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### Selective film formation using self-assembled monolayer

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#### Abstract

A film formation method includes (A) to (C) below: (A) preparing a substrate including, on a surface of the substrate, a first region from which an insulating film is exposed and a second region from which a metal film is exposed; (B) forming a self-assembled monolayer in the second region by supplying an organic compound containing a nitro group, which is a raw material of the self-assembled monolayer, in a head group to the surface of the substrate, and selectively adsorbing the organic compound to the second region among the first region and the second region; and (C) forming a second insulating film in the first region by supplying a raw material gas as a raw material of the second insulating film to the surface of the substrate while formation of the second insulating film in the second region is inhibited by the self-assembled monolayer.

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## **Background/Summary**

### **CROSS-REFERENCE TO RELATED APPLICATIONS**

(1) The present application is a U.S. National Stage Entry of International Patent Application No. PCT/JP2021/032609, filed Sep. 6, 2021, which claims the benefit of priority to Japanese Patent Application No. 2020-156666, filed Sep. 17, 2020, each of which is hereby incorporated herein by reference in its entirety.

### **TECHNICAL FIELD**

(2) The present disclosure relates to a film formation method and a film formation device.

### **BACKGROUND**

(3) Patent Document 1 discloses forming a self-assembled monolayer (SAM) on a metal island, and using a nitro group as an example of a head group of an organic compound as a raw material of the SAM. Similar contents are also disclosed in Patent Documents 2 and 3.

### **PRIOR ART DOCUMENTS**

Patent Documents

(4) Patent Document 1: U.S. Patent Application Publication No. 2006/0213425 Patent Document 2: U.S. Patent Application Publication No. 2019/0322812 Patent Document 3: U.S. Patent Application Publication No. 2010/0021851

(5) An aspect of the present disclosure provides a technique for selectively forming an SAM on a metal film among the metal film and an insulating film.

### **SUMMARY**

(6) A film formation method according to an aspect of the present disclosure includes (A) to (C) below: (A) preparing a substrate including, on a surface of the substrate, a first region from which an insulating film is exposed and a second region from which a metal film is exposed; (B) forming a self-assembled monolayer in the second region by supplying an organic compound containing a nitro group, which is a raw material of the self-assembled monolayer, in a head group to the surface of the substrate, and selectively adsorbing the organic compound to the second region among the first region and the second region; and (C) forming a second insulating film in the first region by supplying a raw material gas as a raw material of the second insulating film to the surface of the substrate while formation of the second insulating film in the second region is inhibited by the self-assembled monolayer.

(7) According to an aspect of the present disclosure, it is possible to selectively form an SAM on a metal film among the metal film and an insulating film.

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## Description

### BRIEF DESCRIPTION OF DRAWINGS

- (1) FIG. 1 is a flowchart illustrating a film formation method according to an embodiment.
- (2) FIG. 2A is a view illustrating a substrate in step S1 according to the embodiment.
- (3) FIG. 2B is a view illustrating the substrate in step S2 according to the embodiment.
- (4) FIG. 2C is a view illustrating the substrate in step S3 according to the embodiment.
- (5) FIG. 3A is a view illustrating a substrate in step S1 according to a first modification.
- (6) FIG. 3B is a view illustrating the substrate in step S2 according to the first modification.
- (7) FIG. 3C is a view illustrating the substrate in step S3 according to the first modification.
- (8) FIG. 4A is a view illustrating a substrate in step S1 according to a second modification.
- (9) FIG. 4B is a view illustrating the substrate in step S2 according to the second modification.
- (10) FIG. 4C is a view illustrating the substrate in step S3 according to the second modification.
- (11) FIG. 5 is a plan view illustrating a film formation device according to an embodiment.
- (12) FIG. 6 is a cross-sectional view illustrating an example of a first processor of FIG. 5.
- (13) FIG. 7 is a diagram showing a result of XPS measurement of a surface state of a Cu substrate obtained in Experiment Example 1.
- (14) FIG. 8 is a diagram showing a result of XPS measurement of a surface state of a Cu substrate obtained in Experiment Example 2.
- (15) FIG. 9 is a diagram showing a result of XPS measurement of a surface state of a Cu substrate obtained in Experiment Example 3.
- (16) FIG. 10 is a diagram showing results of XPS measurement of surface states of various substrates obtained in Experiment Example 4.
- (17) FIG. 11 is a diagram comparing and showing a result of a Cu substrate and a result of a SiO film, which are illustrated in FIG. 10.
- (18) FIG. 12 is a diagram comparing and showing a result of a Co film and the result of the SiO film, which are illustrated in FIG. 10.
- (19) FIG. 13 is a diagram comparing and showing a result of a Ru film and the result of the SiO film, which are illustrated in FIG. 10.
- (20) FIG. 14 is a diagram comparing and showing a result of a W film and the result of the SiO film, which are illustrated in FIG. 10.
- (21) FIG. 15 is a diagram comparing and showing a result of a TiN film and the result of the SiO film, which are illustrated in FIG. 10.

