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**Yamazaki et al.**

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(54) **OXIDE MATERIAL AND SEMICONDUCTOR DEVICE**

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(73) Assignee: **Semiconductor Energy Laboratory Co., Ltd.**, Atsugi (JP)

(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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**Related U.S. Application Data**

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(30) **Foreign Application Priority Data**

Dec. 17, 2010 (JP) ..... 2010-282135  
Jul. 8, 2011 (JP) ..... 2011-151859

(51) **Int. Cl.**  
**H10D 30/67** (2025.01)  
**C01G 19/00** (2006.01)  
(Continued)

(52) **U.S. Cl.**  
CPC ..... **H10D 30/6755** (2025.01); **C01G 19/006** (2013.01); **H10D 30/6757** (2025.01);  
(Continued)

(58) **Field of Classification Search**  
CPC ..... H01L 21/02554; H01L 21/02565  
See application file for complete search history.

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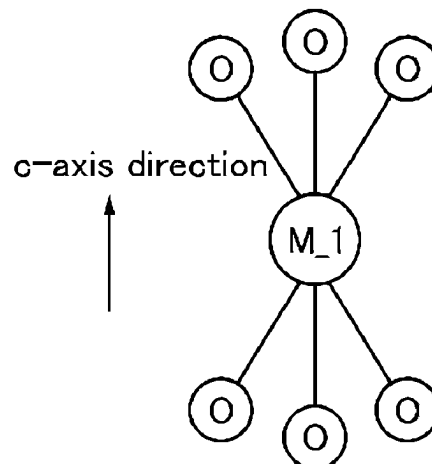
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Robinson Intellectual Property Law Office, P.C.

(57) **ABSTRACT**

An object is to provide a material suitably used for a semiconductor included in a transistor, a diode, or the like. Another object is to provide a semiconductor device including a transistor in which the condition of an electron state at an interface between an oxide semiconductor film and a gate insulating film in contact with the oxide semiconductor film is favorable. Further, another object is to manufacture a highly reliable semiconductor device by giving stable electric characteristics to a transistor in which an oxide semiconductor film is used for a channel. A semiconductor device is formed using an oxide material which includes crystal with c-axis alignment, which has a triangular or hexagonal atomic arrangement when seen from the direction of a surface or an interface and rotates around the c-axis.

**6 Claims, 25 Drawing Sheets**



**Related U.S. Application Data**

continuation of application No. 17/564,556, filed on Dec. 29, 2021, now Pat. No. 11,688,810, which is a continuation of application No. 16/849,113, filed on Apr. 15, 2020, now Pat. No. 11,217,702, which is a continuation of application No. 16/130,588, filed on Sep. 13, 2018, now Pat. No. 11,049,977, which is a continuation of application No. 15/178,949, filed on Jun. 10, 2016, now Pat. No. 10,079,309, which is a continuation of application No. 13/325,700, filed on Dec. 14, 2011, now Pat. No. 9,368,633.

- (51) **Int. Cl.**  
**H10D 62/40** (2025.01)  
**H10D 62/80** (2025.01)  
**U.S. Cl.**  
 CPC ..... **H10D 62/40** (2025.01); **H10D 62/405**  
 (2025.01); **H10D 62/80** (2025.01); **C01P**  
 2002/72 (2013.01)

