semiconductor on at least a side face of a recess portion of a semiconductor substrate that is provided with an interlayer insulating layer having the recess portion and a copper-containing wiring of which at least a part of the surface thereof is exposed on at least a part of the bottom face of the recess portion, a technique whereby provision of a sealing layer for a semiconductor on the wiring exposed on the bottom face of the recess portion can be avoided as far as possible is required.

[0007] Further, in semiconductor device manufacturing processes, there are cases in which the semiconductor device is cleaned with plasma in a state in which the sealing layer for a semiconductor is exposed, and there are also cases in which a layer is formed on the sealing layer for a semiconductor using a plasma CVD method or the like. Therefore, there are cases in which the sealing layer for a semiconductor is requested to have plasma resistance.

[0008] Embodiments of the present invention are made in view of the above problems, and aim to accomplish the following.

Specifically, an aspect of the invention provide a method for manufacturing a semiconductor device whereby formation of a sealing layer for a semiconductor on a wiring that is exposed on the bottom face of a recess portion provided in an interlayer insulating layer is suppressed, but whereby a sealing layer for a semiconductor can be formed on at least a side face of the recess portion.

Another aspect of the invention provide a rinsing liquid with which a sealing layer for a semiconductor present on the exposed face of the wiring can effectively be removed.

Another aspect of the invention provide a rinsing liquid which can improve the plasma resistance of a sealing layer for a semiconductor.

Another aspect of the invention provide a semiconductor device in which diffusion of wiring materials (for example, copper) into an interlayer insulating layer is suppressed, and in which an increase in interconnection resistance of the connection portion between the wirings is suppressed.

Another aspect of the invention provide a semiconductor device in which the plasma resistance of a sealing layer for a semiconductor is improved.

Solution to Problem

[0009]

According to a first aspect of the present invention, there is provided a method for manufacturing a semiconductor device, the method including:

a sealing composition application process of applying a sealing composition for a semiconductor to at least a bottom face and a side face of a recess portion of a semiconductor

substrate, to form a sealing layer for a semiconductor on at least the bottom face and the side face of the recess portion, the sealing composition for a semiconductor including a polymer having a cationic functional group and a weight average molecular weight of from 2,000 to 1,000,000, each of the content of sodium and the content of potassium in the sealing composition for a semiconductor being 10 ppb by mass or less on an elemental basis, and the semiconductor substrate being provided with an interlayer insulating layer having the recess portion and a copper-containing wiring of which at least a part of the surface thereof is exposed on at least a part of the bottom face of the recess portion; and a removal process of subjecting a surface of the semiconductor substrate at a side at which the sealing layer for a semiconductor has been formed to heat treatment under a temperature condition of from 200°C to 425°C, to remove at least a part of the sealing layer for a semiconductor that has been formed on an exposed face of the wiring, wherein the duration of the heat treatment is 30 minutes or less.

According to the above aspect of the method for manufacturing a semiconductor device, a sealing layer for a semiconductor can be formed on at least a side face of the recess portion although formation of a sealing layer for a semiconductor on a wiring exposed on the bottom face of the recess portion formed in the interlayer insulating layer is suppressed.

[0010] In an embodiment, in the method for manufacturing a semiconductor device, the polymer has a cationic functional group equivalent weight of from 27 to 430.

In an embodiment, in the method for manufacturing a semiconductor device, the polymer is polyethyleneimine or a polyethyleneimine derivative.

In an embodiment, the above method for manufacturing a semiconductor device includes a washing process of washing at least the side face and the bottom face of the recess portion with a rinsing liquid having a temperature of from 15°C to 100°C, after the sealing composition application process but before the removal process.

In an embodiment, in the method for manufacturing a semiconductor device, the temperature of the rinsing liquid is from 30°C to 100°C.

In an embodiment, the above method for manufacturing a semiconductor device includes a washing process of washing at least the side face and the bottom face of the recess portion with a rinsing liquid having a pH at 25°C of 6 or lower, after the sealing composition application process but before the removal process.

In an embodiment, in the method for manufacturing a semiconductor device, the rinsing liquid includes a compound having, in one molecule thereof, at least one of a moiety A that blocks an active species or a moiety B that forms a bond with the polymer when heated.