### DETAILED DESCRIPTION

- (22) Hereinafter, embodiments of the present disclosure will be described with reference to the drawings. In each drawing, the same or corresponding components may be denoted by the same reference numerals, and a description thereof may be omitted.
- (23) First, a film formation method according to the present embodiment will be described with reference to FIG. 1 and FIGS. 2A to 2C. The film formation method includes, for example, steps S1 to S3 illustrated in FIG. 1. The film formation method may include steps other than steps S1 to S3. In addition, the film formation method may include repeating steps S2 and S3 multiple times.
- (24) First, in step S1 of FIG. 1, a substrate 1 is prepared as illustrated in FIG. 2A. Preparing the substrate 1 includes, for example, loading a carrier C into a film formation device 100 illustrated in FIG. 5. The carrier C accommodates a plurality of substrates 1.
- (25) The substrate 1 includes a base substrate 10 such as a silicon wafer or a compound semiconductor wafer. The compound semiconductor wafer is not particularly limited, but is, for

example, a GaAs wafer, a SiC wafer, a GaN wafer, or an InP wafer.

(26) The substrate **1** includes an insulating film **11** formed on the base substrate **10**. A conductive film or the like may be formed between the insulating film **11** and the base substrate **10**. The insulating film **11** is, for example, an interlayer insulating film. The interlayer insulating film is preferably a low dielectric constant (low-k) film.

(27) The insulating film **11** is not particularly limited, but is, for example, a SiO film, a SiN film, a SiOC film, a SiON film, or a SiOCN film. Here, the SiO film means a film containing silicon (Si) and oxygen (O). An atomic ratio of Si and O in the SiO film is not limited to 1:1. The same is also applicable to the SiN film, the SiOC film, the SiON film, and the SiOCN film. The insulating film **11** has a recess on a surface **1a** of the substrate **1**. The recess is a trench, a contact hole, or via hole.

(28) The substrate **1** has a metal film **12** that fills an interior of the recess. Although the metal film **12** is not particularly limited, but is, for example, a Cu film, a Co film, a Ru film, or a W film.

(29) The substrate **1** further includes a barrier film **13** formed along the recess. The barrier film **13** suppresses metal diffusion from the metal film **12** to the insulating film **11**. The barrier film **13** is not particularly limited, but is, for example, a TaN film or a TiN film. Here, the TaN film means a film containing tantalum (Ta) and nitrogen (N). An atomic ratio of Ta and N in the TaN film is not limited to 1:1. The same is also applicable to the TiN film.

(30) Table 1 summarizes specific examples of the insulating film **11**, the metal film **12**, and the barrier film **13**.

(31) TABLE-US-00001 TABLE 1 Insulating film Metal film Barrier film SiO film Cu film TaN film SiN film Co film TiN film SiOC film Ru film SiON film W film SiOCN film

(32) In addition, a combination of the insulating film **11**, the metal film **12**, and the barrier film **13** is not particularly limited.

(33) As shown in FIG. 2A, the substrate **1** includes, on its surface **1a**, a first region A1 from which the insulating film **11** is exposed and a second region A2 from which the metal film **12** is exposed. The substrate **1** may further include, on its surface **1a**, a third region A3 from which the barrier film **13** is exposed. The third region A3 is formed between the first region A1 and the second region A2. The structure of the substrate **1** is not limited to the structure illustrated in FIG. 2A, as will be described later.

(34) The substrate **1** may be subjected to a step of removing a natural oxide film before being subjected to step S2 of FIG. 1. The natural oxide film is formed on the surface of the metal film **12**. Removing the natural oxide film includes, for example, supplying hydrogen (H.sub.2) gas to the surface **1a** of the substrate **1**. The hydrogen gas reduces and removes the natural oxide film. The hydrogen gas may be heated to a high temperature to promote a chemical reaction. In addition, the hydrogen gas may be plasmarized to promote the chemical reaction.

(35) Removing the natural oxide film is not limited to a dry process on the surface **1a** of the substrate **1** but may be a wet process. For example, removing the natural oxide film may be performed by supplying a solution such as citric acid (C(OH)(CH<sub>2</sub>COOH)<sub>2</sub>) to the surface **1a** of the substrate **1**. Thereafter, the substrate **1** is cleaned with pure water or the like and dried.