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FIG. 1A

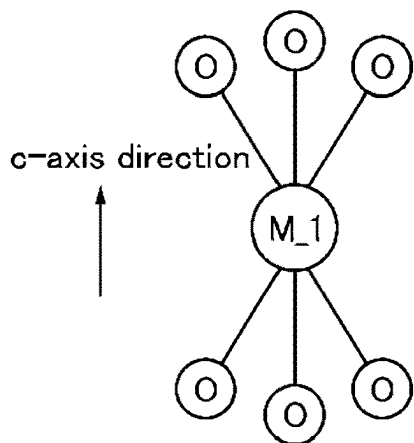


FIG. 1B

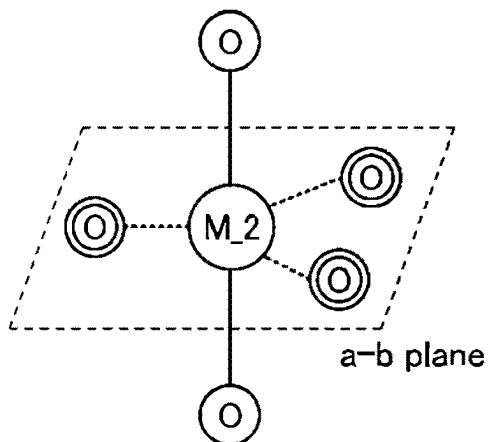


FIG. 1C

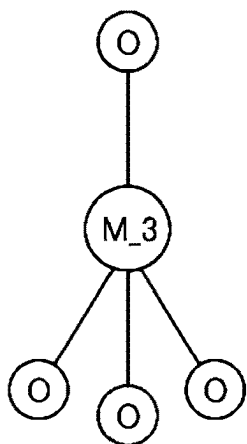


FIG. 1D

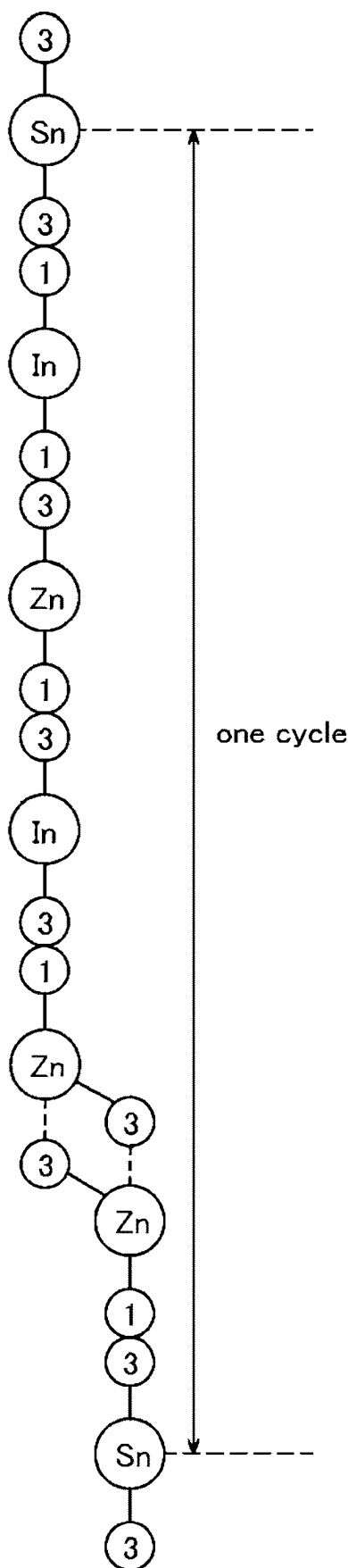


FIG. 2A

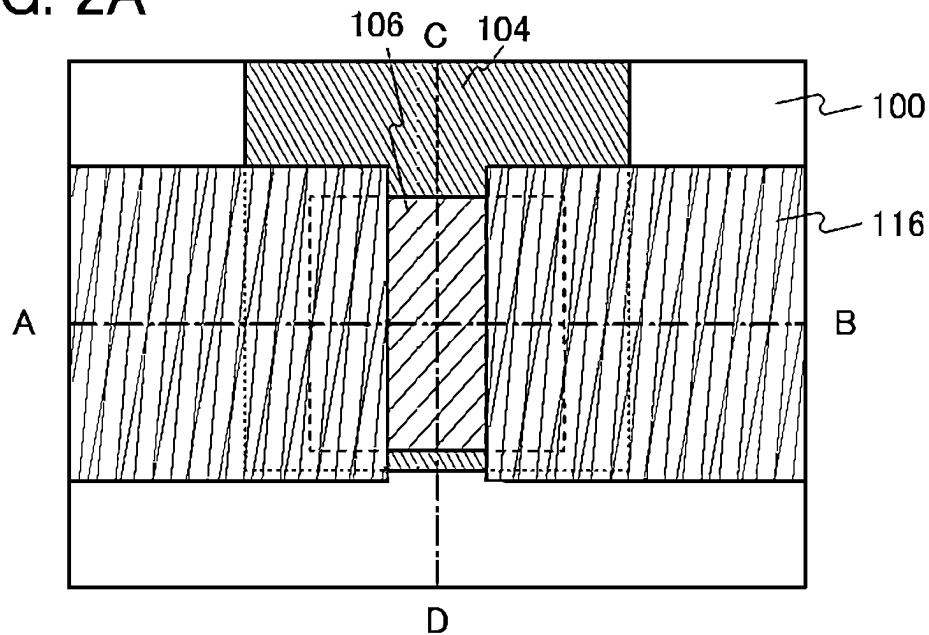


FIG. 2B

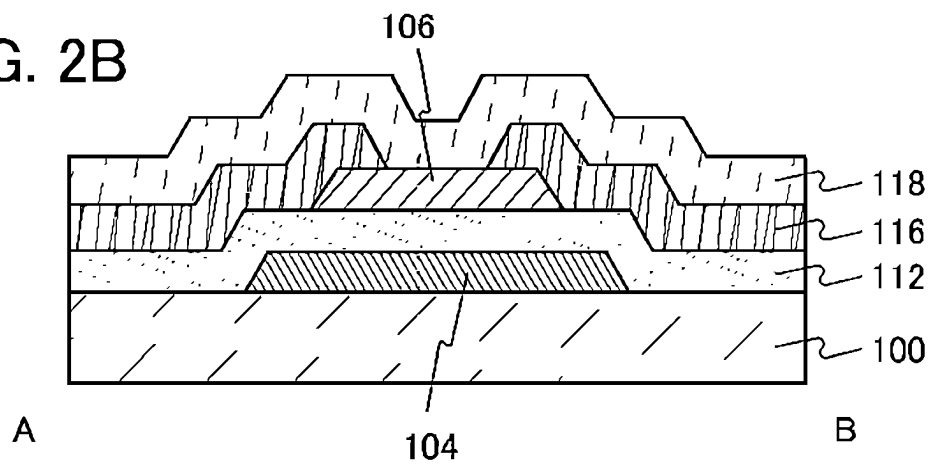


FIG. 2C

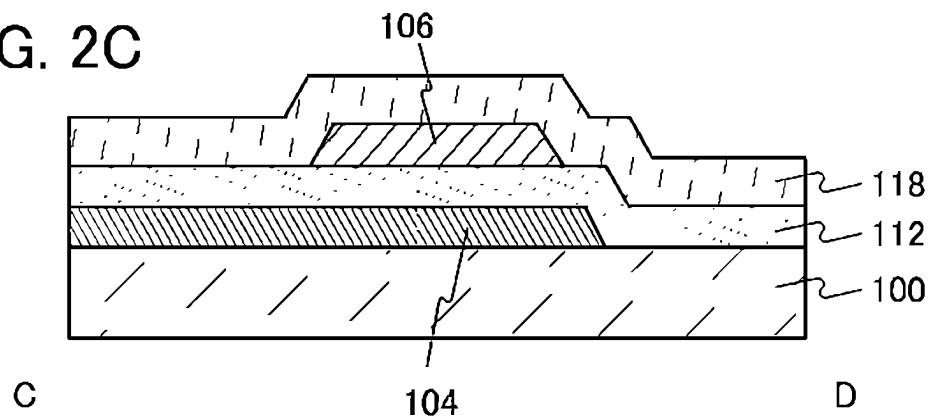


FIG. 3A

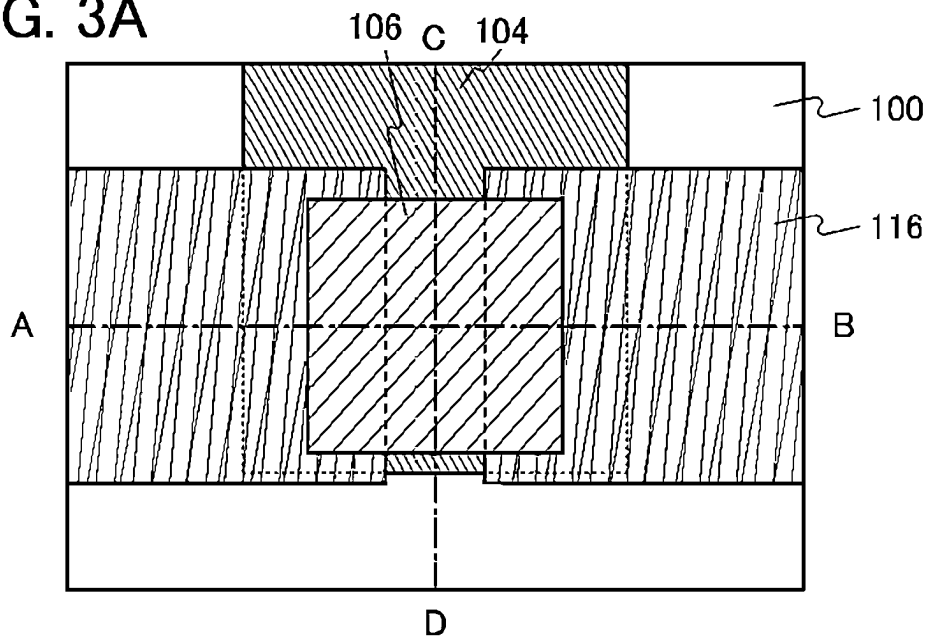


FIG. 3B

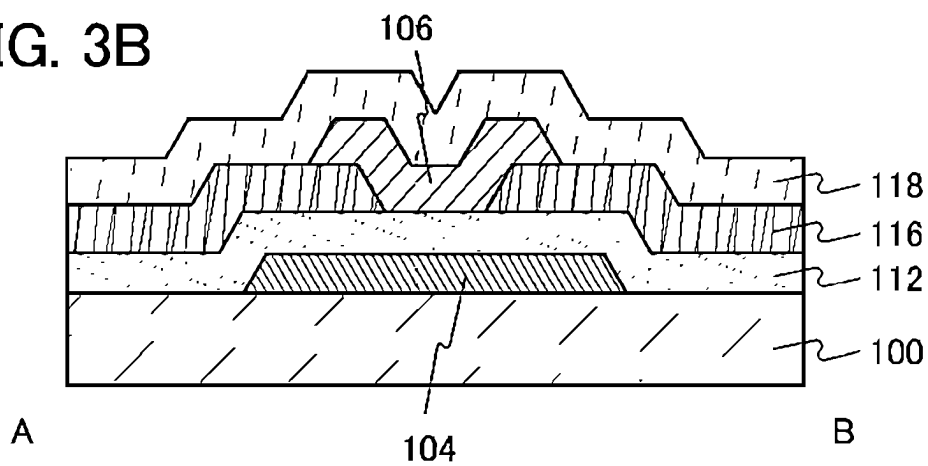


FIG. 3C

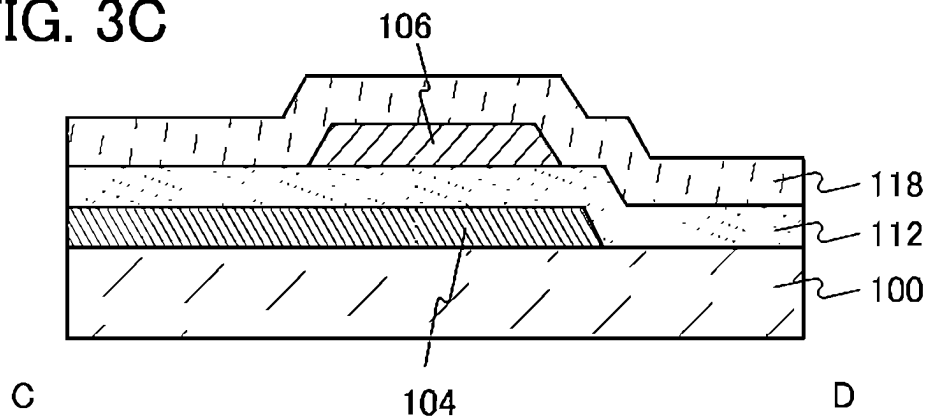


FIG. 4A

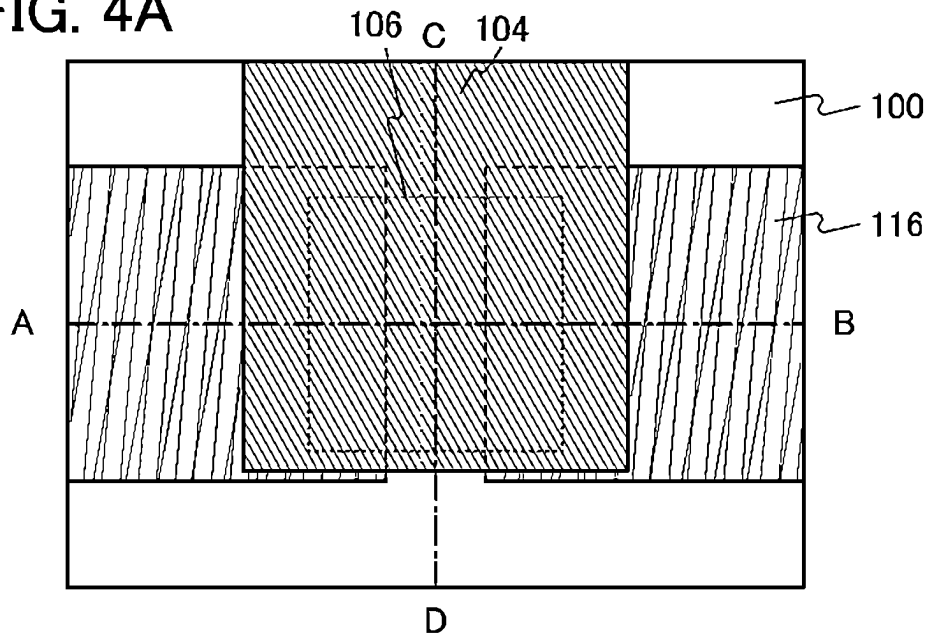


FIG. 4B

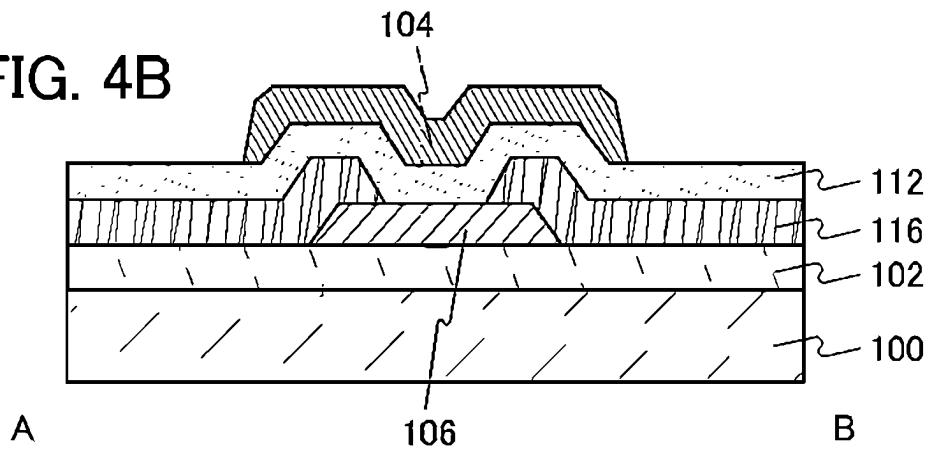


FIG. 4C

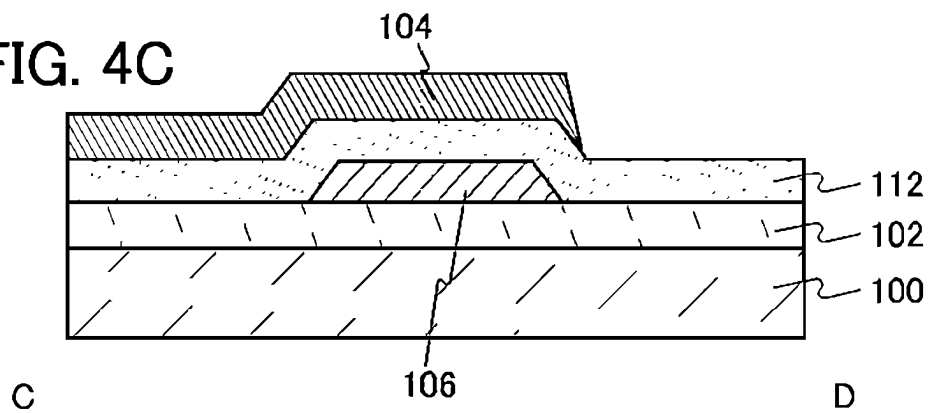


FIG. 5A

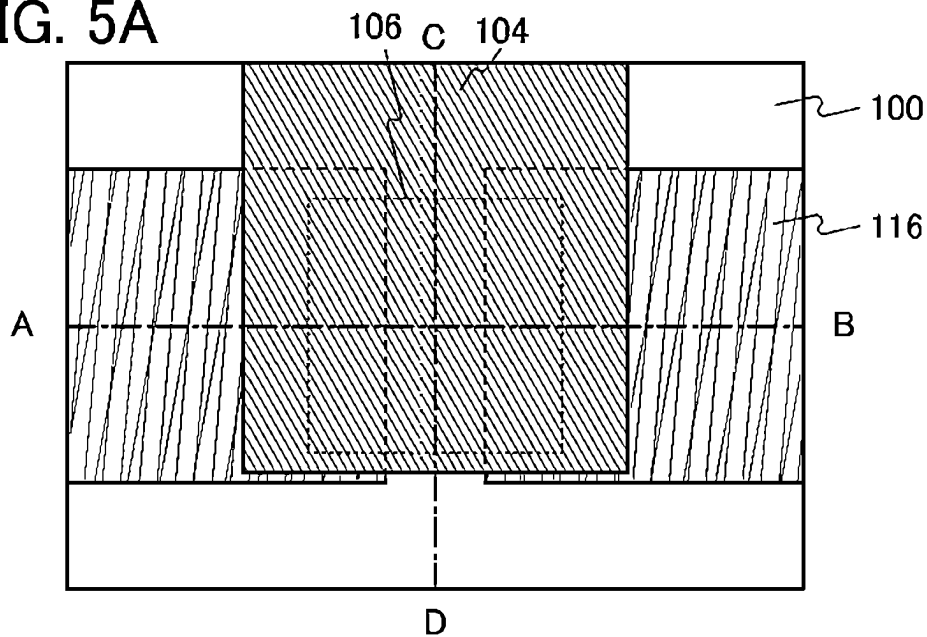


FIG. 5B

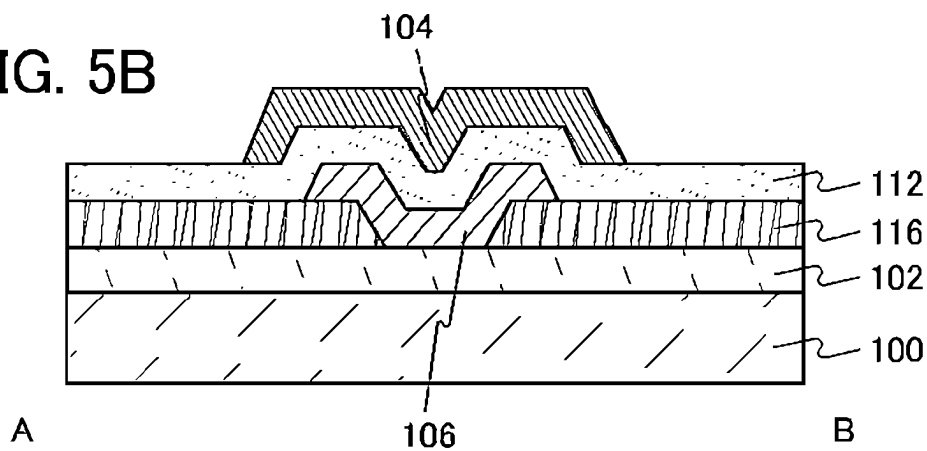


FIG. 5C

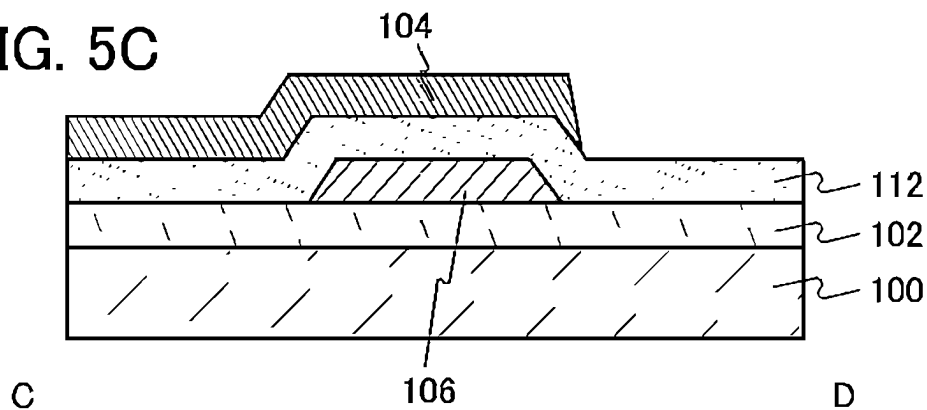




FIG. 6A

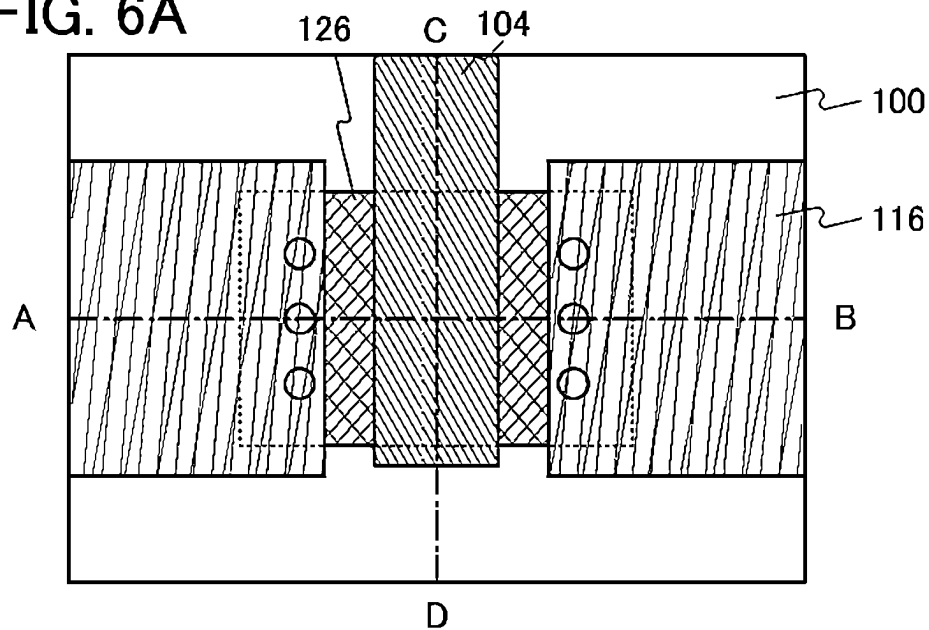


FIG. 6B

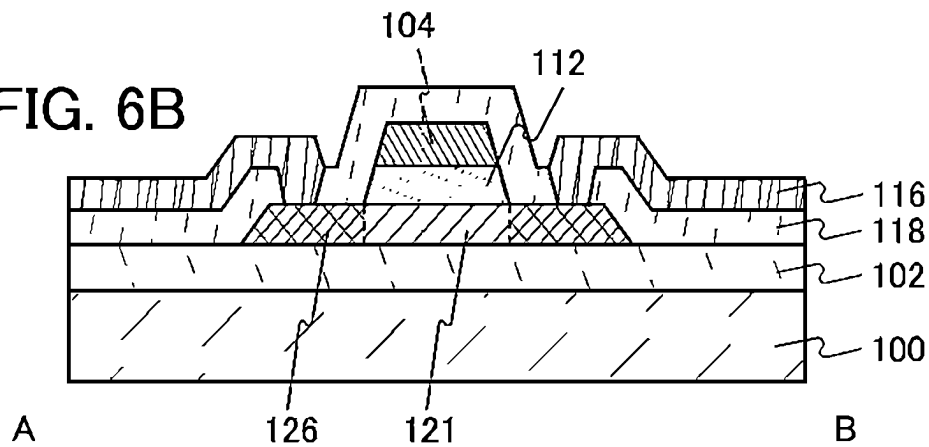


FIG. 6C

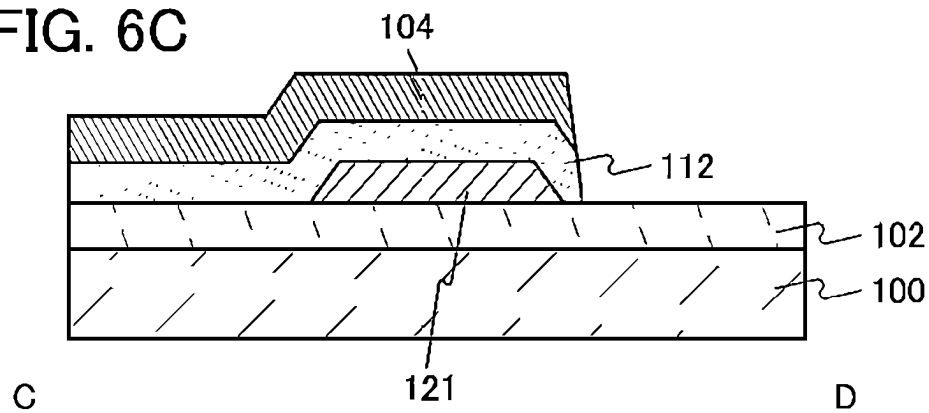


FIG. 7A

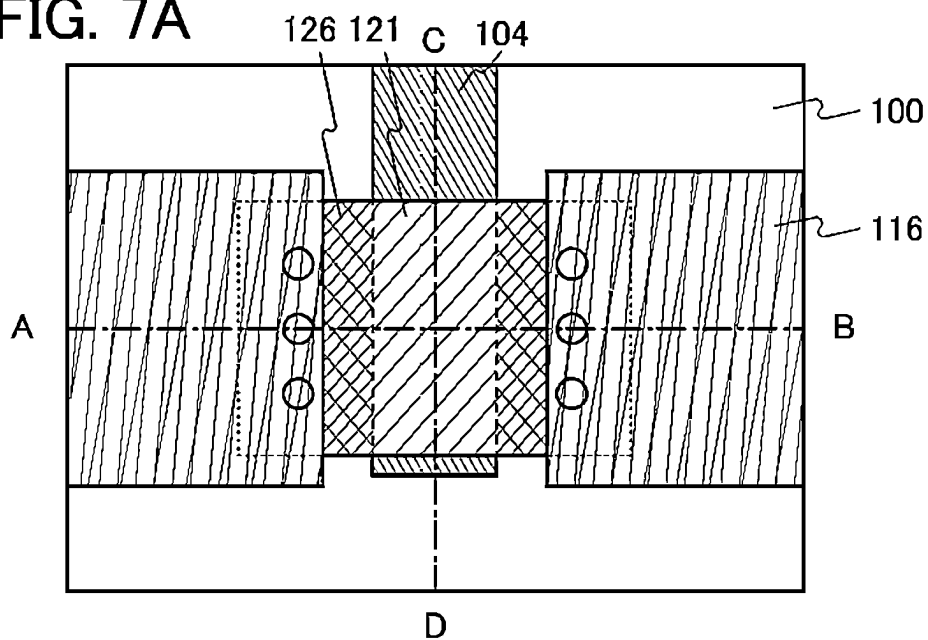


FIG. 7B

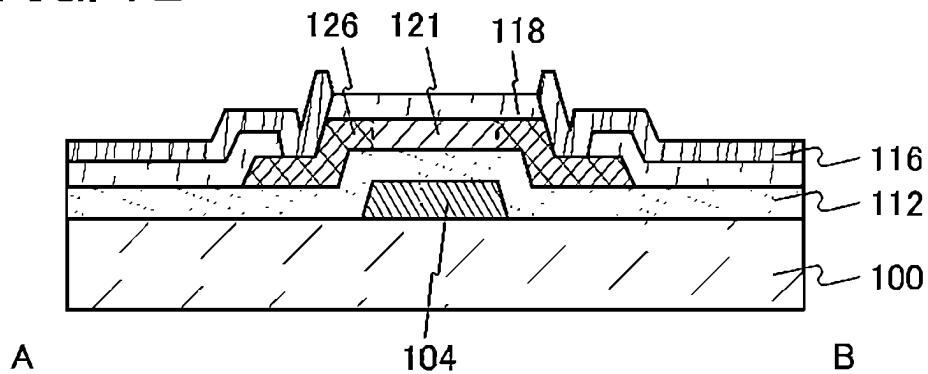


FIG. 7C

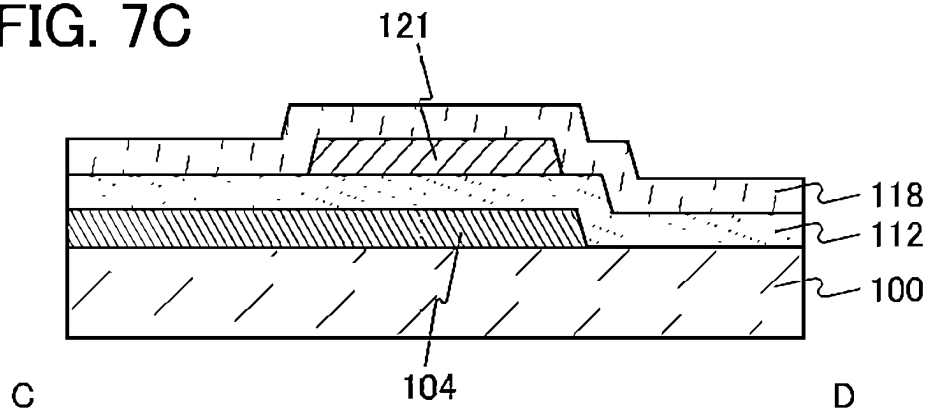




FIG. 9A

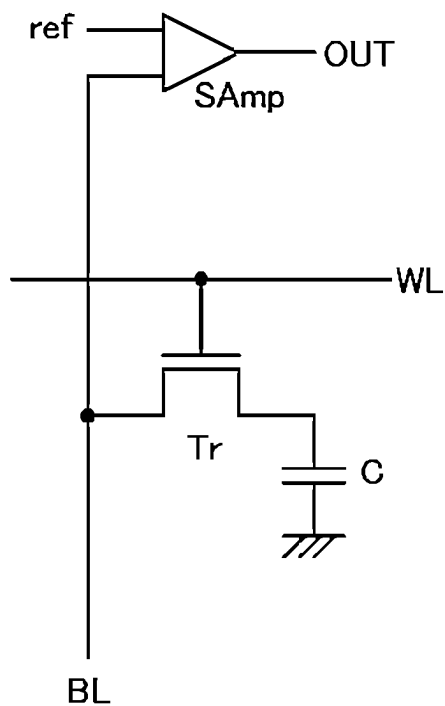


FIG. 9B

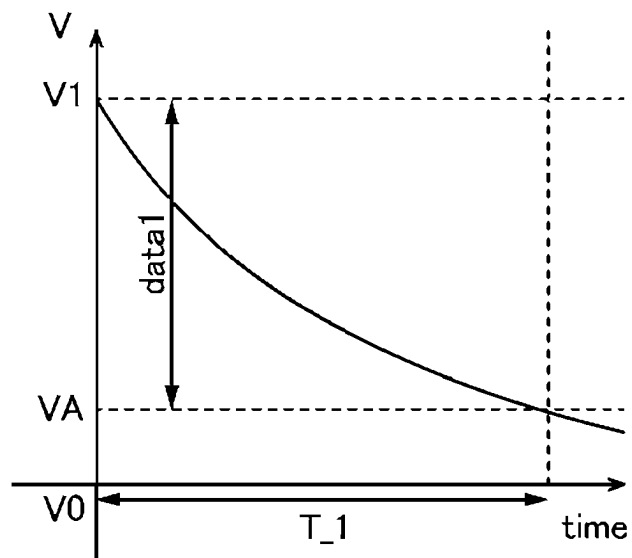


FIG. 10A

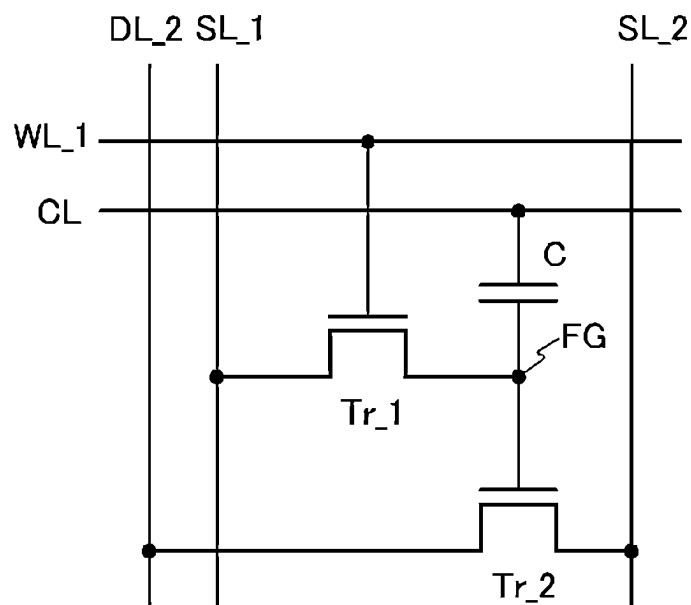


FIG. 10B

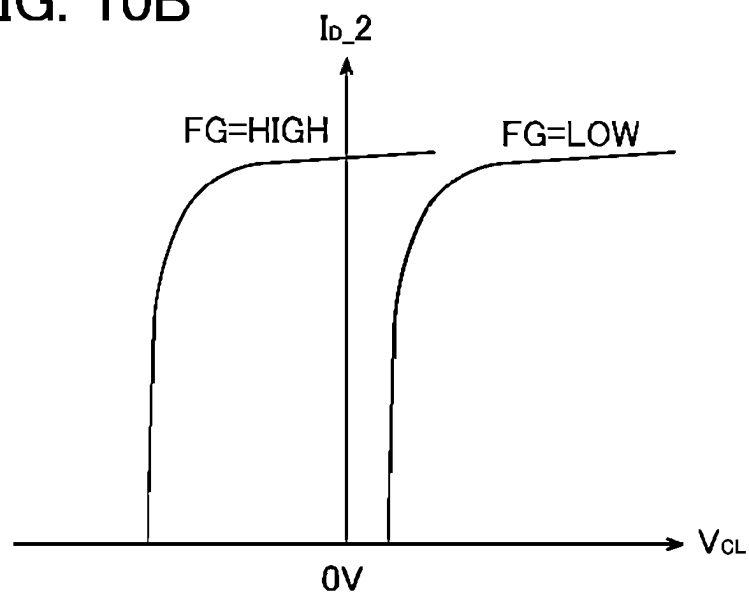


FIG. 11

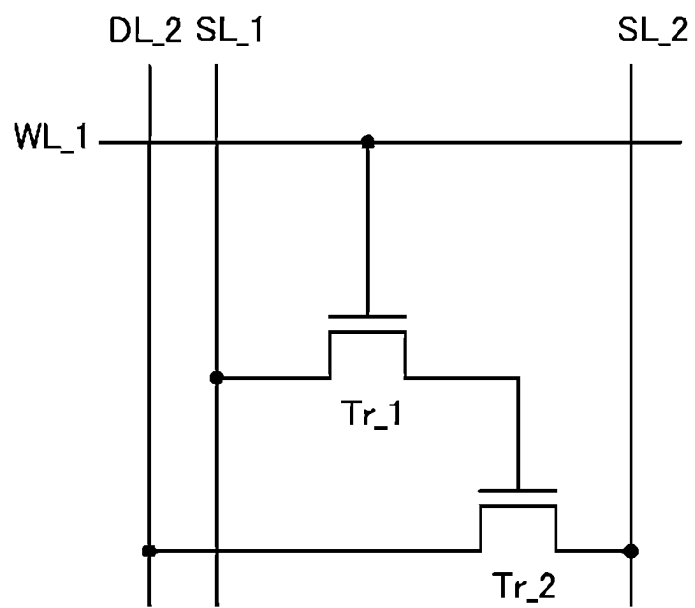


FIG. 12A

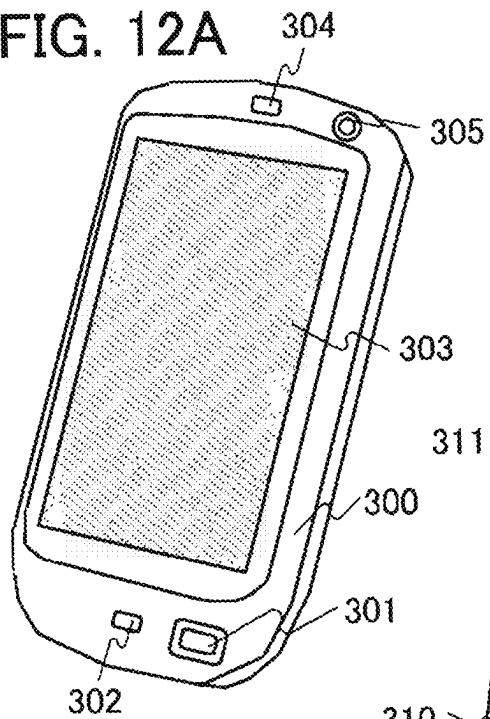


FIG. 12B

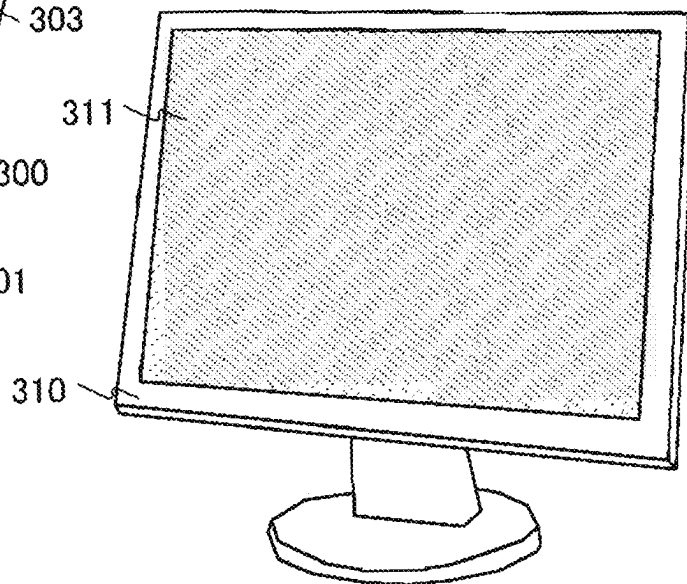


FIG. 12C

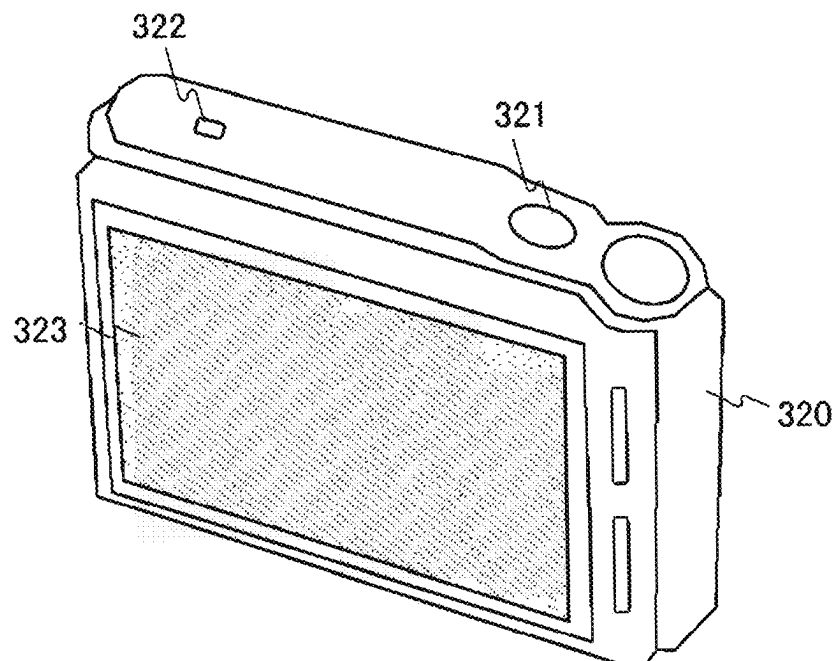


FIG. 13A

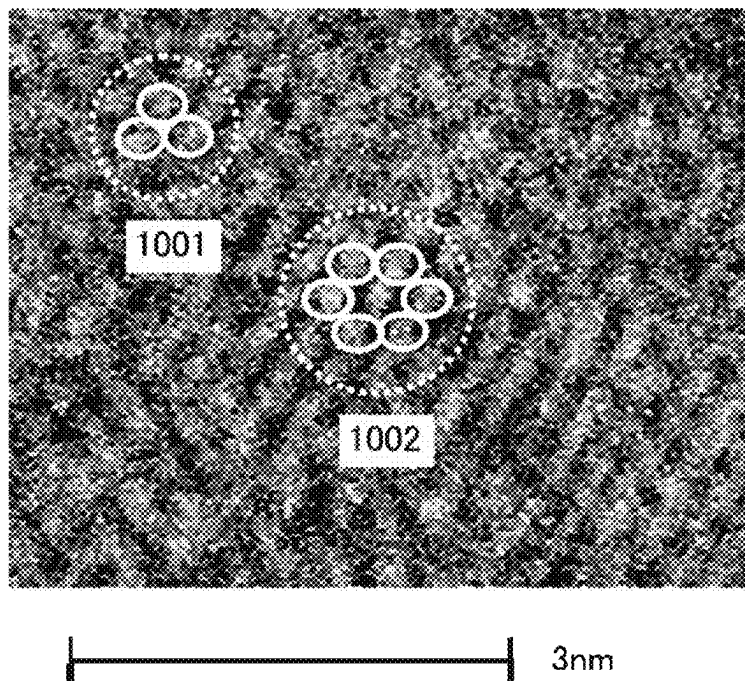


FIG. 13B

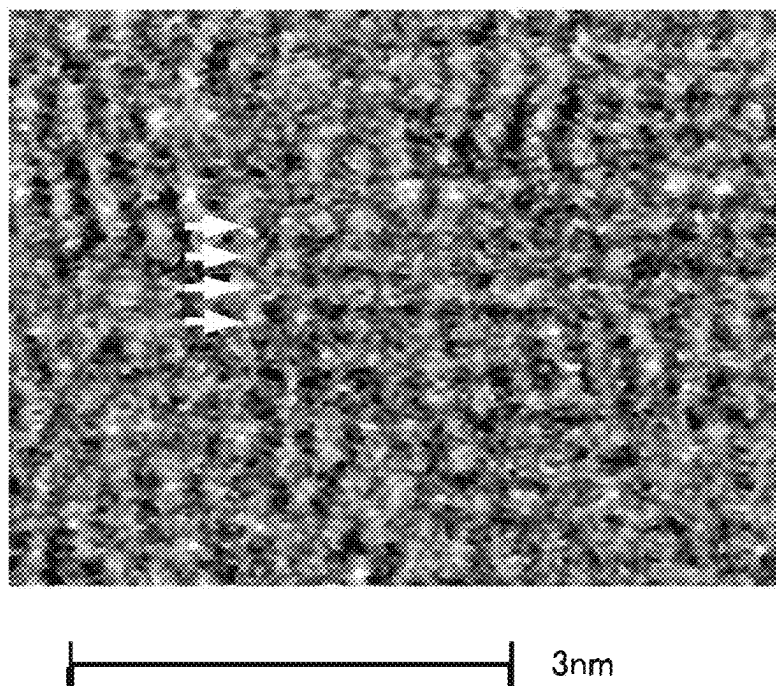




FIG. 14A

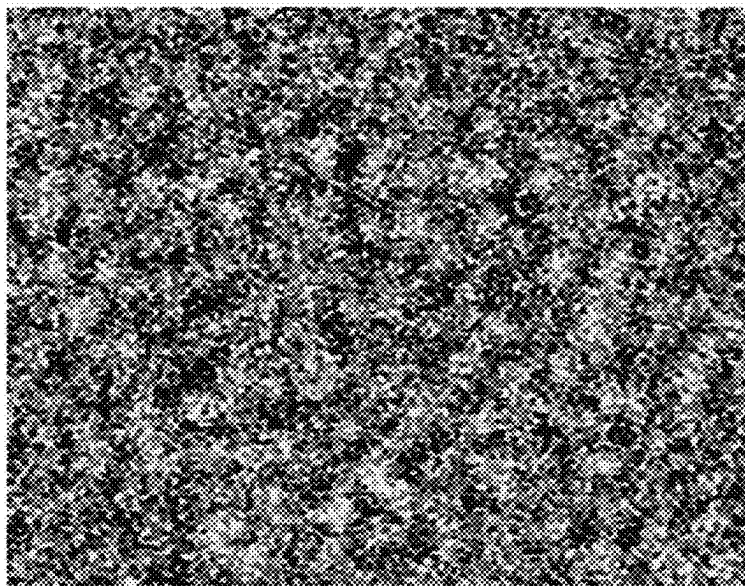


FIG. 14B

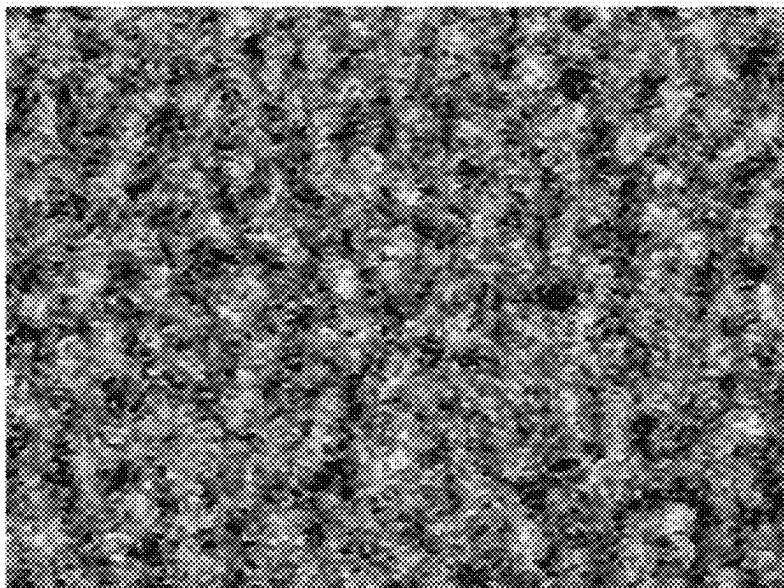


FIG. 15

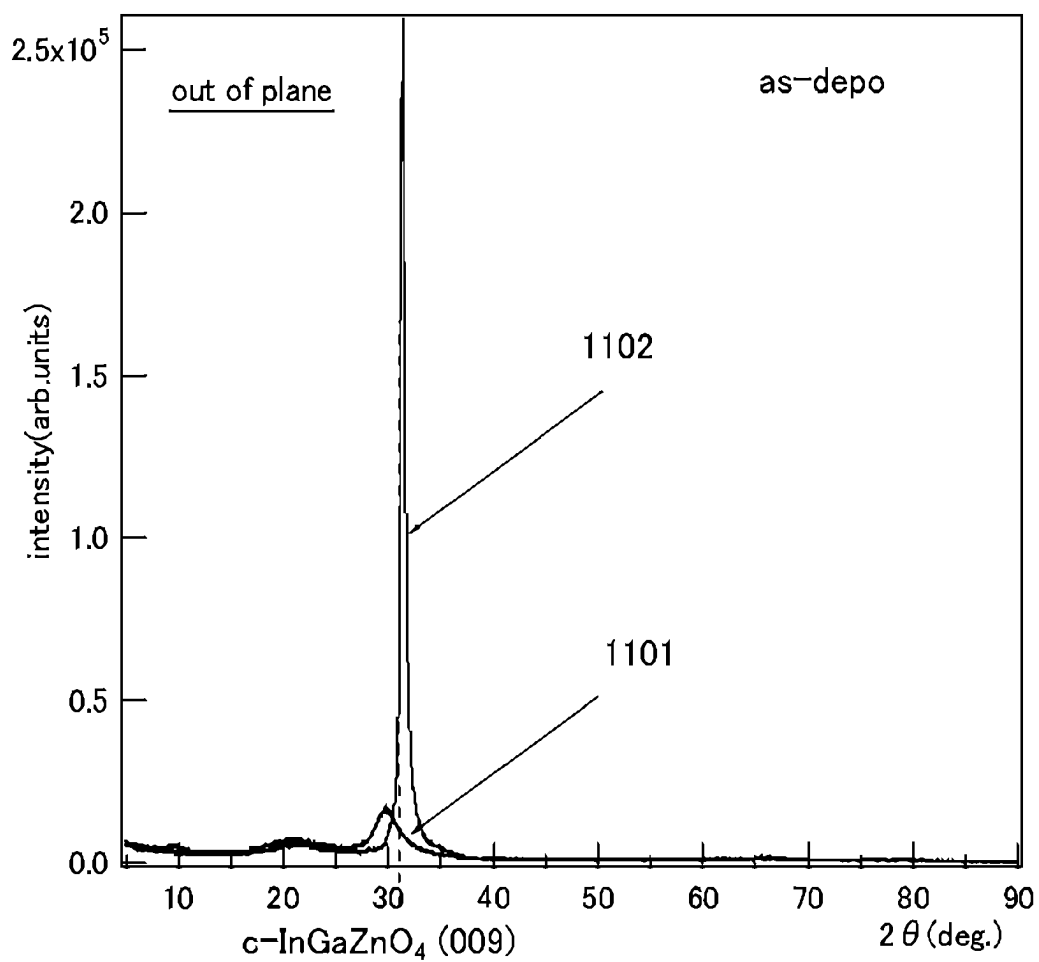


FIG. 16

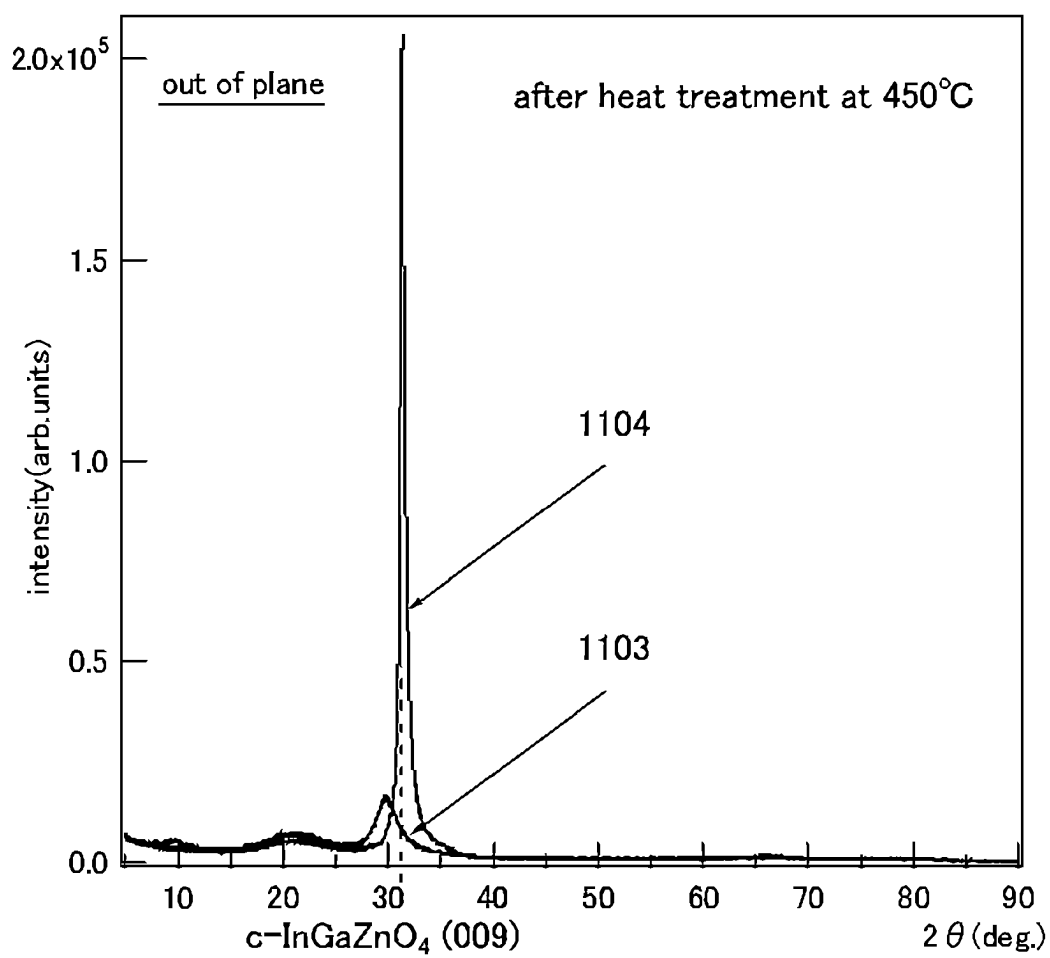


FIG. 17

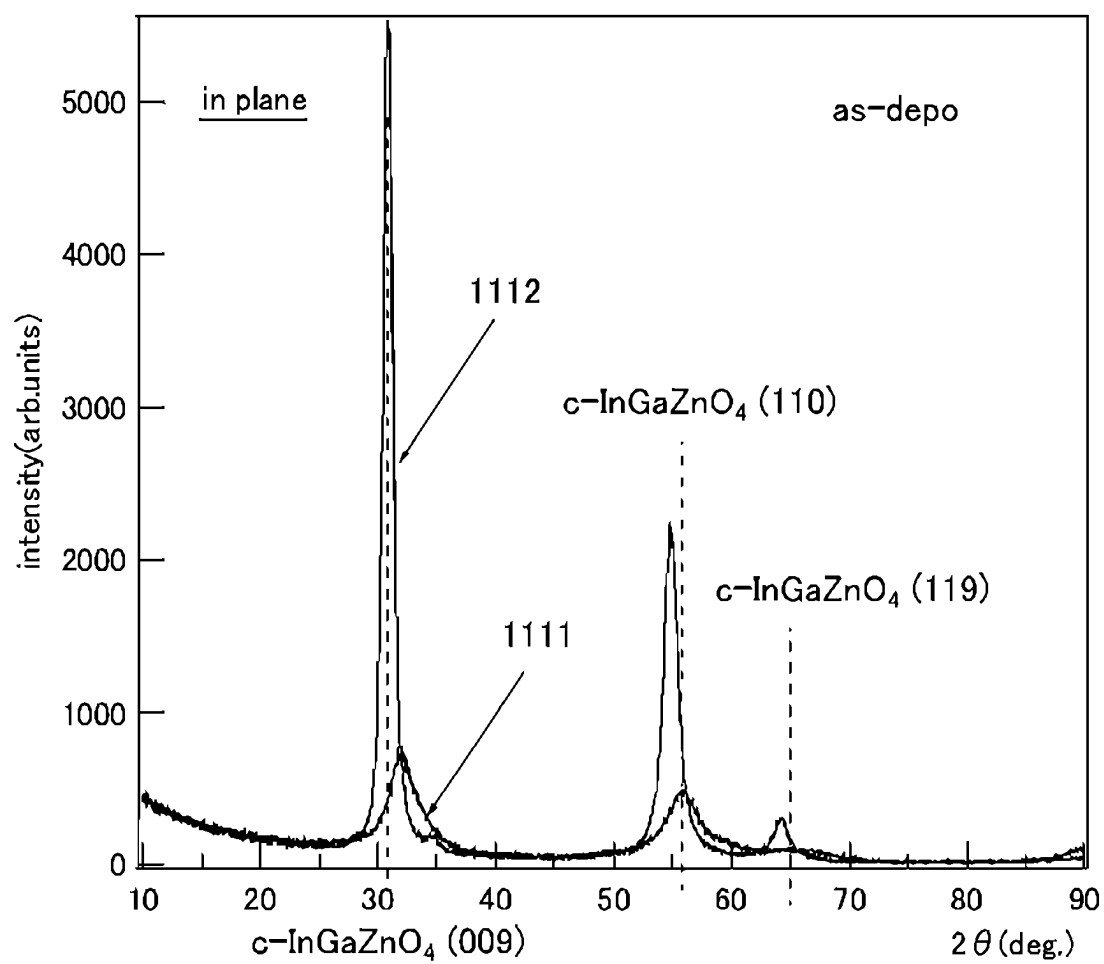


FIG. 18

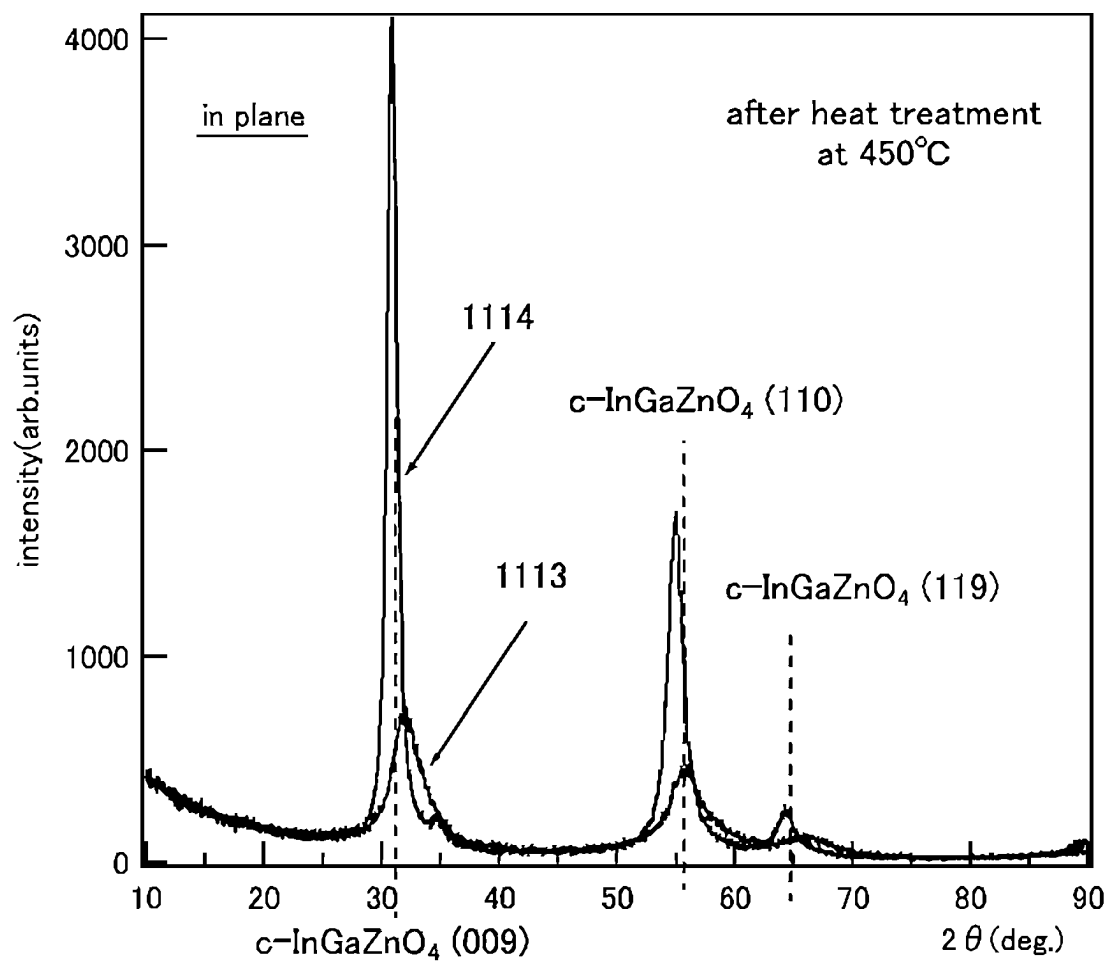


FIG. 19

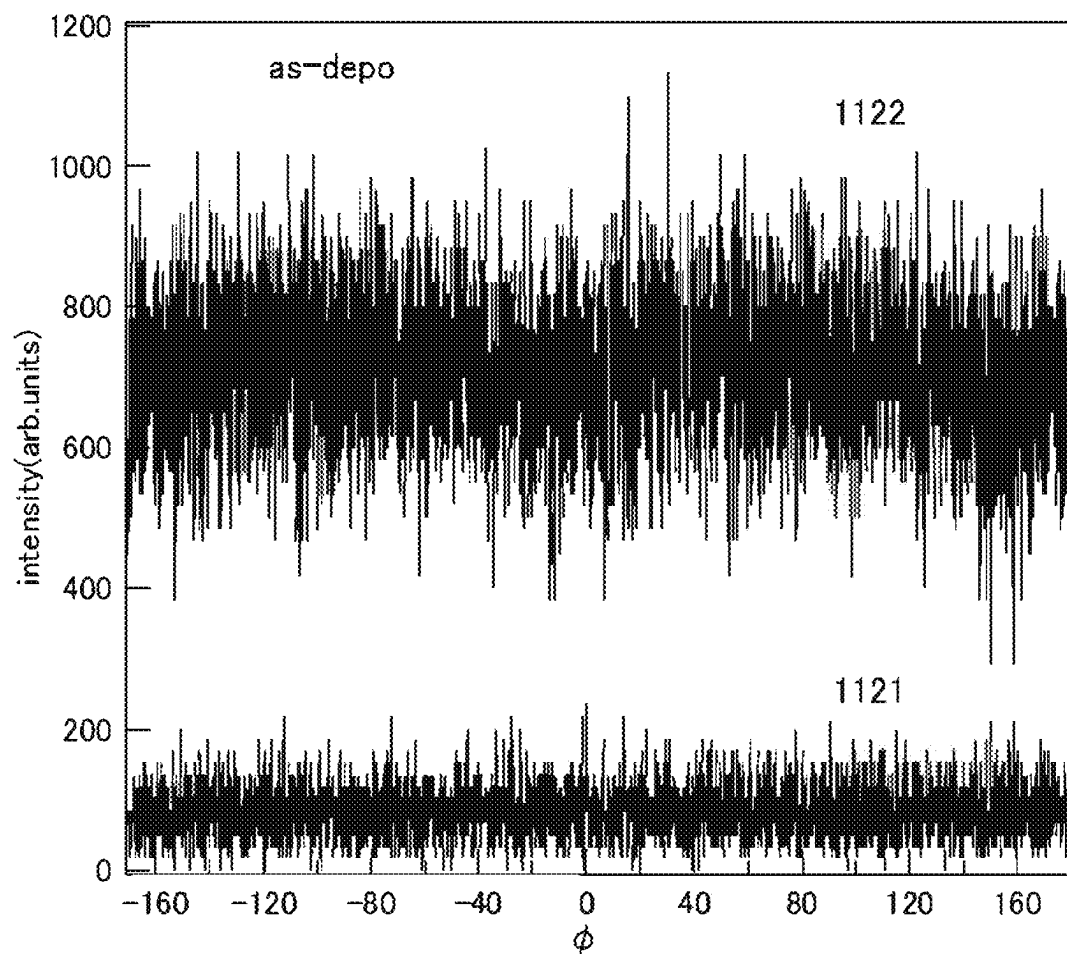


FIG. 20

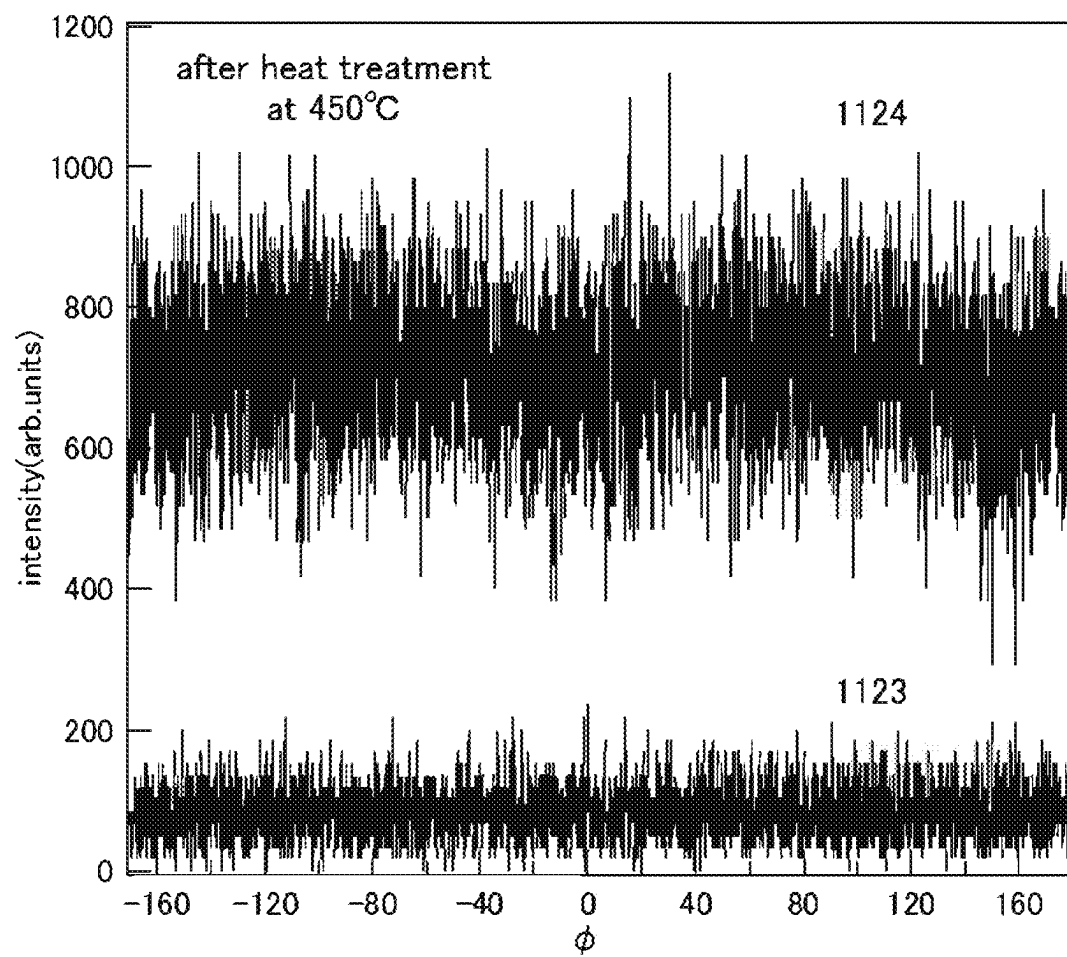


FIG. 21

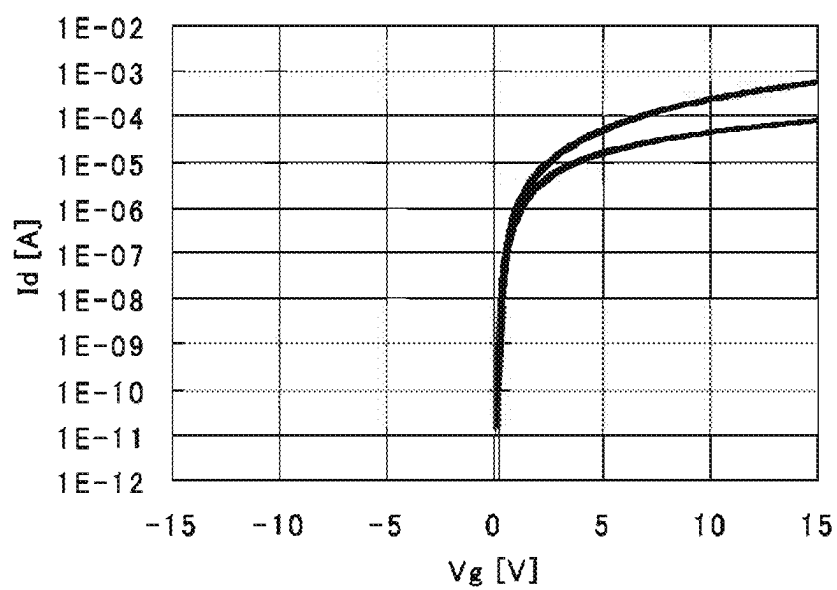




FIG. 22A

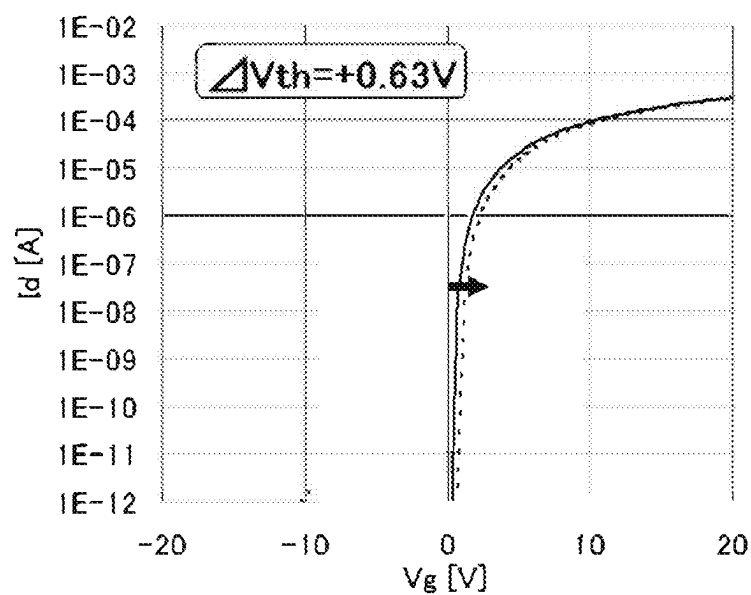


FIG. 22B

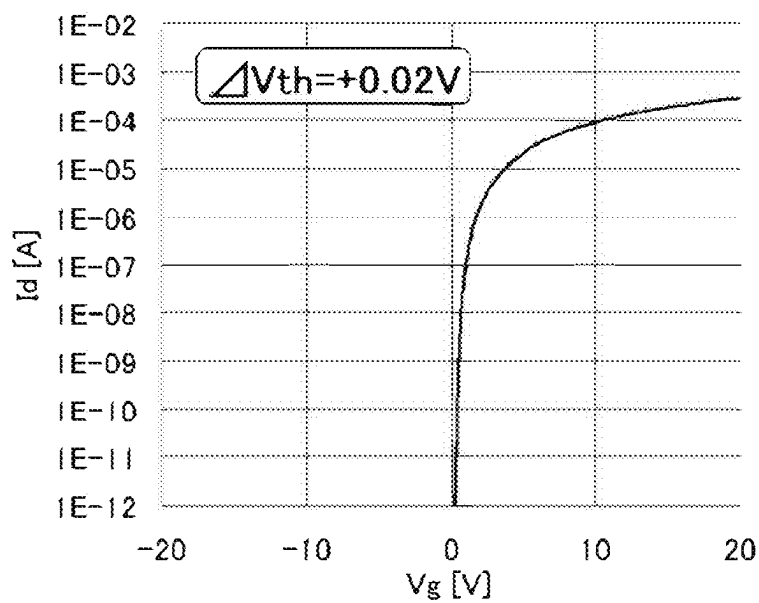


FIG. 23A

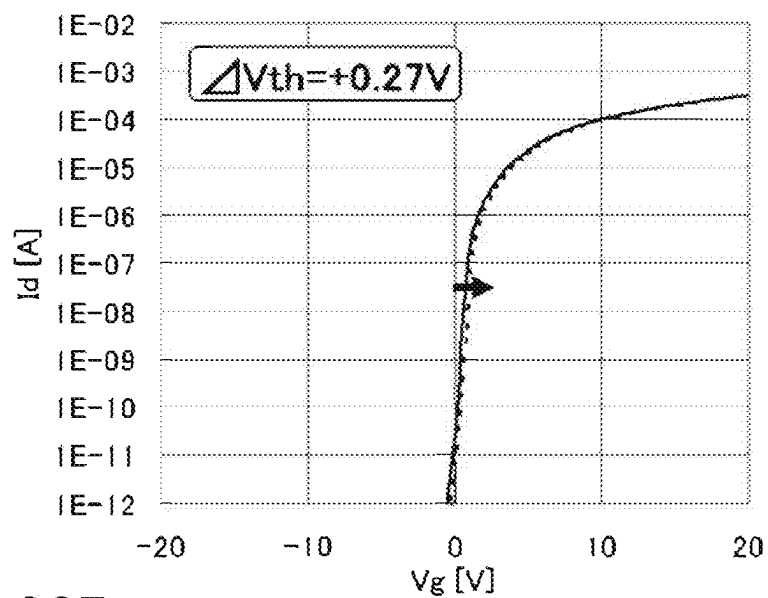


FIG. 23B

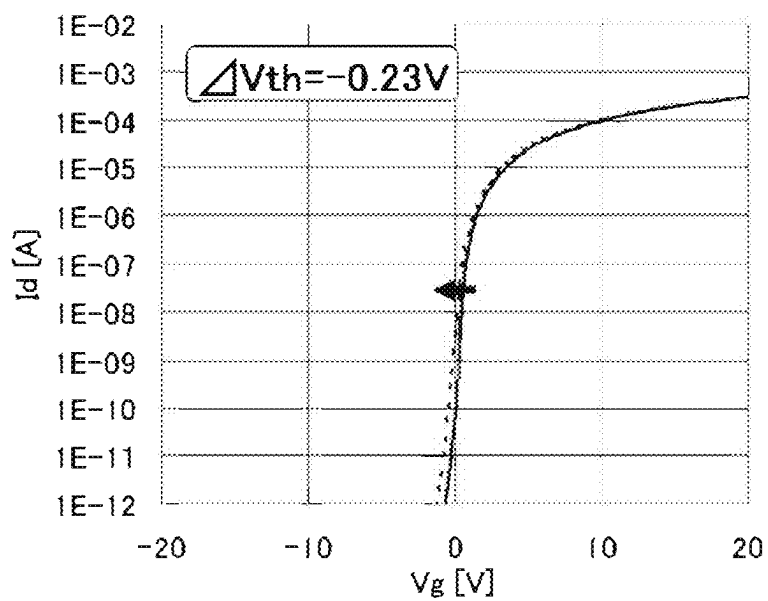


FIG. 24

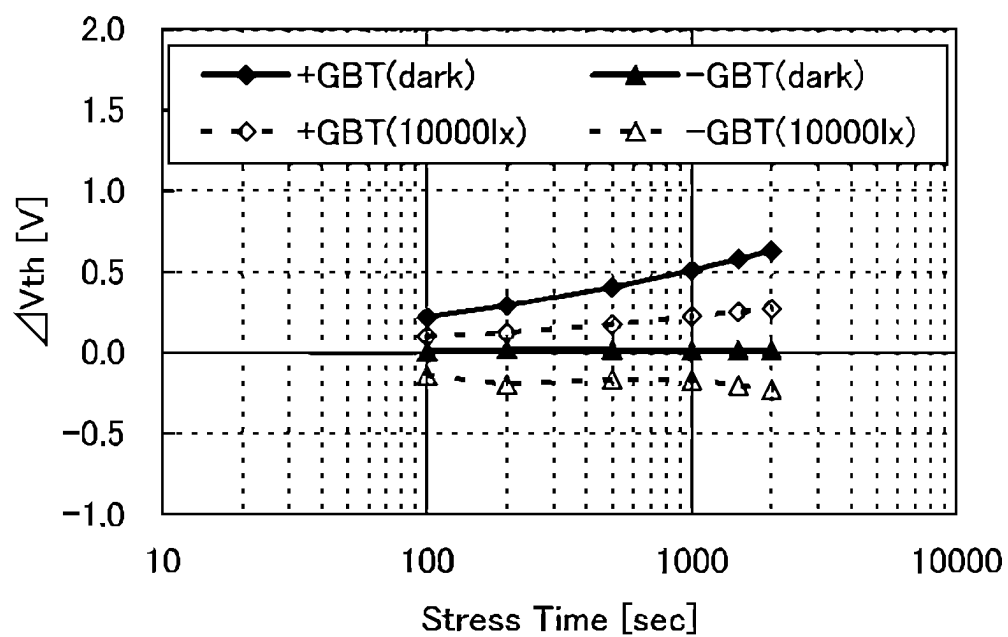


FIG. 25A

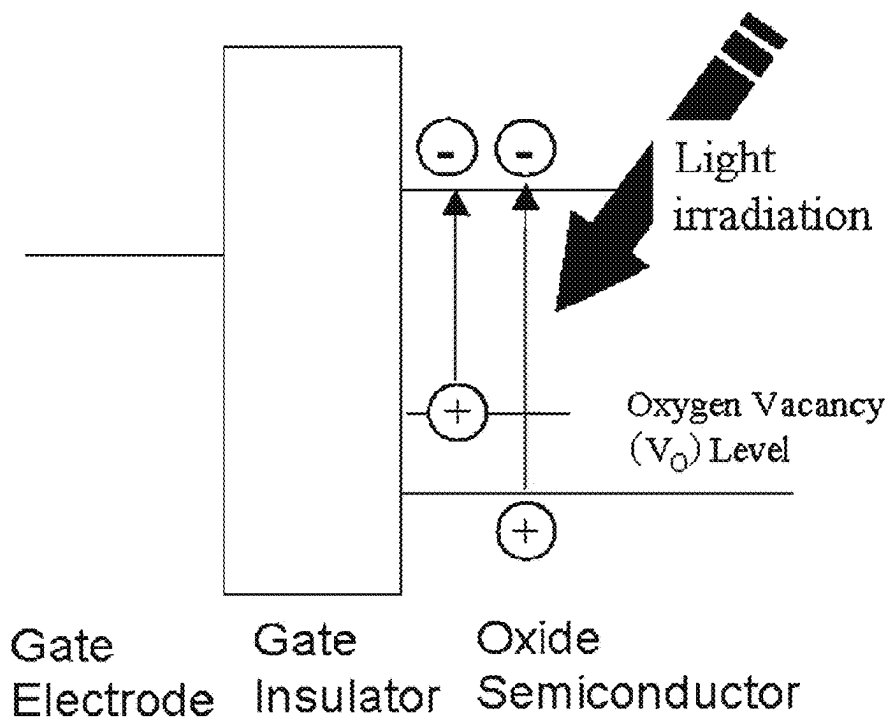
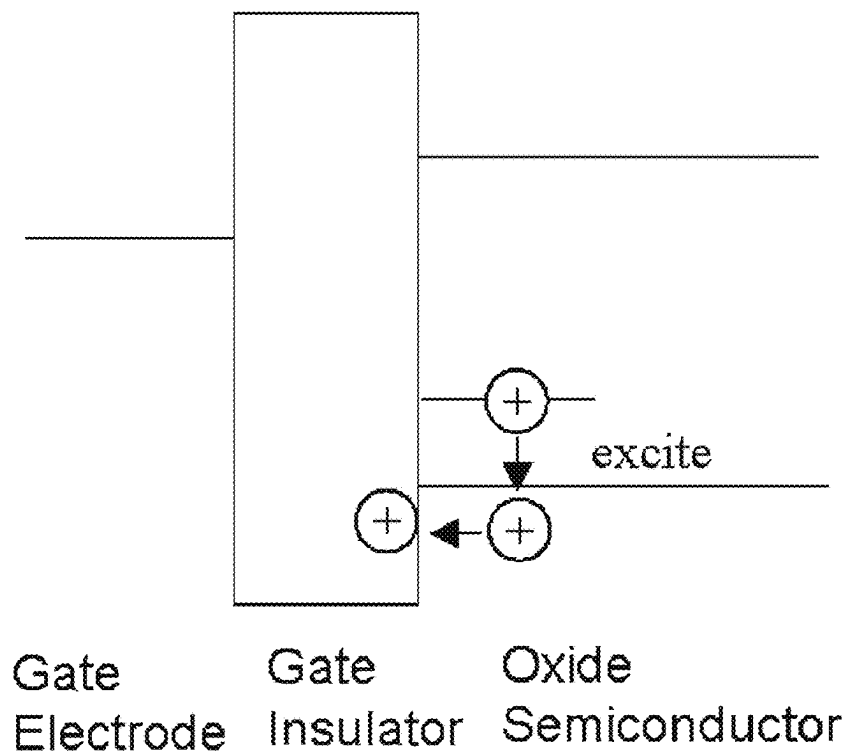


FIG. 25B



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# OXIDE MATERIAL AND SEMICONDUCTOR DEVICE

## TECHNICAL FIELD

The present invention relates to a semiconductor device which includes a circuit including a semiconductor element such as a transistor, and a method for manufacturing the semiconductor device. For example, the present invention relates to a power device which is mounted on a power supply circuit; a semiconductor integrated circuit including a memory, a thyristor, a converter, an image sensor, or the like; and an electronic device on which an electro-optical device typified by a liquid crystal display panel, a light-emitting display device including a light-emitting element, or the like is mounted as a component. Moreover, the present invention relates to an oxide used in the semiconductor device.

In this specification, a "semiconductor device" generally refers to a device which can function by utilizing semiconductor characteristics; an electrooptic device, a display device such as a light-emitting display device, a semiconductor circuit, and an electronic device are all included in semiconductor devices.