[0011] According to a second aspect of the invention, there is provided a rinsing liquid for use in removal of at least a part of the sealing layer for a semiconductor that is formed in the

sealing composition application process in the above method for manufacturing a semiconductor device ~~according to any one of <1> to <7>~~, the rinsing liquid having a pH at 25°C of 6 or lower, wherein the rinsing liquid comprises a compound having, in one molecule thereof, a moiety A that blocks an active species and a moiety B that forms a bond with the polymer when heated, the moiety A is at least one selected from the group consisting of an aromatic ring structure, an alicyclic structure, and a manganese atom, and the moiety B is a carboxyl group.

According to the above aspect of the rinsing liquid, the sealing layer for a semiconductor located on the exposed face of a wiring can effectively be removed.

In an embodiment, the above rinsing liquid is used to remove at least a part of the sealing layer for a semiconductor mentioned in the first invention.

[0012] According to a third aspect of the present invention, there is provided a rinsing liquid for a sealing layer for a semiconductor, the sealing layer being formed on a surface of an interlayer insulating layer of a semiconductor substrate that is provided with the interlayer insulating layer, and being derived from a polymer having a cationic functional group and a weight average molecular weight of from 2,000 to 1,000,000~~, the rinsing liquid including a compound having, in one molecule thereof, at least one of a moiety A that blocks an active species or a moiety B that forms a bond with the polymer when heated~~, wherein the rinsing liquid comprises a compound having, in one molecule thereof, a moiety A that blocks an active species and a moiety B that forms a bond with the polymer when heated, the moiety A is at least one selected from the group consisting of an aromatic ring structure, an alicyclic structure, and a manganese atom and the moiety B is a carboxyl group.

According to the above aspect of the rinsing liquid, the plasma resistance of the sealing layer for a semiconductor can be improved.

[0013] In an embodiment, in the rinsing liquid, the compound has, in one molecule thereof, two or more carboxyl groups as the moiety B, and the compound has, in one molecule thereof, at least one of a structure in which each of two neighboring carbon atoms bonds to a carboxyl group or a structure in which each of two non-central carbon atoms from among three consecutive carbon atoms bonds to a carboxyl group.

~~In an embodiment, in the rinsing liquid, the compound has the moiety A and the moiety B, the moiety A is at least one selected from the group consisting of an aromatic ring structure, an alicyclic structure, a manganese atom, and a silicon atom, and the moiety B is a carboxyl group.~~

[0014] According to a fourth aspect of the present invention, there is provided a semiconductor device including, on a semiconductor substrate: an interlayer insulating layer having a recess portion; a first wiring that includes copper, and that is formed on the recess portion; a sealing layer for a semiconductor that is present at least between a side face of the recess portion of the interlayer insulating layer and the first wiring, and that includes a polymer having a cationic functional group and a weight average molecular weight of from 2,000 to 1,000,000; and a second wiring that contains copper, that has an upper face constituting at least a part of a bottom face of the recess portion, and that is electrically connected to the first wiring via the upper face, wherein the thickness of the sealing layer for a semiconductor in a connection portion between the first wiring and the second wiring is 5 nm or less, wherein the sealing layer for a semiconductor includes at least one selected from the group consisting of an imide bond and an amide bond, and also includes at least one selected from the group consisting of an aromatic ring structure and a manganese atom.

According to the above aspect of the semiconductor device, diffusion of a wiring material (for example, copper) into the interlayer insulating layer is suppressed, and an increase in the interconnection resistance of the connection portion between the wirings is suppressed.

The semiconductor device according to the above aspect cannot be manufactured by known methods for manufacturing semiconductor devices. The semiconductor device according to the above aspect is manufactured, for the first time, by the method for manufacturing a semiconductor device according to the first aspect.

[0015] According to the fifth aspect of the present invention, there is provided a semiconductor device including, on a semiconductor substrate: an interlayer insulating layer; a first wiring that includes copper; and a sealing layer for a semiconductor that is present between the interlayer insulating layer and the first wiring, and that includes a polymer having a cationic functional group and a weight average molecular weight of from 2,000 to 1,000,000, wherein the sealing layer for a semiconductor includes at least one selected from the group consisting of an imide bond and an amide bond, and also includes at least one selected from the group consisting of an aromatic ring structure~~,~~ and a manganese atom~~, and a silicon atom~~.