(36) Subsequently, in step S2 of FIG. 1, as shown in FIG. 2B, an organic compound containing a nitro group, which is a raw material of an SAM **17**, in a head group is supplied to the surface **1a** of the substrate **1**. The nitro group is more easily chemisorbed to the metal film **12** than to the insulating film **11**. Therefore, it is possible to selectively chemisorb the organic component and thus to form the SAM **17** in the second region A2 among the first region A1 and the second region A2.

(37) The nitro group is more easily chemisorbed to the barrier film **13** than to the insulating film **11**. Therefore, as illustrated in FIG. 2B, it is possible to selectively chemisorb the organic compound and thus to form the SAM **17** in the second region A2 and the third region A3, among the first region A1, the second region A2, and the third region A3. Thus, the organic compound

containing a nitro group in a head group may form the SAM **17** over a plurality of regions (e.g., the second region **A2** and the third region **A3**).

(38) The organic compound containing a nitro group in a head group is represented by a chemical formula “R—NO<sub>2</sub>.” R is, for example, a hydrocarbon group or a hydrocarbon group in which at least a part of hydrogen atoms is substituted with halogen elements. The halogen elements include fluorine, chlorine, bromine, iodine, and the like. A specific example of such an organic compound includes CF<sub>3</sub>(CF<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>NO<sub>2</sub>.

(39) The above-mentioned organic compound may be supplied to the surface **1a** of the substrate **1** in a gaseous state or may be supplied to the surface **1a** of the substrate **1** in a liquid state. However, the former may form a denser SAM **17** than the latter. Details will be described later.

(40) Subsequently, in step **S3** of FIG. **1**, as illustrated in FIG. **2C**, a raw material gas as a raw material for a second insulating film **18** is supplied to the surface **1a** of the substrate **1** to form the second insulating film **18** in the first region **A1** while formation of the second insulating film **18** in the second region **A2** is inhibited by the SAM **17**. The second insulating film **18** is formed on the insulating film **11**, and is not formed on the metal film **12**.

(41) As described above, the SAM **17** is formed not only in the second region **A2** but also in the third region **A3**. In this case, in step **S3**, the second insulating film **18** is formed in the first region **A1** while formation of the second insulating film **18** in the second region **A2** and the third region **A3** is inhibited by the SAM **17**. The second insulating film **18** is formed on the insulating film **11**, and is not formed on the metal film **12** and the barrier film **13**. According to the present embodiment, it is possible to reduce a wiring resistance of the substrate **1** compared to a case where the second insulating film **18** is formed on the barrier film **13**.

(42) The second insulating film **18** is formed through a chemical vapor deposition (CVD) method or an atomic layer deposition (ALD) method. The second insulating film **18** is not particularly limited, but is, for example, an AlO film, a SiO film, a SiN film, a ZrO film, a HfO film, or the like. Here, the AlO film means a film containing aluminum (Al) and oxygen (O). An atomic ratio of Al and O in the AlO film is not limited to 1:1. The same is also applicable to the SiO film, the SiN film, the ZrO film, and the HfO film. The second insulating film **18** may be made of the same material as the insulating film **11** or may be made of a different material.

(43) When the AlO film is formed through the ALD method, an Al-containing gas such as trimethylaluminum (TMA) gas and an oxidizing gas such as water vapor (H<sub>2</sub>O gas) are alternately supplied to the surface **1a** of the substrate **1**. Since the water vapor is not adsorbed to the hydrophobic SAM **17**, AlO is selectively deposited in the first region **A1**. A modifying gas such as hydrogen gas may be supplied to the substrate **1** in addition to the Al-containing gas and the oxidizing gas. These raw material gases may be plasmarized to promote a chemical reaction. In addition, these raw material gases may be heated to promote the chemical reaction.

(44) When the HfO film is formed through the ALD method, a Hf-containing gas such as tetrakis(dimethylamide)hafnium (TDMAH: Hf[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>) gas and an oxidizing gas such as water vapor (H<sub>2</sub>O gas) are alternately supplied to the surface **1a** of the substrate **1**. Since the water vapor is not adsorbed to the hydrophobic SAM **17**, HfO is selectively deposited in the second region **A1**. A modifying gas such as hydrogen gas may be supplied to the substrate **1** in addition to the Hf-containing gas and the oxidizing gas. These raw material gases may be plasmarized to promote a chemical reaction. In addition, these raw material gases may be heated to promote the chemical reaction.