## BACKGROUND ART

Many transistors formed over a glass substrate or the like are manufactured using amorphous silicon, polycrystalline silicon, or the like, as typically seen in liquid crystal display devices. Although transistors including amorphous silicon have low field effect mobility, they can be formed over a larger glass substrate. On the other hand, although transistors including polycrystalline silicon have high field effect mobility, they are not suitable for being formed over a larger glass substrate.

Other than a transistor formed using silicon, a technique in which a transistor is formed using an oxide semiconductor and applied to an electronic device or an optical device has attracted attention. For example, a technique of manufacturing a transistor by using zinc oxide or In—Ga—Zn—O-based oxide as oxide semiconductor, and of using the transistor for a switching element of a pixel of a display device and the like is disclosed in Patent Document 1 and Patent Document 2.

## REFERENCE

[Patent Document 1] Japanese Published Patent Application No. 2007-123861

[Patent Document 2] Japanese Published Patent Application No. 2007-096055

## DISCLOSURE OF INVENTION

An object of one embodiment of the present invention is to provide a material suitably used for a semiconductor included in a transistor, a diode, or the like.

Another object is to provide a highly reliable semiconductor device which can be manufactured with use of a large-sized substrate such as a mother glass for mass production.

Electric characteristics of a transistor is easily affected by an electron state at an interface between an oxide semiconductor film and a gate insulating film in contact with the oxide semiconductor film. When the interface between the oxide semiconductor film and the gate insulating film is in

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an amorphous state during the manufacturing the transistor or after manufacture of the transistor, the defect density at the interface is high, and thus electric characteristics of the transistor is likely to be unstable.

Further, electric characteristics of a transistor in which an oxide semiconductor film is used for a channel are changed by irradiation with visible light or ultraviolet light.

In view of such problems, an object of one embodiment of the present invention is to provide a semiconductor device including a transistor in which an electron state at an interface between an oxide semiconductor film and a gate insulating film in contact with the oxide semiconductor film is favorable.

Further, an object of one embodiment of the present invention is to manufacture a highly reliable semiconductor device by giving stable electric characteristics to a transistor in which an oxide semiconductor film is used for a channel.

An oxide material including crystal with c-axis alignment, which has a triangular or hexagonal atomic arrangement when seen from the direction of the a-b plane, a surface, or an interface. In addition, in the crystal, the direction of the a-axis or the b-axis is varied in the a-b plane.

Note that the oxide material may contain zinc. When zinc is contained, it becomes easy to form an oxide material including crystal with c-axis alignment, which has a triangular or hexagonal atomic arrangement when seen from the direction of the a-b plane, a surface, or an interface and in which the direction of the a-axis or the b-axis is varied in the a-b plane.

Alternatively, the oxide material contains two or more kinds of elements selected from indium, gallium, zinc, tin, titanium, and aluminum.

The oxide material can be formed by a sputtering method, a molecular beam epitaxy method, an atomic layer deposition method, a pulsed laser deposition method, or the like.

The oxide material can be formed by stacking two kinds of films whose compositions are different. Alternatively, after two kinds of films are stacked, the oxide material can be formed by crystallizing the films.