According to the above aspect of the semiconductor device, the plasma resistance of the sealing layer for a semiconductor is improved.

The semiconductor device according to the fifth aspect cannot be produced by known methods for manufacturing semiconductor devices. The semiconductor device according to the fifth aspect is produced, for the first time, using the rinsing liquid according to the third aspect.

[0016] In an embodiment, in the semiconductor device, the polymer has a cationic functional group equivalent weight of from 27 to 430.

In an embodiment, in the semiconductor device, the polymer is polyethyleneimine or a polyethyleneimine derivative.

In an embodiment, in the semiconductor device, the interlayer insulating layer is a porous interlayer insulating layer having an average pore radius of from 0.5 nm to 3.0 nm.

Advantageous Effects of Invention

[0017] According to the first aspect, a method for manufacturing a semiconductor device whereby a sealing layer for a semiconductor can be formed on at least the side face of the recess portion although formation of the sealing layer for a semiconductor on a wiring exposed on the bottom face of a recess portion formed in an interlayer insulating layer is suppressed can be provided.

According to the second aspect, a rinsing liquid with which the sealing layer for a semiconductor located on the exposed face of the wiring can effectively be removed can be provided.

According to the third aspect, a rinsing liquid which can improve the plasma resistance of the sealing layer for a semiconductor can be provided.

According to the fourth aspect, a semiconductor device can be provided in which diffusion of a wiring material (for example, copper) into the interlayer insulating layer is suppressed and an increase in the interconnection resistance of the connection portion between the wirings is suppressed.

According to the fifth aspect, a semiconductor device can be provided in which the plasma resistance of the sealing layer for a semiconductor is improved.

BRIEF DESCRIPTION OF DRAWINGS

[0018] Fig. 1 is a schematic cross-sectional diagram schematically illustrating a cross section of a semiconductor substrate before the sealing composition application process, in one example of the method for manufacturing a semiconductor device according to the first invention.

CLAIMS

1. A method for manufacturing a semiconductor device, the method comprising:

a sealing composition application process of applying a sealing composition for a semiconductor to at least a bottom face and a side face of a recess portion of a semiconductor substrate, to form a sealing layer for a semiconductor on at least the bottom face and the side face of the recess portion, the sealing composition for a semiconductor including a polymer having a cationic functional group and a weight average molecular weight of from 2,000 to 1,000,000, each of the content of sodium and the content of potassium in the sealing composition for a semiconductor being 10 ppb by mass or less on an elemental basis, and the semiconductor substrate being provided with an interlayer insulating layer having the recess portion and a copper-containing wiring of which at least a part of a surface thereof is exposed on at least a part of the bottom face of the recess portion; and

a removal process of subjecting a surface of the semiconductor substrate at a side at which the sealing layer for a semiconductor has been formed to heat treatment under a temperature condition of from 200°C to 425°C, to remove at least a part of the sealing layer for a semiconductor that has been formed on an exposed face of the wiring,

wherein the duration of the heat treatment is 30 minutes or less.

2. The method for manufacturing a semiconductor device according to claim 1, wherein the polymer has a cationic functional group equivalent weight of from 27 to 430.

3. The method for manufacturing a semiconductor device according to claim 1 or 2, wherein the polymer is polyethyleneimine or a polyethyleneimine derivative.

4. The method for manufacturing a semiconductor device according to claim 1 or 2, the method comprising a washing process of washing at least the side face and the bottom face of the recess portion with a rinsing liquid having a temperature of from 15°C to 100°C, after the sealing composition application process but before the removal process.

5. The method for manufacturing a semiconductor device according to claim 4, wherein the temperature of the rinsing liquid is from 30°C to 100°C.

6. The method for manufacturing a semiconductor device according to claim 1 or 2, the method comprising a washing process of washing at least the side face and the bottom

face of the recess portion with a rinsing liquid having a pH at 25°C of 6 or lower, after the sealing composition application process but before the removal process.