(45) Next, processing the substrate **1** according to a first modification will be described with reference to FIGS. **3A** to **3C**. As illustrated in FIG. **3A**, the substrate **1** of this modification example further includes, on its surface **1a**, a fourth region **A4** from which a liner film **14** is exposed. The fourth region **A4** is formed between the second region **A2** and the third region **A3**. The liner film **14** is formed on the barrier film **13** to assist formation of the metal film **12**. The metal film **12** is formed on the liner film **14**. The liner film **14** is not particularly limited, but is, for example, a Co

film or a Ru film.

(46) Table 2 summarizes specific examples of the insulating film **11**, the metal film **12**, the barrier film **13**, and the liner film **14**.

(47) TABLE-US-00002 TABLE 2 Insulating film Metal film Barrier film Liner film SiO film Cu film TaN film Co film SiN film TiN film Ru film SiOC film SiON film SiOCN film

(48) In addition, a combination of the insulating film **11**, the metal film **12**, the barrier film **13**, and the liner film **14** is not particularly limited.

(49) However, the nitro group of the organic compound as the raw material of the SAM **17** is more easily chemisorbed to the liner film **14** than to the insulating film **11**.

(50) Therefore, in step S2 of this modification, as illustrated in FIG. 3B, it is possible to selectively chemisorb the organic compound and thus to form the SAM **17** in the second region A2, the third region A3, and the fourth region A4, among the first region A1, the second region A2, the third region A3, and the fourth region A4. The SAM **17** is not formed in the first region A1.

(51) In step S3 of this modification, as illustrated in FIG. 3C, the second insulating film **18** is formed in the first region A1 while formation of the second insulating film **18** in the second region A2, the third region A3, and the fourth region A4 is inhibited by the SAM **17**. The second insulating film **18** is formed on the insulating film **11**, and is not formed on the metal film **12**, the barrier film **13**, and the liner film **14**. According to this modification, it is possible to reduce a wiring resistance of the substrate **1** compared to a case where the second insulating film **18** is formed on the barrier film **13** and the liner film **14**.

(52) Next, processing the substrate **1** according to a second modification will be described with reference to FIGS. 4A to 4C. In the substrate **1** of this modification, the metal film **12** is a cap film, as illustrated in FIG. 4A. A second metal film **15** made of a metal different from that of the metal film **12** is embedded in the recess of the insulating film **11**. The metal film **12** is formed on the second metal film **15**, and the metal film **12** covers the second metal film **15**.

(53) Table 3 summarizes specific examples of the insulating film **11**, the metal film (cap film) **12**, the barrier film **13**, the liner film **14**, and the second metal film **15**.

(54) TABLE-US-00003 TABLE 3 Insulating Metal film Second metal film (Cap film) Barrier film Liner film film SiO film Co film TaN film Co film Cu film SiN film Ru film TiN film Ru film SiOC film SiON film SiOCN film

(55) In addition, a combination of the insulating film **11**, the metal film **12**, the barrier film **13**, the liner film **14**, and the second metal film **15** is not particularly limited.

(56) In step S2 of this modification, as illustrated in FIG. 4B, it is possible to selectively chemisorb the organic compound and thus to form the SAM **17** in the second region A2, the third region A3, and the fourth region A4, among the first region A1, the second region A2, the third region A3, and the fourth region A4. The SAM **17** is not formed in the first region A1.

(57) In step S3 of this modification, as illustrated in FIG. 4C, the second insulating film **18** is formed in the first region A1 while formation of the second insulating film **18** in the second region A2, the third region A3, and the fourth region A4 is inhibited by the SAM **17**. The second insulating film **18** is formed on the insulating film **11**, and is not formed on the metal film **12**, the barrier film **13**, and the liner film **14**. According to this modification, it is possible to reduce a wiring resistance of the substrate **1** compared to a case where the second insulating film **18** is formed on the barrier film **13** and the liner film **14**.

(58) Next, with reference to FIG. 5, the film formation device **100** that executes the above-described film formation method will be described. As illustrated in FIG. 5, the film formation device **100** includes a first processor **200A**, a second processor **200B**, a transporter **400**, and a controller **500**. The first processor **200A** executes step S2 of FIG. 1. The second processor **200B** executes step S3 of FIG. 1. The first processor **200A** and the second processor **200B** have the same structure. Therefore, it is also possible to execute both steps S2 and S3 in FIG. 1 only by the first processor **200A**. The transporter **400** transports the substrate **1** with respect to the first processor

**200A** and the second processor **200B**. The controller **500** controls the first processor **200A**, the second processor **200B**, and the transporter **400**.