One embodiment of the present invention is an oxide material including a plurality of metal oxide layers which are bonded through tetracoordinate oxygen atoms (hereinafter referred to as tetracoordinate O). In addition, one metal oxide layer is a layer which includes a tetracoordinate central metal atom, a pentacoordinate central metal atom, or a central metal atom that can have either five ligands or six ligands and extends in a planar direction by bonding the central metal atoms through a tricoordinate oxygen atom (hereinafter referred to as tricoordinate O) or tetracoordinate O.

In the case where the oxide material has conductivity, the oxide material can be used for a material of a gate electrode of a transistor. The gate electrode may be formed by stacking a film including the oxide material and a metal film.

In the case where the oxide material has conductivity, the oxide material can be used for a source electrode and a drain electrode of a transistor. Note that the source electrode and the drain electrode may be formed by stacking the oxide material and a metal film.

In the case where the oxide material has semiconductor characteristics, a film including the oxide material can be used for an active layer of a transistor. In that case, the film including the oxide material is, for example, provided in contact with a conductive film functioning as a source electrode and a drain electrode and an insulating film in the transistor. Note that the insulating film functions as a gate

insulating film, a base insulating film, or an interlayer insulating film in the transistor.

According to one embodiment of the present invention, a semiconductor device having excellent electric characteristics can be provided.

Further, mass production of highly reliable semiconductor devices can be performed with use of a large-sized substrate such as a mother glass.

#### BRIEF DESCRIPTION OF DRAWINGS

FIGS. 1A to 1D illustrate a structure of an oxide material according to one embodiment of the present invention.

FIGS. 2A to 2C are a top view and cross-sectional views illustrating an example of a semiconductor device which is one embodiment of the present invention.

FIGS. 3A to 3C are a top view and cross-sectional views illustrating an example of a semiconductor device which is one embodiment of the present invention.

FIGS. 4A to 4C are a top view and cross-sectional views illustrating an example of a semiconductor device which is one embodiment of the present invention.

FIGS. 5A to 5C are a top view and cross-sectional views illustrating an example of a semiconductor device which is one embodiment of the present invention.

FIGS. 6A to 6C are a top view and cross-sectional views illustrating an example of a semiconductor device which is one embodiment of the present invention.

FIGS. 7A to 7C are a top view and cross-sectional views illustrating an example of a semiconductor device which is one embodiment of the present invention.

FIG. 8 is a circuit diagram illustrating an example of a liquid crystal display device including a transistor which is one embodiment of the present invention.

FIGS. 9A and 9B are a circuit diagram illustrating an example of a semiconductor memory device including a transistor which is one embodiment of the present invention and a graph showing electric characteristics.

FIGS. 10A and 10B are a circuit diagram illustrating an example of a semiconductor memory device including a transistor which is one embodiment of the present invention and a graph showing electric characteristics.

FIG. 11 is a circuit diagram illustrating an example of a semiconductor memory device including a transistor which is one embodiment of the present invention.

FIGS. 12A to 12C are perspective views each illustrating an example of an electronic device which is one embodiment of the present invention.

FIGS. 13A and 13B show a planar image and a cross-sectional image of an oxide film including CAAC, which are obtained with HAADF-STEM.

