b* in the thermistor film **5** was about 50 at % which is substantially constant in the thickness direction. Accordingly, it can be ascertained that the oxygen concentration of the second region **5***b* in the thermistor film **5** of the thermistor element **4** according to Example 1 is higher than the oxygen concentration of the first region **5***a*. As illustrated in FIGS. **13** and **14**, when the thermistor film **5** is divided into three regions including a region close to the second surface-side electrode **6***c*, a region far from the second surface-side electrode **6***c*, and a region including a central part in the thickness direction, it can be ascertained in any of the three regions that the oxygen concentration of the second region **5***b* is higher than the oxygen concentration of the first region **5***a*.

Test Example 1

[0146] An insulating film with a thickness of 200 nm formed of aluminum oxide (Al_2O_3) was formed on the whole surface of a silicon substrate, a thermistor material film with a thickness of 100 nm formed of an oxide having a spinel crystal structure was formed on the whole surface thereof, and thus a stacked sample according to Test Example 1 was obtained.

[0147] An oxide having a spinel crystal structure (Co:Mn:Ni=43.7 at %:42.3 at %:14.0 at %) including Co and Mn as base metal elements and Ni as an additive element was used as the material of the thermistor material film.

Test Example 2

[0148] Similarly to Test Example 1, a stacked sample according to Test Example 2 was obtained in the same ways except that an oxide having a spinel crystal structure (Mn:Ni:Fe:Cu:Zr=35.1 at %:32.8 at %:24.1 at %:4.9 at %:3.1 at %) including Mn and Ni as base metal elements and Fe, Cu, and Zr as additive elements was used as the material of the thermistor material film.

[0149] In the thermistor material films of the stacked samples according to Test Example 1 and Test Example 2, a current was made to flow in the in-plane direction, and resistivity was measured using a four-probe sheet resistance measuring instrument (product name: Prometrix RS75; manufactured by KLA-Tencor Corporation). Results thereof are shown in Table 1.

[0150] Test samples were manufactured by film-processing the stacked samples according to Test Example 1 and Test Example 2 using a dual beam FIB (focus ion beam) processing and observation device (product name: Helios450F1; manufactured by Thermo Fisher Inc.).

[0151] On the obtained test samples, energy distributed X-ray analysis (EDS) (product name: NSS (NORAN SYSTEM SEVEN); manufactured by Thermo Fisher Inc.) was performed while scanning the test sample from the insulating film side of the thermistor material film to the surface side thereof using a scanning transmission electron microscope (STEM) (product name: ARM200F; manufactured by JEOL LTD.). Accordingly, the oxygen (O) concentration in the thickness direction in the cross-sections of the thermistor material films of the stacked samples according to Test Example 1 and Test Example 2 were measured.

[0152] Thereafter, an arithmetic means was calculated and used as an average oxygen concentration of the thermistor material film using the measurement results of the oxygen (O) concentration at the measuring points in a region including a central part when the thermistor film **5** was divided into three regions including a region close to the insulating film, a region far from the insulating film (a region close to the surface), and a region including a central part in the thickness direction. An interval in the thickness direction between the measuring points was 2.4 nm. Results thereof are shown in Table 1.

[0153] Heat treatment (annealing) in the atmospheric air at 250° C. for 1 hour was performed on the stacked samples according to Test Example 1 and Test Example 2. Thereafter, in the same way as before heat treatment was performed, a current was made to flow in the in-plane direction in the thermistor material films of the stacked samples according to Test Example 1 and Test Example 2, and resistivity was measured. Results thereof are shown in Table 1.

[0154] Test samples were taken from the stacked samples according to Test Example 1 and Test Example 2 after heat treatment (annealing) was performed in the same way as before heat treatment was performed, and the oxygen concentration in the thickness direction was measured and an average oxygen concentration of the thermistor material film was calculated in the same way as before heat treatment was performed. Results thereof are shown in Table 1.

TABLE 1

	Test Example 1		Test Example 2	
Annealing	Resistivity Ω · cm	Oxygen concentration at %	Resistivity Ω · cm	Oxygen concentration at %
After heat treatment	577	50	1565	52
Before heat treatment	480	37	1300	41

[0155] As shown in Table 1, in any of Test Example 1 and Test Example 2, the oxygen concentration in the thermistor material film after heat treatment was performed was higher than that in the thermistor material film before heat treatment was performed. In any of Test Example 1 and Test Example 2, the resistivity in the thermistor material film in which the oxygen concentration after heat treatment was relatively high was higher than that in the thermistor material film in which the oxygen concentration before heat treatment is relatively low.

[0156] While embodiments of the disclosure have been described and illustrated above, it should be understood that these are exemplary of the disclosure and are not to be considered as limiting. Additions, omissions, substitutions, and other modifications can be made without departing from the spirit or scope of the present disclosure. Accordingly, the invention is not to be considered as being limited by the foregoing description, and is only limited by the scope of the appended claims.

What is claimed is:

1. A thermistor element comprising:

a thermistor film formed of an oxide having a spinel crystal structure;

a first surface-side electrode provided in contact with a first surface of the thermistor film; and

a second surface-side electrode provided in contact with a second surface of the thermistor film,

wherein the first surface-side electrode includes a first electrode and a second electrode that is disposed to be separated from the first electrode in a plan view, and at least a part of the first electrode and at least a part of the second electrode are disposed to overlap the second surface-side electrode in a plan view, and

in the thermistor film, an oxygen concentration of a second region located between the first electrode and the second electrode in a plan view is higher than an oxygen concentration of a first region consisting of a region that overlaps the first electrode and the second surface-side electrode in a plan view and a region that overlaps the second electrode and the second surface-side electrode in a plan view.

2. An electromagnetic wave sensor comprising at least one of the thermistor element according to claim **1**.

3. The electromagnetic wave sensor according to claim **2**, wherein the at least one of the thermistor element includes a plurality of the thermistor elements, and

the thermistor elements are arranged in an array.

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