(59) The transporter **400** includes a first transport chamber **401** and a first transport mechanism **402**. An internal atmosphere of the first transport chamber **401** is atmospheric atmosphere. The first transport mechanism **402** is provided inside the first transport chamber **401**. The first transport mechanism **402** includes an arm **403** that holds the substrate **1**, and travels along a rail **404**. The rail **404** extends in a direction along which carriers **C** are arranged.

(60) In addition, the transporter **400** includes a second transport chamber **411** and a second transport mechanism **412**. The internal atmosphere of the second transport chamber **411** is a vacuum atmosphere. The second transport mechanism **412** is provided inside the second transport chamber **411**. The second transport mechanism **412** includes an arm **413** that holds the substrate **1**, and the arm **413** is disposed to be movable in the vertical direction and the horizontal direction and to be rotatable around the vertical axis. The first processor **200A** and the second processor **200B** are connected to the second transport chamber **411** via different gate valves **G**.

(61) In addition, the transporter **400** includes load-lock chambers **421** between the first transport chamber **401** and the second transport chamber **411**. An internal atmospheres of the load-lock chambers **421** are switched between a vacuum atmosphere and atmospheric atmosphere by a pressure regulating mechanism (not illustrated). Thus, an interior of the second transport chamber **411** can always be maintained in a vacuum atmosphere. In addition, it is possible to suppress an inflow of a gas from the first transport chamber **401** to the second transport chamber **411**. Gate valves **G** are provided between the first transport chamber **401** and the load-lock chambers **421**, and between the second transport chamber **411** and the load-lock chambers **421**.

(62) The controller **500** is, for example, a computer and includes a central processing unit (CPU) **501** and a storage medium **502** such as a memory. The storage medium **502** stores programs for controlling various processes executed in the film formation device **100**. The controller **500** controls operations of the film formation device **100** by causing the CPU **501** to execute the programs stored in the storage medium **502**. The controller **500** controls the first processor **200A**, the second processor **200B**, and the transporter **400** to execute the above-described film formation method.

(63) Next, operations of the film formation device **100** will be described. First, the first transport mechanism **402** takes out the substrate **1** from the carrier **C**, transports the taken-out substrate **1** to the load-lock chamber **421**, and withdraws the substrate **1** from the load-lock chamber **421**. Subsequently, the internal atmosphere of the load-lock chamber **421** is switched from atmospheric atmosphere to the vacuum atmosphere. Thereafter, the second transport mechanism **412** takes out the substrate **1** from the load-lock chamber **421** and transports the taken-out substrate **1** to the first processor **200A**.

(64) Subsequently, the first processor **200A** executes step **S2**. Thereafter, the second transport mechanism **412** takes out the substrate **1** from the first processor **200A** and transports the taken-out substrate **1** to the second processor **200B**. During this period, since it is possible to maintain a surrounding atmosphere of the substrate **1** to be a vacuum atmosphere, the substrate **1** can be suppressed from being oxidized.

(65) Subsequently, the second processor **200B** executes step **S3**. Thereafter, the second transport mechanism **412** takes out the substrate **1** from the second processor **301**, transports the taken-out substrate **1** to the load-lock chamber **421**, and withdraws the substrate **1** from the load-lock chamber **421**. Subsequently, the internal atmosphere of the load-lock chamber **421** is switched from the vacuum atmosphere to atmospheric atmosphere. Thereafter, the first transport mechanism **402** takes out the substrate **1** from the load-lock chamber **421** and accommodates the taken-out substrate **1** in the carrier **C**. Then, processing the substrate **1** is completed.

(66) Next, the first processor **200A** will be described with reference to FIG. **6**. Since the second processor **200B** is configured in the same manner as the first processor **200A**, illustration and



description thereof will be omitted.

(67) The first processor **200A** includes a substantially cylindrical and airtight processing container **210**. A gas exhaust chamber **211** is provided in a central portion of a bottom wall of the processing container **210**. The gas exhaust chamber **211** has, for example, a substantially cylindrical shape that protrudes downward. A gas exhaust pipe **212** is connected to the gas exhaust chamber **211**, for example, on a side surface of the gas exhaust chamber **211**.

(68) A gas exhaust source **272** is connected to the gas exhaust pipe **212** via a pressure controller **271**. The pressure controller **271** includes a pressure regulating valve such as a butterfly valve. The gas exhaust pipe **212** is configured such that a pressure inside the processing container **210** can be reduced by the gas exhaust source **272**. The pressure controller **271** and the gas exhaust source **272** constitute a gas discharge mechanism **270** configured to discharge a gas inside the processing container **210**.