FIGS. 14A and 14B show a planar image and a cross-sectional image of an oxide film which does not include CAAC, which are obtained with HAADF-STEM.

FIG. 15 shows XRD spectra of oxide films including CAAC as deposited (as-depo).

FIG. 16 shows XRD spectra of oxide films including CAAC after heat treatment.

FIG. 17 shows XRD spectra of oxide films including CAAC as deposited (as-depo).

FIG. 18 shows XRD spectra of oxide films including CAAC after heat treatment.

FIG. 19 shows XRD spectra of oxide films including CAAC as deposited (as-depo).

FIG. 20 shows XRD spectra of oxide films including CAAC after heat treatment.

FIG. 21 is a graph showing Vg-Id curves of a transistor.

FIGS. 22A and 22B are graphs showing results of a +BT test and a -BT test.

FIGS. 23A and 23B are graphs showing results of a +BT test and a -BT test performed while transistors are irradiated with light.

FIG. 24 is a graph showing time dependence of the amount of shift in the threshold voltage  $V_{th}$  ( $\Delta V_{th}$ ) on various kinds of stress conditions.

FIGS. 25A and 25B are schematic diagrams showing mechanism of negative-bias temperature stress photodegradation.

#### BEST MODE FOR CARRYING OUT THE INVENTION

Hereinafter, embodiments of the present invention will be described in detail with reference to the accompanying drawings. However, the present invention is not limited to the description below, and it is easily understood by those skilled in the art that modes and details disclosed herein can be modified in various ways unless departing from the spirit and the scope of the present invention. Therefore, the present invention is not construed as being limited to description of the embodiments. In describing structures of the present invention with reference to the drawings, the same reference numerals are used in common for the same portions in different drawings. Note that the same hatch pattern is applied to similar parts, and the similar parts are not especially denoted by reference numerals in some cases.

Before the present invention is described, terms used in this specification will be briefly explained. First, when one of a source and a drain of a transistor is called a drain, the other is called a source in this specification. That is, they are not distinguished depending on the potential level. Therefore, a portion called a source in this specification can be alternatively referred to as a drain.

Note that voltage refers to a potential difference between a predetermined potential and a reference potential (e.g., a ground potential) in many cases. Accordingly, voltage, potential and a potential difference can be referred to as potential, voltage, and a voltage difference, respectively.

Further, even when the expression "to be connected" is used in this specification, there is a case in which no physical connection is made in an actual circuit and a wiring is just extended.

Note that the ordinal numbers such as "first" and "second" in this specification are used for convenience and do not denote the order of steps or the stacking order of layers. In addition, the ordinal numbers in this specification do not denote particular names which specify the present invention.

#### Embodiment 1

In this embodiment, a method for forming an oxide film including a crystal with c-axis alignment, which has a triangular or hexagonal atomic arrangement when seen from the direction of an a-b plane, a surface, or an interface, will be described. In the crystal, metal atoms are arranged in a layered manner, or metal atoms and oxygen atoms are arranged in a layered manner along the c-axis, and the direction of the a-axis or the b-axis is varied in the a-b plane (or the surface, or at the interface) (the crystal rotates around the c-axis). Such a crystal is also referred to as a c-axis aligned crystal (CAAC).