7. The method for manufacturing a semiconductor device according to claim 6, wherein the rinsing liquid includes a compound having, in one molecule thereof, at least one of a moiety A that blocks an active species or a moiety B that forms a bond with the polymer when heated.

8. A rinsing liquid for use in removal of at least a part of the sealing layer for a semiconductor that is formed in the sealing composition application process in the method for manufacturing a semiconductor device according to claim 1 or 2, the rinsing liquid having a pH at 25°C of 6 or lower,

wherein the rinsing liquid comprises a compound having, in one molecule thereof, a moiety A that blocks an active species and a moiety B that forms a bond with the polymer when heated, the moiety A is at least one selected from the group consisting of an aromatic ring structure, an alicyclic structure, and a manganese atom, and the moiety B is a carboxyl group.

9. A rinsing liquid for a sealing layer for a semiconductor, the sealing layer being formed on a surface of an interlayer insulating layer of a semiconductor substrate that includes the interlayer insulating layer, and being derived from a polymer having a cationic functional group and a weight average molecular weight of from 2,000 to 1,000,000,

~~the rinsing liquid comprising a compound having, in one molecule thereof, at least one of a moiety A that blocks an active species or a moiety B that forms a bond with the polymer when heated,~~

wherein the rinsing liquid comprises a compound having, in one molecule thereof, a moiety A that blocks an active species and a moiety B that forms a bond with the polymer when heated, the moiety A is at least one selected from the group consisting of an aromatic ring structure, an alicyclic structure, and a manganese atom, and the moiety B is a carboxyl group.

10. The rinsing liquid according to claim 9, wherein the compound has, in one molecule thereof, two or more carboxyl groups as the moiety B, and

wherein the compound has, in one molecule thereof, at least one of a structure in which each of two neighboring carbon atoms bonds to a carboxyl group or a structure in

which each of two non-central carbon atoms from among three consecutive carbon atoms bonds to a carboxyl group.

~~11. The rinsing liquid according to claim 9, wherein the compound has the moiety A and the moiety B, the moiety A is at least one selected from the group consisting of an aromatic ring structure, an alicyclic structure, a manganese atom, and a silicon atom, and the moiety B is a carboxyl group.~~

~~12~~11. A semiconductor device comprising, on a semiconductor substrate:

an interlayer insulating layer having a recess portion;

a first wiring that includes copper, and that is formed on the recess portion;

a sealing layer for a semiconductor that is present at least between a side face of the recess portion of the interlayer insulating layer and the first wiring, and that includes a polymer having a cationic functional group and a weight average molecular weight of from 2,000 to 1,000,000; and

a second wiring that contains copper, that has an upper face constituting at least a part of a bottom face of the recess portion, and that is electrically connected to the first wiring via the upper face,

wherein a thickness of the sealing layer for a semiconductor in a connection portion between the first wiring and the second wiring is 5 nm or less,

wherein the sealing layer for a semiconductor includes at least one selected from the group consisting of an imide bond and an amide bond, and also includes at least one selected from the group consisting of an aromatic ring structure and a manganese atom.

~~13~~12. A semiconductor device comprising, on a semiconductor substrate:

an interlayer insulating layer;

a first wiring that includes copper; and

a sealing layer for a semiconductor that is present between the interlayer insulating layer and the first wiring, and that includes a polymer having a cationic functional group and a weight average molecular weight of from 2,000 to 1,000,000,

wherein the sealing layer for a semiconductor includes at least one selected from the group consisting of an imide bond and an amide bond, and also includes at least one selected from the group consisting of an aromatic ring structure, and a manganese atom~~, and a silicon atom~~.

~~14~~13. The semiconductor device according to claim ~~12~~11 or ~~13~~12, wherein the polymer has a cationic functional group equivalent weight of from 27 to 430.

~~15~~14. The semiconductor device according to claim ~~12~~11 or ~~13~~12, wherein the polymer is polyethyleneimine or a polyethyleneimine derivative.

~~16~~15. The semiconductor device according to claim ~~12~~11 or ~~13~~12, wherein the interlayer insulating layer is a porous interlayer insulating layer having an average pore radius of from 0.5 nm to 3.0 nm.