(69) A transport port **215** is provided in the side surface of the processing container **210**. The transport port **215** is opened and closed by a gate valve G. Loading and unloading the substrate **1** between an interior of the processing container **210** and the second transport chamber **411** (see FIG. 5) may be performed via the transport port **215**.

(70) A stage **220**, which is a holder configured to hold the substrate **1**, is provided in the processing container **210**. The stage **220** holds the substrate **1** horizontally with the surface **1a** of the substrate **1** facing upward. The stage **220** has a substantially circular shape in a plan view and is supported by a support **221**. In a surface of the stage **220**, a substantially circular recess **222** for placing the substrate **1** having a diameter of, for example, 300 mm is formed. The recess **222** has an inner diameter slightly larger than the diameter of the substrate **1**. A depth of the recess **222** is substantially the same as, for example, a thickness of the substrate **1**. The stage **220** is made of a ceramic material such as aluminum nitride (AlN). The stage **220** may be made of a metallic material such as nickel (Ni). Instead of the recess **222**, a guide ring configured to guide the substrate **1** may be provided on a peripheral edge of the surface of the stage **220**.

(71) A lower electrode **223**, which is grounded, for example, is embedded in the stage **220**. A heating mechanism **224** is embedded below the lower electrode **223**. The heating mechanism **224** heats the substrate **1** placed on the stage **220** to a set temperature by receiving power from a power supply (not illustrated) based on a control signal from the controller **500** (see FIG. 5). When the entire stage **220** is made of metal, the entire stage **220** functions as a lower electrode, and thus it is not necessary to embed the lower electrode **223** in the stage **220**. The stage **220** is provided with a plurality of (e.g., three) lifting pins **231** configured to hold and lift the substrate **1** placed on the stage **220**. A material of the lifting pins **231** may be, for example, ceramic such as alumina (Al.sub.2O.sub.3), quartz, or the like. Lower ends of the lifting pins **231** are installed on a support plate **232**. The support plate **232** is connected to a lifting mechanism **234** provided outside the processing container **210** via a lifting shaft **233**.

(72) The lifting mechanism **234** is installed, for example, below the gas exhaust chamber **211**. A bellows **235** is provided between an opening **219** for the lifting shaft **233** formed in a bottom surface of the gas exhaust chamber **211** and the lifting mechanism **234**. The support plate **232** may have a shape configured to be raised and lowered without interfering with the support **221** of the stage **220**. The lifting pins **231** are configured to be raised and lowered by the lifting mechanism **234** between a position above the surface of the stage **220** and a position below the surface of the stage **220**.

(73) A gas supply **240** is provided on a ceiling wall **217** of the processing container **210** via an insulating member **218**. The gas supply **240** constitutes an upper electrode and faces the lower electrode **223**. A radio-frequency power supply **252** is connected to the gas supply **240** via a matcher **251**. By supplying radio-frequency power of 450 kHz to 100 MHz from the radio-frequency power supply **252** to the upper electrode (the gas supply **240**), a radio-frequency electric field is generated between the upper electrode (the gas supply **240**) and the lower electrode **223** to

generate capacitively coupled plasma. A plasma generator **250** configured to generate plasma includes the matcher **251** and the radio-frequency power supply **252**. The plasma generator **250** is not limited to generate capacitively coupled plasma, and may generate other plasma such as inductively coupled plasma.

(74) The gas supply **240** includes a hollow gas supply chamber **241**. In a bottom surface of the gas supply chamber **241**, a plurality of holes **242** configured to disperse and supply a processing gas into the processing container **210** is arranged, for example, evenly. A heating mechanism **243** is embedded in the gas supply **240**, for example, above the gas supply chamber **241**. The heating mechanism **243** is heated to a set temperature by receiving power from a power supply (not illustrated) based on a control signal from the controller **500**.

(75) A gas supply mechanism **260** is connected to the gas supply chamber **241** via a gas path **261**. The gas supply mechanism **260** supplies a gas, which is used in at least one of steps S2 and S3 in FIG. 1, to the gas supply chamber **241** via the gas path **261**. Although not illustrated, the gas supply mechanism **260** includes an individual pipe for each type of gases, an opening/closing valve provided in a middle of the individual pipe, and a flow controller provided in a middle of the individual pipe. When the opening/closing valve opens the individual pipe, a gas is supplied from a source thereof to the gas path **261**. A supply amount of the gas is controlled by the flow controller. On the other hand, when the opening/closing valve closes the individual pipe, the supply of the gas from the source to the gas path **261** is stopped.