In a broad sense, an oxide including CAAC means a non-single-crystal oxide material including a phase which has a triangular, hexagonal, regular triangular, or regular

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hexagonal atomic arrangement when seen from the direction perpendicular to the a-b plane and in which metal atoms are arranged in a layered manner or metal atoms and oxygen atoms are arranged in a layered manner when seen from the direction perpendicular to the c-axis direction. Further, the oxide film including CAAC may have a grain boundary, which is a film having a novel structure in which crystals are not necessarily aligned in the a-b plane direction.

CAAC is not single crystal. In addition, the oxide film including CAAC is not composed of only an amorphous component. Although the oxide film including CAAC includes a crystallized portion (crystalline portion), a boundary between one crystalline portion and another crystalline portion is not clear in some cases.

Nitrogen may be substituted for part of oxygen included in the oxide film including CAAC. The c-axes of individual crystalline portions including CAAC may be aligned in a certain direction (e.g., a direction perpendicular to a surface of a substrate over which the oxide film including CAAC is formed or a surface of the oxide film including CAAC). Alternatively, the normals of the a-b planes of the individual crystalline portions including CAAC may be aligned in a certain direction (e.g., a direction perpendicular to a surface of a substrate over which the oxide film including CAAC is formed or a surface of the oxide film including CAAC).

The oxide film including CAAC becomes a conductor, a semiconductor, or an insulator depending on its composition or the like. The CAAC transmits or does not transmit visible light depending on its composition or the like.

An example of an oxide including such a CAAC is a material which is formed into a film shape and has a triangular or hexagonal atomic arrangement when observed from the direction perpendicular to a surface of the film, a surface of a supporting substrate, or an interface and in which metal atoms are arranged in a layered manner or metal atoms and oxygen atoms (or nitrogen atoms) are arranged in a layered manner when a cross section of the film is observed.

The CAAC will be described in detail with reference to FIGS. 1A to 1D. In FIGS. 1A to 1D, the vertical direction corresponds to the c-axis direction and a plane perpendicular to a flat surface in FIGS. 1A to 1D corresponds to the a-b plane, unless otherwise specified. When the expressions "an upper half" and "a lower half" are simply used, they refer to an upper half above the a-b plane and a lower half below the a-b plane (an upper half and a lower half with respect to the a-b plane).

FIG. 1A illustrates a structure having one hexacoordinate metal atom M<sub>1</sub> and six tetracoordinate O proximate to the metal atom M<sub>1</sub>. Such a structure in which one metal atom and proximate oxygen atoms to the metal atom are only illustrated is called a subunit here. The structure in FIG. 1A is actually an octahedral structure, but is illustrated as a planar structure for simplicity. Note that three tetracoordinate O exist in each of an upper half and a lower half in FIG. 1A. Although the subunit including only one metal atom is typically illustrated, actually, a plurality of subunits are bonded through tricoordinate O or tetracoordinate O to extend in a planar direction, so that a metal oxide layer is formed.

FIG. 1B illustrates a structure having one pentacoordinate metal atom M<sub>2</sub>, three tricoordinate O proximate to the metal atom M<sub>2</sub>, and two tetracoordinate O proximate to the metal atom M<sub>2</sub>. All the tricoordinate O atoms exist on the a-b plane. One tetracoordinate O exists in each of an upper half and a lower half in FIG. 1B.

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FIG. 1C illustrates a structure having one tetracoordinate metal atom M<sub>3</sub> and four tetracoordinate O proximate to the metal atom M<sub>3</sub>. In FIG. 1C, one tetracoordinate O exists in an upper half and three tetracoordinate O exist in a lower half.

A metal atom whose coordination number is 4, 5, or 6 is bonded to another metal atom through a tetracoordinate O. Specifically, a metal atom is bonded to another metal atom through tetracoordinate O, the number of which is four in total. For example, in the case where the hexacoordinate metal atom M<sub>1</sub> is bonded through three tetracoordinate O atoms in the upper half, it is bonded to the pentacoordinate metal atom M<sub>2</sub> through tetracoordinate O in the upper half of the pentacoordinate metal atom M<sub>2</sub>, the pentacoordinate metal atom M<sub>2</sub> through tetracoordinate O in the lower half of the pentacoordinate metal atom M<sub>2</sub>, or the tetracoordinate metal atom M<sub>3</sub> through the tetracoordinate O in the upper half of the tetracoordinate metal atom M<sub>3</sub>.

Besides, subunits are bonded to each other so that the total electric charge in the layered structure is 0.

Here, electric charge of a tricoordinate O for making one bond and electric charge of a tetracoordinate O for making one bond can be assumed to be -0.667 and -0.5, respectively. For example, electric charge of (hexacoordinate or pentacoordinate) In, electric charge of (tetracoordinate) Zn, electric charge of (pentacoordinate) Ga, and electric charge of (pentacoordinate or hexacoordinate) Sn are +3, +2, +3, and +4, respectively. Therefore, electric charge of each of a subunit including In, a subunit including Zn, and a subunit including Ga is 0. Thus, the total electric charge of a layered structure having a combination of such subunits is always 0. On the other hand, electric charge of a subunit including Sn is +1. Therefore, electric charge of -1, which cancels +1, is needed to form a layered structure including Sn. As a structure having electric charge of -1, a structure in which two subunits including Zn are bonded can be given. For example, when one subunit including Sn is combined with one structure in which two subunits including Zn are bonded, electric charge is canceled, whereby the total electric charge in the layered structure can be 0.

FIG. 1D illustrates an In—Sn—Zn—O-based layered structure. For simplicity, tricoordinate O is omitted, and as for tetracoordinate O, only the number of tetracoordinate O is shown. An In atom can have either five ligands or six ligands. When a structure in which one cycle illustrated in FIG. 1D is repeated is formed, In—Sn—Zn—O-based crystal (In<sub>2</sub>SnZn<sub>3</sub>O<sub>8</sub>) can be obtained. Note that a layered structure of the In—Sn—Zn—O-based crystal can be expressed as a composition formula, In<sub>2</sub>SnZn<sub>3</sub>O<sub>7</sub>(ZnO)<sub>m</sub> (m is 0 or a natural number). In addition, in a similar manner, with use of an In—Sn—Ga—Zn—O-based material, an In—Ga—Zn—O-based material, an In—Si—Zn—O-based material, an In—Al—Zn—O-based material, a Sn—Ga—Zn—O-based material, an Al—Ga—Zn—O-based material, a Sn—Al—Zn—O-based material, an In—Zn—O-based material, a Sn—Zn—O-based material, an Al—Zn—O-based material, a Zn—Mg—O-based material, a Sn—Mg—O-based material, an In—Mg—O-based material, an In—Ga—O-based material, an In—O-based material, a Sn—O-based material, a Zn—O-based material, or the like, crystal of oxide can be obtained.

Next, a method for forming an oxide film including CAAC is described.

First, a first oxide film is formed over a substrate by a sputtering method, a molecular beam epitaxy method, an atomic layer deposition method, or a pulsed laser deposition method. Note that by heating the substrate at the time of film

formation, an oxide film in which the ratio of a crystalline region to an amorphous region is high can be obtained. For example, the substrate temperature is higher than or equal to 150° C. and lower than or equal to 450° C., preferably, higher than or equal to 200° C. and lower than or equal to 350° C.

Crystallization of the oxide film including CAAC can be further promoted by increasing the substrate temperature.

Next, the substrate may be subjected to first heat treatment. With the first heat treatment, the ratio of the crystalline region to the amorphous region in the oxide film can be further increased. The first heat treatment may be performed at a temperature, for example, higher than or equal to 200° C. and lower than the strain point of the substrate, and is preferably performed at a temperature higher than or equal to 250° C. and lower than or equal to 450° C. The first heat treatment is performed in an oxidizing atmosphere, an inert atmosphere, or a reduced-pressure atmosphere, but the atmosphere is not limited thereto. The treatment time is 3 minutes to 24 hours. As the treatment time is prolonged, the ratio of the crystalline region to the amorphous region in the oxide film can be increased. However, heat treatment for longer than 24 hours is not preferable because the productivity is reduced.

The oxidizing atmosphere is an atmosphere containing an oxidizing gas. The oxidizing gas is oxygen, ozone, nitrous oxide, or the like, and it is preferable that the oxidation gas does not contain water, hydrogen, and the like. For example, the purity of oxygen, ozone, or nitrous oxide to be introduced into a heat treatment apparatus is greater than or equal to 8N (99.999999%), preferably greater than or equal to 9N (99.9999999%), i.e., the impurity concentration is lower than or equal to 1 ppm, preferably, lower than 0.1 ppm. As the oxidizing atmosphere, an oxidizing gas and an inert gas may be mixed to be used. In that case, the mixture contains an oxidizing gas at a concentration of higher than or equal to 10 ppm.

Further, an inert atmosphere refers to an atmosphere containing an inert gas (such as nitrogen or a rare gas (e.g., helium, neon, argon, krypton, or xenon)) as the main component. Specifically, the concentration of a reactive gas such as an oxidizing gas is lower than 10 ppm.

For the first heat treatment, a rapid thermal anneal (RTA) apparatus can be used. With use of the RTA apparatus, only in a short time, the heat treatment can be performed at a temperature higher than or equal to the strain point of the substrate. Thus, the time required for formation of the oxide film in which the ratio of a crystalline region to an amorphous region is high can be shortened.

Further, a material represented by  $\text{InMO}_3(\text{ZnO})_m$  ( $m$  is larger than 0) may be used as the oxide. Here,  $M$  represents one or more metal elements selected from Ga, Al, Mn, and Co. For example,  $M$  may be Ga, Ga and Al, Ga and Mn, Ga and Co, or the like.

Specifically, an In—Ga—Zn—O-based material containing nitrogen at a concentration higher than or equal to  $5 \times 10^{19}$  atoms/cm<sup>3</sup>, preferably higher than or equal to  $1 \times 10^{20}$  atoms/cm<sup>3</sup>, and lower than 7 at. %, becomes an oxide having a c-axis-aligned hexagonal crystal structure, which includes one layer containing Ga and Zn between an In—O crystal plane (a crystal plane containing indium and oxygen) and another In—O crystal plane (a crystal plane containing indium and oxygen). Alternatively, in the In—Ga—Zn—O-based oxide material containing nitrogen with the above range, a plurality of layers containing Ga and Zn may be provided between the In—O crystal planes.

Next, a second oxide film may be formed over the first oxide film, whereby an oxide stack may be formed. The second oxide film can be formed by the same method as the first oxide film.

When the substrate is heated while the second oxide film is formed, the second oxide film can be crystallized with use of the first oxide film as a seed crystal. At this time, to compose the first oxide film and the second oxide film using the same kind of element is referred to as “homo-growth”. Alternatively, to compose the first oxide film and the second oxide film using elements, at least one kind of which differs between the first oxide film and the second oxide film, is referred to as “hetero-growth”.

Note that second heat treatment may be performed after the second oxide film is formed. The second heat treatment may be performed in a manner similar to that of the first heat treatment. With the second heat treatment, an oxide stack in which the ratio of a crystalline region to an amorphous region is high can be obtained. Further, with the second heat treatment, the second oxide film can be crystallized with use of the first oxide film as a seed crystal. At this time, homo-growth in which the first oxide film and the second oxide film are composed of the same element may be caused. Alternatively, hetero-growth in which the first oxide film and the second oxide film are composed of elements, at least one kind of which differs between the first oxide film and the second oxide film, may be caused.

Through the above steps, an oxide film including CAAC can be formed.

This embodiment can be implemented in appropriate combination with the other embodiments.

## Embodiment 2

In this embodiment, an example of a transistor which includes the oxide film including CAAC described in Embodiment 1 will be described with reference to FIGS. 2A to 2C.

FIG. 2A is a top view of a transistor. FIGS. 2B and 2C illustrate a cross section A-B and a cross section C-D taken along a dashed-dotted line A-B and a dashed-dotted line C-D shown in FIG. 2A.

The cross section A-B of FIG. 2B is described in detail below.

The cross section A-B is a cross section of the transistor including a substrate 100, a gate electrode 104 over the substrate 100, a gate insulating film 112 covering the substrate 100 and the gate electrode 104, a semiconductor film 106 over the gate electrode 104 with the gate insulating film 112 positioned therebetween, a pair of electrodes 116 which is over the semiconductor film 106 and partly in contact with the semiconductor film 106, and an interlayer insulating film 118 covering the gate insulating film 112, the semiconductor film 106, and the pair of electrodes 116.

The gate electrode 104 may be formed to have a single-layer structure or a stacked-layer structure, using at least one of the following materials: one of Al, Ti, Cr, Co, Ni, Cu, Y, Zr, Mo, Ag, Ta, and W; a nitride of any of these elements; an oxide of any of these elements; and an alloy of any of these elements. Alternatively, the gate electrode 104 can include a conductive film formed using the oxide film including CAAC described in Embodiment 1 (an oxide conductive film). The composition of the oxide conductive film may control the work function.

Since an oxide conductive film has higher resistance than a metal film, in the case of using an oxide conductive film for the gate electrode 104, it is preferable to use a stacked



structure of the oxide conductive layer and a low-resistance film in order to reduce resistance of the gate electrode **104**. The low-resistance film is formed using a material selected from the aforementioned materials, so that the sheet resistance is lower than or equal to 10  $\Omega/\text{sq}$ . Note that in the stacked structure, the oxide conductive film is formed on the gate insulating film **112** side.

Note that in the top view of FIG. 2A, the lateral length and the longitudinal length of the gate electrode **104** are larger than those of the semiconductor film **106**, so that degradation and generation of electric charge due to light are suppressed in the semiconductor film **106**; however, the size is not limited thereto. The lateral length and the longitudinal length of the semiconductor film **106** in the top view may be larger than those of the gate electrode **104**.

There is no particular limitation on the substrate **100** as long as it has at least heat resistance high enough to withstand heat treatment performed later. For example, a glass substrate, a ceramic substrate, a quartz substrate, or a sapphire substrate may be used as the substrate **100**. Alternatively, a single crystal semiconductor substrate or a polycrystalline semiconductor substrate made of silicon, silicon carbide, or the like, a compound semiconductor substrate made of silicon germanium, or the like, an SOI (silicon on insulator) substrate, or the like may be used. Still alternatively, any of these substrates further provided with a semiconductor element may be used as the substrate **100**.

A flexible substrate may alternatively be used as the substrate **100**. In that case, a transistor is formed directly on the flexible substrate. Note that as a method for providing the transistor over the flexible substrate, there is also a method in which a non-flexible substrate is used as the substrate **100**, the transistor is formed thereover, and then the transistor is separated and transferred to a flexible substrate. In that case, a separation layer is preferably provided between the substrate **100** and the transistor.

As the semiconductor film **106**, a silicon film, a germanium film, a silicon germanium film, a silicon carbide film, a gallium nitride film, or a semiconductor film formed using the oxide film including CAAC described in Embodiment 1 (an oxide semiconductor film) may be used. Since the oxide semiconductor film can be formed easily and have high field-effect mobility without laser beam treatment or the like, it is preferably used as a material of the semiconductor film **106**. In addition, a transistor in which the interface level of an interface between the oxide semiconductor film and the gate insulating film in contact with the oxide semiconductor film is low can be obtained.

The gate insulating film **112** and the interlayer insulating film **118** may be formed to have a stacked-layer structure or a single-layer structure using, for example, silicon oxide, silicon oxynitride, silicon nitride oxide, silicon nitride, aluminum oxide, hafnium oxide, yttrium oxide, zirconium oxide, or the like. For example, the gate insulating film **112** and the interlayer insulating film **118** may be formed by a thermal oxidation method, a CVD method, a sputtering method, or the like. As each of the gate insulating film **112** and the interlayer insulating film **118**, a film from which oxygen is released by heating may be used. With use of such a film from which oxygen is released by heating, defects generated in the semiconductor film **106** can be repaired and electric characteristics of the transistor can be inhibited from being degraded.

In this specification, silicon oxynitride refers to a substance that contains more oxygen than nitrogen and for example, silicon oxynitride includes oxygen, nitrogen, silicon, and hydrogen at concentrations higher than or equal to

50 at. % and lower than or equal to 70 at. %, higher than or equal to 0.5 at. % and lower than or equal to 15 at. %, higher than or equal to 25 at. % and lower than or equal to 35 at. %, and higher than or equal to 0 at. % and lower than or equal to 10 at. %, respectively. Further, a silicon nitride oxide film refers to a substance that contains more nitrogen than oxygen and includes oxygen, nitrogen, silicon, and hydrogen at concentrations higher than or equal to 5 at. % and lower than or equal to 30 at. %, higher than or equal to 20 at. % and lower than or equal to 55 at. %, higher than or equal to 25 at. % and lower than or equal to 35 at. %, and higher than or equal to 10 at. % and lower than or equal to 25 at. %, respectively. Note that the above ranges are ranges for cases where measurement is performed using Rutherford backscattering spectrometry (RBS) and hydrogen forward scattering spectrometry (HFS). In addition, the total of the percentages of the constituent elements does not exceed 100 at. %.

In the case where a material of the pair of electrodes **116** diffuses to the semiconductor film **106** and adversely affects the transistor characteristics, each of the gate insulating film **112** and the interlayer insulating film **118** may be an insulating film through which the material of the pair of electrodes **116** is not easily diffused. The interlayer insulating film **118** serves as a protective film of the semiconductor film **106**.

To release oxygen by heating means that the released amount of oxygen which is converted to oxygen atoms is greater than or equal to  $1 \times 10^{18}$  atoms/cm<sup>3</sup>, preferably greater than or equal to  $3 \times 10^{20}$  atoms/cm<sup>3</sup> in thermal desorption spectroscopy (TDS).

Here, a method in which the amount of released oxygen is measured on an oxygen atom basis using TDS analysis will now be described.

The amount of released gas in TDS analysis is proportional to the integral value of a spectrum. Therefore, the amount of released gas can be calculated from the ratio between the measured integral value of a spectrum and the reference value of a standard sample. The reference value of a standard sample refers to the ratio of the density of a predetermined atom contained in a sample to the integral value of a spectrum.

For example, the number of the released oxygen molecules ( $N_{O_2}$ ) from an insulating film can be found according to a Numerical Expression 1 with the TDS analysis results of a silicon wafer containing hydrogen at a predetermined density which is the standard sample and the TDS analysis results of the insulating film. Here, all spectra in a mass number of 32 which are obtained by the TDS analysis are assumed to originate from an oxygen molecule. CH<sub>3</sub>OH, which is given as a gas having a mass number of 32, is not taken into consideration on the assumption that it is unlikely to be present. Further, an oxygen molecule including an oxygen atom having a mass number of 17 or 18 which is an isotope of an oxygen atom is also not taken into consideration because the proportion of such a molecule in the natural world is minimal.

$$N_{O_2} = N_{H_2} / S_{H_2} \times S_{O_2} \times \alpha \quad (\text{Numerical Expression 1})$$

$N_{H_2}$  is the value obtained by conversion of the number of hydrogen molecules desorbed from the standard sample into densities.  $S_{H_2}$  is the integral value of a spectrum when the standard sample is subjected to TDS analysis. Here, the reference value of the standard sample is set to  $N_{H_2}/S_{H_2}$ .  $S_{O_2}$

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is the integral value of a spectrum when the insulating film is subjected to TDS analysis.  $\alpha$  is a coefficient affecting the intensity of the spectrum in the TDS analysis. Refer to Japanese Published Patent Application No. H6-275697 for details of the Numerical Expression 1. Note that the amount of released oxygen from the above insulating film is measured with a thermal desorption spectroscopy apparatus produced by ESCO Ltd., EMD-WA1000S/W using a silicon wafer containing a hydrogen atom at  $1 \times 10^{16}$  atoms/cm<sup>3</sup> as the standard sample.

Further, in the TDS analysis, oxygen is partly detected as an oxygen atom. The ratio between oxygen molecules and oxygen atoms can be calculated from the ionization rate of the oxygen molecules. Note that, since the above includes the ionization rate of the oxygen molecules, the number of the released oxygen atoms can also be estimated through the evaluation of the number of the released oxygen molecules.

Note that  $N_{O_2}$  is the number of the released oxygen molecules. The amount of released oxygen on an oxygen atom basis is twice the number of the released oxygen molecules.

In the above structure, the film from which oxygen is released by heating may be an oxygen-excess silicon oxide ( $SiO_X$  ( $X > 2$ )). In the oxygen-excess silicon oxide ( $SiO_X$  ( $X > 2$ )), the number of oxygen atoms per unit volume is more than twice the number of silicon atoms per unit volume. The number of silicon atoms and the number of oxygen atoms per unit volume are measured by Rutherford backscattering spectrometry.

By supplying oxygen from the gate insulating film 112 or the interlayer insulating film 118 to the semiconductor film 106 that is an oxide semiconductor film, the interface state density between the semiconductor film 106 and the gate insulating film 112 or the interface state density between the semiconductor film 106 and the interlayer insulating film 118 can be decreased. As a result, carrier trapping at the interface between the semiconductor film 106 and the gate insulating film 112 or the interface between the semiconductor film 106 and the interlayer insulating film 118 can be suppressed, and thus a transistor with less degradation in electric characteristics can be obtained.

Further, electric charge is generated owing to an oxygen vacancy in the oxide semiconductor film in some cases. In general, part of oxygen vacancy in an oxide semiconductor film serves as a donor and causes release of an electron which is a carrier. As a result, the threshold voltage of a transistor shifts in the negative direction. Oxygen is sufficiently supplied from the gate insulating film 112 or the interlayer insulating film 118 to the semiconductor film 106 that is an oxide semiconductor film, whereby the density of oxygen vacancy in the oxide semiconductor film, which causes the negative shift of the threshold voltage, can be reduced.

In other words, a film from which oxygen is released by heating is used for the gate insulating film 112 or the interlayer insulating film 118, the interface state density at an interface between the semiconductor film 106 and the gate insulating film 112 or the interface state density at an interface between the semiconductor film 106 and the interlayer insulating film 118 and the oxygen vacancy density in the semiconductor film 106 that is an oxide semiconductor film can be reduced. Thus, the influence of carrier trapping at the interface between the semiconductor film 106 that is an oxide semiconductor film and the gate insulating film 112 or at the interface between the semiconductor film 106 and the interlayer insulating film 118 can be reduced.

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The pair of electrodes 116 may be formed using the metal, the metal nitride, the metal oxide, or the alloy, which is given as the material for the gate electrode 104, or the like as appropriate.

When a film including copper (Cu) is used for the pair of electrodes 116, the resistance of a wiring can be reduced, and generation of wiring delays or the like even in a large-sized display device can be reduced. In the case of using Cu for the pair of electrodes 116, adhesion to the substrate 100 is decreased depending on the material of the substrate 100; thus, it is preferable for the pair of electrodes 116 to have a stacked-layer structure including a film with high adhesion to the substrate 100. As a film with high adhesion to the substrate 100, a film containing Ti, Mo, Mn, Al, or the like may be used. For example, a Cu—Mn—Al alloy may be used.

With the described-above structure, a transistor whose threshold voltage is controlled and electric characteristics are excellent can be obtained. Therefore, a semiconductor device with low power consumption, favorable electric characteristics, and high reliability can be manufactured with high productivity.

This embodiment can be implemented in appropriate combination with the other embodiments.

## Embodiment 3

In this embodiment, a transistor having a structure different from that of the transistor described in Embodiments 2 will be described.

FIGS. 3A to 3C are a top view and cross-sectional views of a transistor which is one embodiment of the present invention. FIGS. 3B and 3C illustrate a cross section A-B and a cross section C-D taken along a dashed-dotted line A-B and a dashed-dotted line C-D in FIG. 3A.

The cross section A-B illustrated in FIG. 3B is described in detail below.

The cross section A-B is a cross-section of the transistor which includes the substrate 100, the gate electrode 104 over the substrate 100, the gate insulating film 112 covering the substrate 100 and the gate electrode 104, the pair of electrodes 116 over the gate insulating film 112, the semiconductor film 106 which is over the gate electrode 104 with the gate insulating film 112 positioned therebetween and partly in contact with the pair of electrodes 116, and the interlayer insulating film 118 covering the gate insulating film 112, and the pair of electrodes 116, and the semiconductor film 106.

The gate electrode 104 and the semiconductor film 106 in this embodiment have structures similar to those of the gate electrode 104 and the semiconductor film 106 in Embodiment 2. With use of the gate electrode including the oxide film including CAAC described in Embodiment 1, the work function is controlled, and the threshold voltage of the transistor can be controlled. In addition, with use of the oxide semiconductor film described in Embodiment 1 as the semiconductor film 106, a transistor in which the interface state density at an interface between the oxide semiconductor film and the gate insulating film in contact with the oxide semiconductor film is low can be obtained.

FIGS. 4A to 4C are a top view and cross-sectional views of a transistor which is one embodiment of the present invention. FIGS. 4B and 4C illustrate a cross section A-B and a cross section C-D taken along a dashed-dotted line A-B and a dashed-dotted line C-D shown in FIG. 4A.

The cross section A-B of FIG. 4B is described in detail below.

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The cross section A-B is a cross section of the transistor which includes the substrate **100**, a base insulating film **102** over the substrate **100**, the semiconductor film **106** over the base insulating film **102**, the pair of electrodes **116** which is over the semiconductor film **106** and partly in contact with the semiconductor film **106**, the gate insulating film **112** covering the semiconductor film **106** and the pair of electrodes **116**, and the gate electrode **104** over the semiconductor film **106** with the gate insulating film **112** positioned therebetween.

The base insulating film **102** can have a structure similar to that of the gate insulating film **112** and that of the interlayer insulating film **118**.

FIGS. **5A** to **5C** are a top view and cross-sectional views of a transistor which is one embodiment of the present invention. FIGS. **5B** and **5C** illustrate a cross section A-B and a cross section C-D taken along a dashed-dotted line A-B and a dashed-dotted line C-D shown in FIG. **5A**.

The cross section A-B of FIG. **5B** is described in detail below.

The cross section A-B is a cross section of the transistor which includes the substrate **100**, the base insulating film **102** over the substrate **100**, the pair of electrodes **116** over the base insulating film **102**, the semiconductor film **106** which is over the pair of electrodes **116** and partly in contact with the pair of electrodes **116**, the gate insulating film **112** covering the semiconductor film **106** and the pair of electrodes **116**, and the gate electrode **104** over the semiconductor film **106** with the gate insulating film **112** positioned therebetween.

Note that in each of FIG. **3A**, FIG. **4A**, and FIG. **5A**, the lateral length and the longitudinal length of the gate electrode **104** are larger than those of the semiconductor film **106**, so that degradation and generation of electric charge due to light are suppressed in the semiconductor film **106**; however, the size is not limited thereto. The lateral length and the longitudinal length of the semiconductor film **106** in the top views may be larger than those of the gate electrode **104**.

FIGS. **6A** to **6C** are a top view and cross-sectional views of a transistor which is one embodiment of the present invention. FIGS. **6B** and **6C** illustrate a cross section A-B and a cross section C-D taken along a dashed-dotted line A-B and a dashed-dotted line C-D shown in FIG. **6A**.

The cross section A-B of FIG. **6B** is described in detail below.

The cross section A-B is a cross section of the transistor which includes the substrate **100**, the base insulating film **102** over the substrate **100**, a semiconductor film having a region **126** and a region **121** over the base insulating film **102**, the gate insulating film **112** over the region **121**, the gate electrode **104** over the gate insulating film **112**, the interlayer insulating film **118** covering the base insulating film **102**, the region **126**, the gate insulating film **112**, and the gate electrode **104**, and the pair of electrodes **116** in contact with the region **126** through an opening portion which is formed in the interlayer insulating film **118** to expose the region **126**.

The gate insulating film **112** and the gate electrode **104** may have substantially the same shape seen from the top surface. The shape can be obtained by processing the gate electrode **104** and the gate insulating film **112** together with use of one mask. Note that after formation of the gate electrode **104** and the gate insulating film **112**, the width of the gate electrode **104** may be narrowed by performing plasma treatment or chemical treatment.

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The region **121** may have substantially the same shape as the gate insulating film **112** or the gate electrode **104** when seen from the top surface. The shape is obtained by forming the region **126** of the semiconductor film with use of the gate insulating film **112** or the gate electrode **104** as a mask. For example, with use of the gate insulating film **112** or the gate electrode **104** as a mask, an impurity (such as boron, phosphorus, hydrogen, a rare gas, or nitrogen) is introduced to the semiconductor film, so that a region whose resistance is reduced is formed. The thus formed region can be the region **126**. Note that the region **121** is a region in the semiconductor film where the region **126** is not formed.

The region **121** functions as a channel region of the transistor. Further, the region **126** functions as a source region and a drain region of the transistor.

FIGS. **7A** to **7C** are a top view and cross-sectional views of a transistor which is one embodiment of the present invention. FIGS. **7B** and **7C** illustrate a cross section A-B and a cross section C-D taken along a dashed-dotted line A-B and a dashed-dotted line C-D in FIG. **7A**.

The cross-section A-B of FIG. **7B** is described in detail below.

The cross section A-B is a cross-section of the transistor which includes the substrate **100**, the gate electrode **104** over the substrate **100**, the gate insulating film **112** over the gate electrode **104**, a semiconductor film having the region **126** and the region **121** over the gate electrode **104** with the gate insulating film **112** positioned therebetween, the interlayer insulating film **118** covering the semiconductor film and the gate insulating film **112**, and the pair of electrodes **116** in contact with the region **126** through an opening portion which is formed in the interlayer insulating film **118** to expose the region **126**.

In FIGS. **7A** to **7C**, the gate insulating film **112** and the gate electrode **104**, and the region **121** have substantially the same shape seen from the top surface; however, they are not limited thereto. The gate insulating film **112** and the gate electrode **104**, and the region **121** may have different shapes from each other.

With the described-above structure, a transistor whose threshold voltage is controlled and electric characteristics are excellent can be obtained. Therefore, a semiconductor device with low power consumption, favorable electric characteristics, and high reliability can be manufactured with high productivity.

This embodiment can be implemented in appropriate combination with the other embodiments.

#### Embodiment 4

In this embodiment, a liquid crystal display device manufactured using the transistor described in Embodiment 2 or Embodiment 3 will be described. Note that although an example in which one embodiment of the present invention is applied to the liquid crystal display device is described in this embodiment, application is not limited thereto. For example, application of one embodiment of the present invention to an electroluminescence (EL) display device is readily conceived by those skilled in the art.

FIG. **8** is a circuit diagram of an active matrix liquid crystal display device. The liquid crystal display device includes source lines SL<sub>1</sub> to SL<sub>a</sub>, gate lines GL<sub>1</sub> to GL<sub>b</sub>, and a plurality of pixels **200**. Each pixel **200** includes a transistor **230**, a capacitor **220**, and a liquid crystal element **210**. A pixel portion in the liquid crystal display device is constituted by arranging such a plurality of pixels **200**. In the

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case where the source line or the gate line is simply mentioned, it is denoted as the source line SL or the gate line GL.

As the transistor **230**, the transistor described in Embodiment 2 or Embodiment 3 is used. With use of the transistor which is one embodiment of the present invention, a display device with low power consumption, favorable electric characteristics, and high reliability can be obtained.

The gate line GL is connected to a gate of the transistor **230**, the source line SL is connected to a source of the transistor **230**, and a drain of the transistor **230** is connected to one of capacitor electrodes of the capacitor **220** and one of pixel electrodes of the liquid crystal element **210**. The other capacitor electrode of the capacitor **220** and the other pixel electrode of the liquid crystal element **210** are connected to a common electrode. Note that the common electrode may be formed using the same material and in the same layer as the gate line GL.

Further, the gate line GL is connected to a gate driver circuit. The gate driver circuit may include the transistor described in Embodiment 2 or Embodiment 3. Since the threshold voltage of the transistor is controlled, the off-state current can be decreased, and the voltage used for turning the transistor on can be low. Thus, power consumption can be reduced.

The source line SL is connected to a source driver circuit. The source driver circuit may include the transistor described in Embodiment 2 or Embodiment 3. Since the threshold voltage of the transistor is controlled, the off-state current can be decreased, and the voltage used for turning the transistor on can be low. Thus, power consumption can be reduced.

One of or both the gate driver circuit and the source driver circuit may be formed over a substrate which is separately prepared, and a connection method such as a chip on glass (COG) method, a wire bonding method, or a tape automated bonding (TAB) method may be employed.

Since the transistor is easily broken by static electricity or the like, a protection circuit is preferably provided. The protection circuit is preferably formed using a nonlinear element.

When a potential is applied to the gate line GL to be higher than or equal to the threshold voltage of the transistor **230**, electric charge supplied from the source line SL flows as a drain current of the transistor **230** and is stored in the capacitor **220**. After charging for one column is performed, the transistors **230** in the column are turned off, and the voltage is not given from the source line SL. However, the necessary voltage can be held by the electric charge stored in the capacitor **220**. Then, the capacitors **220** in the next column are charged. In such a manner, charging for the first column to  $\alpha$ -th column is performed.

Since the threshold voltage of the transistor **230** is controlled, the electric charge stored in the capacitor **220** is barely likely to be discharged, and capacitance of the capacitor **220** can be reduced, so that power consumption needed for charging can be reduced.

Further, in the case where a transistor whose off-state current is small (such as a transistor including an oxide semiconductor film) is used as the transistor **230**, a time period during which the voltage is held can be made longer. By this effect, the frequency of rewriting display can be reduced in the case of an image with little motion (including a still image); thus, further reduction in power consumption can be achieved. In addition, capacitance of the capacitor **220** can be further reduced, so that power consumption needed for charging can be reduced.

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As described above, according to one embodiment of the present invention, a liquid crystal display device with high reliability and low power consumption can be obtained.

This embodiment can be implemented in appropriate combination with the other embodiments.

#### Embodiment 5

In this embodiment, an example of manufacturing a semiconductor memory device using the transistor described in Embodiment 2 or Embodiment 3 will be described.

Typical examples of volatile semiconductor memory devices include a dynamic random access memory (DRAM) which stores data by selecting a transistor included in a memory element and storing electric charge in a capacitor and a static random access memory (SRAM) which holds stored data using a circuit such as a flip-flop.

Typical examples of nonvolatile semiconductor memory devices include a flash memory which has a floating gate between a gate electrode and a channel formation region of a transistor and stores data by holding electric charge in the floating gate.

The transistor described in Embodiment 2 or Embodiment 3 can be applied to some of transistors included in the above semiconductor memory device.

First, a volatile memory to which the transistor described in Embodiment 2 or Embodiment 3 is applied is described with reference to FIGS. 9A and 9B.

A memory cell includes a bit line BL, a word line WL, a sense amplifier SAmp, a transistor Tr, and a capacitor C (see FIG. 9A).

It is known that the voltage held by the capacitor C is gradually reduced over time due to the off-state current of the transistor Tr as shown in FIG. 9B. After a certain period of time, the voltage originally charged from V0 to V1 is decreased to VA which is a limit for reading data 1. This period is called a holding period T<sub>1</sub>. In the case of a two-level memory cell, refresh operation needs to be performed within the holding period T<sub>1</sub>.

When the transistor described in Embodiment 2 or Embodiment 3 is employed as the transistor Tr, the holding period T<sub>1</sub> can be made longer because the threshold voltage of the transistor is controlled. That is, frequency of the refresh operation can be reduced, which results in reduction in power consumption.

When the transistor whose off-state current is small is used as the transistor Tr, the time period for holding the voltage can further be prolonged, so that the power consumption can be further reduced. For example, when a DRAM is formed using a transistor in which a highly purified oxide semiconductor film is included and the off-state current is less than or equal to  $1 \times 10^{-21}$  A, preferably less than or equal to  $1 \times 10^{-24}$  A, data can be held for several days to several decades without supply of power.

As described above, according to one embodiment of the present invention, a volatile memory with high reliability and low power consumption can be obtained.

Next, a nonvolatile memory to which the transistor described in Embodiment 2 or Embodiment 3 is applied is described with reference to FIGS. 10A and 10B.

FIG. 10A is a circuit diagram of a nonvolatile memory. The nonvolatile memory includes a transistor Tr<sub>1</sub>, a word line WL<sub>1</sub> connected to a gate of the transistor Tr<sub>1</sub>, a source wiring SL<sub>1</sub> connected to a source of the transistor Tr<sub>1</sub>, a transistor Tr<sub>2</sub>, a source wiring SL<sub>2</sub> connected to a source of the transistor Tr<sub>2</sub>, a drain wiring DL<sub>2</sub> connected to a drain of the transistor Tr<sub>2</sub>, a capacitor C, a

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capacitor wiring CL connected to one of ends of the capacitor C, and a floating gate FG connected to the other end of the capacitor C, a drain of the transistor Tr<sub>1</sub>, and a gate of the transistor Tr<sub>2</sub>.

The nonvolatile memory described in this embodiment utilizes variation in the threshold voltage of the transistor Tr<sub>2</sub>, which depends on the potential of the floating gate FG. For example, FIG. 10B is a graph showing a relation between the drain current  $I_{D2}$  flowing through the transistor Tr<sub>2</sub> and the voltage  $V_{CL}$  of the capacitor wiring CL.

The floating gate FG can control voltage through the transistor Tr<sub>1</sub>. For example, the potential of the source wiring SL<sub>1</sub> is set to VDD. In this case, when the potential of the word line WL<sub>1</sub> is set to be higher than or equal to the potential obtained by adding VDD to the threshold voltage  $V_{th}$  of the transistor Tr<sub>1</sub>, the potential of the floating gate FG can be HIGH. Further, when the potential of the word line WL<sub>1</sub> is set to be lower than or equal to the threshold voltage  $V_{th}$  of the transistor Tr<sub>1</sub>, the potential of the floating gate FG can be LOW.