#### Experiment Example 1

(76) In Experiment Example 1, a Cu substrate was prepared, a natural oxide film on a surface of the Cu substrate was removed, a raw material of an SAM was supplied to the surface of the Cu substrate, and the Cu substrate was heated to fix the SAM. Thereafter, the surface state of the Cu substrate was measured with an X-ray photoelectron spectroscopy (XPS) device.

(77) In removing the natural oxide film, the Cu substrate was immersed for one minute in an aqueous solution having a citric acid concentration of 1% by volume and a temperature of 65 degrees C. Thereafter, the Cu substrate was cleaned with pure water, and then dried with N.sub.2 gas.

(78) In supplying the raw material of the SAM, the Cu substrate was immersed for thirty minutes in a room-temperature toluene solution having a concentration of the raw material of the SAM of 0.1% by volume. Thereafter, the Cu substrate was washed with toluene at room temperature, and then dried with N.sub.2 gas. CF.sub.3(CF.sub.2).sub.5CH.sub.2CH.sub.2NO.sub.2 was used as the raw material of the SAM.

(79) In fixing the SAM, the Cu substrate was heated for ten minutes on a hot plate having a temperature of 60 degrees C., and then heated for four minutes on a hot plate having a temperature of 120 degrees C.

(80) FIG. 7 shows a result of XPS measurement of a surface state of the Cu substrate obtained in Experiment Example 1. As shown in FIG. 7, since a peak of fluorine (F), which is a constituent element of the SAM, is recognized, it can be seen that the SAM was formed on the surface of the Cu substrate.

#### Experiment Example 2

(81) In Experiment Example 2, a Cu substrate was processed under the same conditions as in Experiment Example 1, except that a processing temperature was changed from room temperature to 85 degrees C. when supplying the raw material of the SAM to the surface of the Cu substrate. Specifically, in supplying the raw material of the SAM, the Cu substrate was immersed for five minutes in a toluene solution having a concentration of the raw material of the SAM of 0.1% by volume and a temperature of 85 degrees C. Thereafter, the Cu substrate was washed with toluene at 85 degrees C., and dried with N.sub.2 gas.

(82) FIG. 8 shows a result of XPS measurement of a surface state of the Cu substrate obtained in Experiment Example 2. As shown in FIG. 8, since a peak of fluorine (F), which is a constituent

element of the SAM, is recognized, it can be seen that the SAM was formed on the surface of the Cu substrate.

(83) In addition, since the peak of fluorine in FIG. 8 is larger than the peak of fluorine in FIG. 7, it can be seen that, by changing the processing temperature from room temperature to 85 degrees C. when supplying the raw material of the SAM to the surface of the Cu substrate, the SAM is formed on the surface of the Cu substrate at a higher density.

#### Experiment Example 3

(84) In Experiment Example 3, the Cu substrate was processed under the same conditions as in Experimental Example 2, except that the raw material of the SAM was supplied to the surface of the Cu substrate in a gaseous state instead of being supplied in a liquid state. Specifically, in supplying the raw material of the SAM in Experiment Example 3, first, both a toluene solution having concentration of the raw material of the SAM of 0.1% by volume and a Cu substrate were accommodated in a container, and the Cu substrate was placed above a liquid surface. In that state, the entire container was uniformly heated from outside by a heater. A heating temperature was 85 degrees C., and a heating time was five minutes. Thus, the raw material of the SAM was supplied to the surface of the Cu substrate in a gaseous state.

(85) FIG. 9 shows a result of XPS measurement of a surface state of the Cu substrate obtained in Experiment Example 3. As shown in FIG. 9, since a peak of fluorine (F), which is a constituent element of the SAM, is recognized, it can be seen that the SAM was formed on the surface of the Cu substrate.

(86) In addition, since the peak of fluorine in FIG. 9 is larger than the peak of fluorine in FIG. 8, it can be seen that by supplying the SAM to the Cu substrate surface in a gaseous state instead of in a liquid state, the SAM is formed on the Cu substrate surface at a higher density.

#### Experiment Example 4

(87) In Experiment Example 4, except that various substrates were prepared instead of the Cu substrate, the substrates were processed under the same conditions as in Experiment Example 2. As the substrates, a substrate having a Co film on a surface thereof, a substrate having a Ru film on a surface thereof, a substrate having a W film on a surface thereof, a substrate having a TiN film on a surface thereof, and a substrate having a SiO film on a surface thereof were prepared. The SiO film was a silicon thermal oxide film.