Thus, either a  $V_{CL}$ - $I_{D2}$  curve (FG=LOW) or a  $V_{CL}$ - $I_{D2}$  curve (FG=HIGH) can be obtained. In the case where FG=LOW, the drain current  $I_{D2}$  is small when  $V_{CL}$  is 0 V, so that data 0 is given. In the case where FG=HIGH, the drain current  $I_{D2}$  is large when  $V_{CL}$  is 0 V, so that data 1 is given. In such a manner, data can be stored.

When the transistor described in Embodiment 2 or Embodiment 3 is employed as the transistor Tr<sub>1</sub>, the off-state current of the transistor can be extremely reduced; thus, unintentional leakage of the electric charge stored in the floating gate FG, between the source and the drain of the transistor Tr<sub>1</sub>, can be suppressed. As a result, data can be held for a long time. Further, since the threshold voltage of the transistor Tr<sub>1</sub> is controlled in accordance with one embodiment of the present invention, the voltage needed for writing can be reduced, and thus power consumption can be less than that of the flash memory or the like.

Note that the transistor described in Embodiment 2 or Embodiment 3 can be applied to the transistor Tr<sub>2</sub>.

Next, a structure of the nonvolatile memory shown in FIG. 10A without the capacitor is described with reference to FIG. 11.

FIG. 11 is a circuit diagram of a nonvolatile memory. The nonvolatile memory includes the transistor Tr<sub>1</sub>, a word line WL<sub>1</sub> connected to the gate of the transistor Tr<sub>1</sub>, the source wiring SL<sub>1</sub> connected to the source of the transistor Tr<sub>1</sub>, the transistor Tr<sub>2</sub>, the source wiring SL<sub>2</sub> connected to the source of the transistor Tr<sub>2</sub>, and the drain wiring DL<sub>2</sub> connected to the drain of the transistor Tr<sub>2</sub>. The gate of the transistor Tr<sub>2</sub> is connected to the drain of the transistor Tr<sub>1</sub>.

In the case where the transistor whose off-state current is small is used as the transistor Tr<sub>1</sub>, electric charge can be held between the drain of the transistor Tr<sub>1</sub> and the gate of the transistor Tr<sub>2</sub> without the capacitor. The structure without the capacitor makes it possible to reduce an area of a memory, and the integration degree can be more increased than that of the structure with a capacitor.

Although the nonvolatile memory including four or five wirings is described in this embodiment, a structure of the nonvolatile memory is not limited thereto. For example, a structure in which one wiring functions as the source wiring SL<sub>1</sub> and the drain wiring DL<sub>2</sub> may be employed.

As described above, according to one embodiment of the present invention, a semiconductor memory device with high reliability and low power consumption can be obtained.

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This embodiment can be implemented in appropriate combination with the other embodiments.

#### Embodiment 6

In this embodiment, examples of electronic devices to which Embodiment 2 or Embodiment 3 is applied will be described.

FIG. 12A illustrates a portable information terminal, which includes a housing 300, a button 301, a microphone 302, a display portion 303, a speaker 304, and a camera 305, and has a function as a mobile phone. One embodiment of the present invention can be applied to the display portion 303 and the camera 305. Although not illustrated, one embodiment of the present invention can also be applied to an arithmetic unit, a wireless circuit, or a memory device inside the main body.

FIG. 12B illustrates a display which includes a housing 310 and a display portion 311. One embodiment of the present invention can be applied to the display portion 311. When one embodiment of the present invention is employed, a display having high display quality can be provided even in the case where the size of the display portion 311 is increased.

FIG. 12C illustrates a digital still camera which includes a housing 320, a button 321, a microphone 322, and a display portion 323. One embodiment of the present invention can be applied to the display portion 323. Although not illustrated, one embodiment of the present invention can also be applied to a memory device or an image sensor.

When one embodiment of the present invention is employed, cost of an electric device can be reduced. Further, a display device having high display quality can be obtained.

This embodiment can be implemented in appropriate combination with the other embodiments.

#### Example 1

FIGS. 13A and 13B show a planar image and a cross-sectional image of an oxide including CAAC, which are obtained with high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM). FIGS. 14A and 14B show a planar image and a cross-sectional image of an amorphous oxide, which are obtained with HAADF-STEM.

Sample 1 and Sample 2 were In—Ga—Zn—O-based oxide films each formed over a quartz substrate by a DC sputtering method. The other deposition conditions were as follows: a power of 0.5 kW; a deposition pressure of 0.4 Pa; a deposition gas including Ar (35 sccm) and O<sub>2</sub> (15 sccm); and a distance of 60 mm between a target and a substrate. As the target, an In—Ga—Zn—O (In<sub>2</sub>O<sub>3</sub>:Ga<sub>2</sub>O<sub>3</sub>:ZnO=1:1:2 [molar ratio]) target was used. Note that the thickness was 100 nm.

Here, in the case of Sample 1, the substrate temperature was 400° C., and in the case of Sample 2, the substrate temperature was room temperature. Heat treatment was not performed after film formation.

From the planar image showing a region 1001 and a region 1002 in FIG. 13A, atoms were arranged to have a triangular or hexagonal shape seen from the direction of the a-b plane, a top surface, or an interface. Further, from the cross-sectional image in FIG. 13B, metal atoms were arranged in the direction indicated by arrows. In other words, metal atoms, or metal atoms and oxygen atoms were

arranged in a layered manner in the c-axis direction. As a result, it is found that Sample 1 is an oxide film including CAAC.

From the planar image of FIG. 14A, arrangement of atoms in a triangular or hexagonal shape seen from the direction of a top surface or an interface was not observed. Further, from the cross-sectional image of FIG. 14B, metal atoms, or metal atoms and oxygen atoms were not arranged in a layered manner. As a result, it is found that Sample 2 is not an oxide film including CAAC.

As described above, an oxide film including CAAC was able to be obtained.

#### Example 2

In this example, an example in which a crystal state of an oxide film including CAAC was evaluated by a X-ray diffraction (XRD) method will be described.

Sample 3 and Sample 4 were In—Ga—Zn—O-based oxide films each formed over a quartz substrate by a DC sputtering method. The other deposition conditions were as follows: a power of 0.5 kW; a deposition pressure of 0.4 Pa; a distance of 60 mm between a target and a substrate; and a substrate temperature of 400° C. As the target, an In—Ga—Zn—O (In<sub>2</sub>O<sub>3</sub>:Ga<sub>2</sub>O<sub>3</sub>:ZnO=1:1:2 [molar ratio]) target was used. Note that the thickness was 300 nm.

A deposition gas for Sample 3 was O<sub>2</sub> (40 sccm), and a deposition gas for Sample 4 was N<sub>2</sub> (40 sccm).

FIG. 15 and FIG. 16 each show XRD spectra obtained by an out-of-plane method. FIG. 15 shows XRD spectra after deposition (as-depo), and FIG. 16 shows XRD spectra after heat treatment at 450° C. for an hour in an N<sub>2</sub> atmosphere, which was performed after the deposition. Here, a solid line 1101 and a solid line 1103 each indicate an XRD spectrum of Sample 3, and a solid line 1102 and a solid line 1104 each indicate an XRD spectrum of Sample 4.

From FIG. 15 and FIG. 16, the samples which were formed under both conditions each had a peak at a position corresponding to the (009) plane, which means the presence of strong alignment in the c-axis direction. Thus, it was found that Sample 3 and Sample 4 had c-axis alignment. In particular, Sample 4 had high peak intensity at a position corresponding to the (009) plane. Further, in Sample 3, the peak position corresponding to the (009) plane was shifted to a smaller angle side.

FIG. 17 and FIG. 18 each show XRD spectra obtained by an in-plane method. FIG. 17 shows XRD spectra after deposition (as-depo), and FIG. 18 shows XRD spectra after heat treatment at 450° C. for an hour in an N<sub>2</sub> atmosphere, which was performed after deposition. Here, a solid line 1111 and a solid line 1113 each indicate an XRD spectrum of Sample 3, and a solid line 1112 and a solid line 1114 each indicate an XRD spectrum of Sample 4.

From FIG. 17 and FIG. 18, the samples which were formed under both conditions each had a peak at a position corresponding to the (009) plane, which means presence of strong alignment in the c-axis direction. In addition, it was also found that there were a peak at a position corresponding to the (110) plane and a peak at a position corresponding to the (119) plane.

FIG. 19 and FIG. 20 each show XRD spectra measured under conditions where an optical system was fixed to correspond to the peak position (2θ) of the (110) plane obtained by the in-plane method and the samples were rotated around a normal on the sample surface as an axis. Here a solid line 1121 and a solid line 1123 each indicate an

XRD spectrum of Sample 3, and a solid line 1122 and a solid line 1124 each indicate an XRD spectrum of Sample 4.

From FIG. 19 and FIG. 20, the samples which were formed under both conditions each had no peak.

According to FIG. 15, FIG. 16, FIG. 17, FIG. 18, FIG. 19, and FIG. 20, it was found that the measured samples had characteristics of CAAC, which is not single crystal and has a different property from polycrystal. Note that although In—Ga—Zn—O-based oxide films are described in this example, a material is not particularly limited thereto. In the case of an In—Sn—Zn—O-based oxide film, an oxide film including CAAC can be obtained.

#### Example 3

A transistor was manufactured using an In—Ga—Zn—O-based oxide film (with a thickness of 35 nm) including CAAC over a glass substrate (600 mm×720 mm), and initial characteristics thereof is shown in FIG. 21. The manufactured transistor was a bottom-gate transistor having the structure illustrated in FIGS. 2A to 2C, in which the channel length L was 3 μm and the channel width W was 50 μm. Further, the thickness of a gate insulating film of the transistor was 100 nm.

FIG. 21 shows data on V<sub>g</sub>-I<sub>d</sub> curves (where V<sub>d</sub>=1 V, and V<sub>d</sub>=10 V) obtained by measurement at 20 points in the substrate. The substantially same values are plotted and overlap, which means that the transistor formed using an In—Ga—Zn—O-based oxide film including CAAC has favorable uniformity. In FIG. 21, the V<sub>g</sub>-I<sub>d</sub> curve on the upper side shows data obtained when V<sub>d</sub>=10 V, and the V<sub>g</sub>-I<sub>d</sub> curve on the lower side shows data obtained when V<sub>d</sub>=1.

The average value of the threshold voltages V<sub>th</sub> measured in the transistor was 1.34 V, and the average value of the field-effect mobilities measured in the transistor was 10.7 cm<sup>2</sup>/Vs. Note that the threshold voltage V<sub>th</sub> is a value calculated by using a curve expressed by the square root of I<sub>d</sub> in the V<sub>g</sub>-I<sub>d</sub> curve (V<sub>d</sub>=10 V) (hereinafter, the curve is also referred to as a √I<sub>d</sub> curve).

In order to evaluate reliability of the transistor, a plurality of transistors each including an In—Ga—Zn—O-based oxide film (with a thickness of 35 nm) including CAAC were newly manufactured over a 5-inch substrate, and were subjected to BT tests. Each of the manufactured transistors was a bottom-gate transistor having the structure illustrated in FIGS. 2A to 2C, which had a channel length L of 6 μm and a channel width W of 50 μm. In addition, the thickness of a gate insulating film in each transistor was 100 nm.

The BT test is one kind of accelerated test and can evaluate change in characteristics, caused by long-term usage, of transistors in a short time. In particular, the amount of shift in threshold voltage of the transistor between before and after the BT test is an important indicator for examining reliability. As the amount of shift in the threshold voltage V<sub>th</sub> (ΔV<sub>th</sub>) between before and after the BT test is small, the transistor has higher reliability.

Specifically, the temperature of the substrate over which the transistor is formed (substrate temperature) is set at fixed temperature, a source and a drain of the transistor are set at the same potential, and a gate is supplied with potential different from those of the source and the drain for a certain period. The substrate temperature may be determined as appropriate in accordance with the test purpose. A BT test in which a potential applied to a gate is higher than the potential of a source and a drain is referred to as +BT test and

a BT test in which a potential applied to a gate is lower than the potential of a source and a drain is referred to as -BT test.

The stress condition of a BT test can be determined in accordance with a substrate temperature, the electric field intensity applied to a gate insulating film, and a time period of application of electric field. The intensity of the electric field applied to the gate insulating film is determined in accordance with a value obtained by dividing a potential difference between the gate and the source and drain by the thickness of the gate insulating film. For example, in the case where the intensity of the electric field applied to the gate insulating film with a thickness of 100 nm is to be 2 MV/cm, the potential difference may be set to 20 V.

Note that a voltage refers to the difference between potentials of two points, and a potential refers to electrostatic energy (electric potential energy) of a unit charge at a given point in an electrostatic field. Note that in general, a difference between a potential of one point and a reference potential (e.g., a ground potential) is merely called a potential or a voltage, and a potential and a voltage are used as synonymous words in many cases. Thus, in this specification, a potential may be rephrased as a voltage and a voltage may be rephrased as a potential unless otherwise specified.

Conditions of the BT tests were as follows: the substrate temperature was 80° C.; the intensity of an electric field applied to the gate insulating film was 3 MV/cm; and the application time (also called stress time) was 100 seconds, 200 seconds, 500 seconds, 1000 seconds, 1500 seconds, and 2000 seconds. Under the above conditions, +BT tests and -BT tests were performed.

FIG. 22A shows a result of the +BT test performed for 2000 seconds, and FIG. 22B shows a result of the -BT test performed for 2000 seconds.

In FIG. 22A, the threshold voltage  $V_{th}$  after the +BT test was shifted by 0.63 V in the positive direction from the threshold voltage value in the initial characteristics. In FIG. 22B, the threshold voltage  $V_{th}$  after the -BT test was shifted by 0.02 V in the positive direction from the threshold voltage value in the initial characteristics. In both of the BT tests, the amount of shift in the threshold voltage ( $\Delta V_{th}$ ) is less than or equal to 1 V, which proves that the transistor manufactured using an In—Ga—Zn—O-based oxide film including CAAC can have high reliability.

In the BT test, it is important to use a transistor which has been never subjected to a BT test. For example, if a -BT test is performed with use of a transistor which has been once subjected to a +BT test, the results of the -BT test cannot be evaluated correctly due to influence of the +BT test which has been performed previously. Further, the same applies to the case where a +BT test is performed on a transistor which has been once subjected to a +BT test. Note that the same does not apply to the case where a BT test is intentionally repeated in consideration of these influences.

FIG. 23A shows a result of a +BT test performed while a transistor was irradiated with light with use of an LED light source (white light with 10000 lux), which is also called positive-bias temperature stress photodegradation. FIG. 23B shows a result of a -BT test performed while a transistor was irradiated with light with use of an LED light source, which is also called negative-bias temperature stress photodegradation. In FIG. 23A, the threshold voltage  $V_{th}$  after the +BT test is shifted by 0.27 V in the positive direction from the threshold voltage value in the initial characteristics. In FIG. 23B, the threshold voltage  $V_{th}$  after the -BT test is shifted by 0.23 V in the positive direction from the threshold voltage value in the initial characteristics. In both of the BT tests

with light irradiation, the amount of shift in the threshold voltage ( $\Delta V_{th}$ ) is less than or equal to 1 V, which proves that the transistor manufactured using an In—Ga—Zn—O-based oxide film including CAAC can have high reliability.

FIG. 24 shows time dependence of the amount of shift in the threshold voltage  $V_{th}$  ( $\Delta V_{th}$ ) on various kinds of stress conditions. The vertical axis represents the amount of shift in the threshold voltage  $V_{th}$  ( $\Delta V_{th}$ ) on a linear scale, and the horizontal axis represents the stress time on a logarithmic scale.

FIGS. 25A and 25B are schematic diagrams showing mechanism of negative-bias stress temperature photodegradation. FIGS. 25A and 25B each illustrate an interface between an oxide semiconductor and a gate insulating film. As illustrated in FIG. 25A, when a transistor is irradiated with light, a hole is generated. The hole is trapped or detrapped. As illustrated in FIG. 25B, the hole is drawn to the gate insulating film and thereby becoming fixed charge which causes a shift of the threshold voltage  $V_{th}$  in the negative direction. Thus, no oxygen vacancy level is important for elimination of negative-bias temperature stress photodegradation. That is, a reduction in oxygen vacancy is effective for prevention of negative-bias temperature stress photodegradation. A crystalline surface is less likely than an amorphous surface to transmit oxygen; thus, a transistor including an In—Ga—Zn—O-based oxide film including CAAC has high reliability. In addition, in order to reduce oxygen vacancy, a film from which oxygen is released by heating is used as a gate insulating film and an interlayer insulating film, and heat treatment is performed in an oxygen atmosphere, which are effective for improving reliability.

#### EXPLANATION OF REFERENCE

100: substrate, 102: base insulating film, 104: gate electrode, 106: semiconductor film, 112: gate insulating film, 116: electrode, 118: interlayer insulating film, 121: region, 126: region, 200: pixel, 210: liquid crystal element, 220: capacitor, 230: transistor, 300: housing, 301: button, 302: microphone, 303: display portion, 304: speaker, 305: camera, 310: housing, 311: display portion, 320: housing, 321: button, 322: microphone, 323: display portion, 1001: region, 1002: region, 1101: solid line, 1102: solid line, 1103: solid line, 1104: solid line, 1111: solid line, 1112: solid line, 1113: solid line, 1114: solid line, 1121: solid line, 1122: solid line, 1123: solid line, 1124: solid line

This application is based on Japanese Patent Application serial no. 2010-282135 filed with Japan Patent Office on Dec. 17, 2010 and Japanese Patent Application serial no. 2011-151859 filed with Japan Patent Office on Jul. 8, 2011, the entire contents of which are hereby incorporated by reference.

The invention claimed is:

1. A semiconductor device comprising:

an oxide semiconductor layer comprising a stack of a first film and a second film;

an insulating layer over the oxide semiconductor layer; and

a gate electrode over the insulating layer,

wherein the second film is positioned over the first film, wherein one of the first film and the second film comprises an In—Sn—Ga—Zn—O-based oxide semiconductor film,

wherein each of the first film and the second film comprises a crystal,

wherein the second film comprises c-axis aligned crystals,  
and  
wherein the c-axis aligned crystals in the second film have  
different a-axis directions and b-axis directions from  
each other. 5

2. The semiconductor device according to claim 1,  
wherein the first film and the second film have a different  
composition from each other.

3. The semiconductor device according to claim 1,  
wherein the insulating layer is in contact with the oxide 10  
semiconductor layer, and  
wherein the insulating layer comprises silicon and oxy-  
gen.

4. The semiconductor device according to claim 1,  
wherein the insulating layer is in contact with the second 15  
film, and  
wherein the insulating layer comprises silicon and oxy-  
gen.

5. The semiconductor device according to claim 1, further  
comprising: 20

a source electrode and a drain electrode each in contact  
with the oxide semiconductor layer,  
wherein one of the source electrode and the drain elec-  
trode is electrically connected to a display element.

6. The semiconductor device according to claim 5, 25  
wherein the display element is a liquid crystal element.

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