(88) In addition, in supplying the raw material of the SAM in Experiment Example 4, the substrates were immersed for five minutes in a toluene solution having a concentration of the raw material of the SAM of 0.1% by volume and a temperature of 85 degrees C., in the same manner as in the supplying of the raw material of the SAM in Experiment Example 2. Thereafter, the substrates were cleaned with toluene at 85 degrees C., and dried with N.sub.2 gas.

(89) FIG. 10 shows results of XPS measurement of surface states of the various substrates obtained in Experiment Example 4. FIG. 10 also shows the result of XPS measurement of the surface state of the Cu substrate of Experiment Example 2. As is clear from FIGS. 10 to 15, the raw material of the SAM is more easily adsorbed to Cu, Co, Ru, W, and TiN than to SiO.

(90) Therefore, it can be seen that an organic compound containing a nitro group in a head group is capable of forming an SAM not only in a region in which a metal film is exposed but also in a region in which a barrier film is exposed or a region in which a liner film is exposed. In addition, the SAM is capable of inhibiting not only formation of the second insulating film on the metal film, but also formation of the second insulating film on the barrier film or the liner film. Therefore, it is possible to reduce the wiring resistance of the substrate 1.

(91) Although the embodiments of the film formation method and the film formation device according to the present disclosure have been described above, the present disclosure is not limited to the above-described embodiments or the like. Various changes, modifications, substitutions, additions, deletions, and combinations may be made within the scope of the claims. Of course, these also fall within the technical scope of the present disclosure.

(92) This application claims priority based on Japanese Patent Application No. 2020-156666 filed with the Japan Patent Office on Sep. 17, 2020, and the disclosure of Japanese Patent Application No. 2020-156666 is incorporated herein in its entirety by reference.

#### EXPLANATION OF REFERENCE NUMERALS

(93) **1**: substrate, **1a**: surface, **11**: insulating film, **12**: metal film, **17**: self-assembled monolayer (SAM), **18**: second insulating film, **A1**: first region, **A2**: second region

### Claims

1. A film formation method comprising: preparing a substrate in which a first insulating film and a first metal film are formed, wherein a surface of the substrate includes a first region from which the first insulating film is exposed and a second region from which the first metal film is exposed; forming a self-assembled monolayer on the first metal film in the second region by supplying, as a raw material of the self-assembled monolayer, an organic compound containing a nitro group in a head group to the surface of the substrate, and selectively adsorbing the organic compound to the second region among the first region and the second region; and forming a second insulating film on the first insulating film in the first region by supplying a raw material gas as a raw material of the second insulating film to the surface of the substrate while formation of the second insulating film in the second region is inhibited by the self-assembled monolayer.
2. The film formation method of claim 1, wherein the first insulating film has a recess in the surface of the substrate, and wherein the first metal film is formed in the recess.
3. The film formation method of claim 2, wherein the substrate further includes, on the surface of the substrate, a third region from which a barrier film is exposed, and wherein the film formation method further comprises: forming the self-assembled monolayer in the second region and the third region by selectively adsorbing the organic compound to the second region and the third region, among the first region, the second region, and the third region; and forming the second insulating film in the first region while formation of the second insulating film in the second region and the third region is inhibited by the self-assembled monolayer.
4. The film formation method of claim 3, wherein the barrier film is a TaN film or a TiN film.
5. The film formation method of claim 4, wherein the substrate further includes, on the surface of the substrate, a fourth region from which a liner film is exposed, and wherein the film formation method further comprises: forming the self-assembled monolayer in the second region, the third region, and the fourth region by selectively adsorbing the organic compound to the second region, the third region, and the fourth region, among the first region, the second region, the third region, and the fourth region; and forming the second insulating film in the first region while formation of the second insulating film in the second region, the third region, and the fourth region is inhibited by the self-assembled monolayer.
6. The film formation method of claim 5, wherein the liner film is a Co film or a Ru film.
7. The film formation method of claim 6, wherein a second metal film made of a metal different from the first metal film is buried inside the recess, and wherein the first metal film is a cap film that covers the second metal film.
8. The film formation method of claim 7, wherein the second metal film is a Cu film, and wherein the cap film as the first metal film is a Co film or a Ru film.
9. The film formation method of claim 8, wherein the first insulating film is a SiN film, a SiO film, a SiOC film, a SiON film, or a SiOCN film.
10. The film formation method of claim 9, further comprising supplying the organic compound in a gaseous state to the surface of the substrate.
11. The film formation method of claim 3, wherein the substrate further includes, on the surface of the substrate, a fourth region from which a liner film is exposed, and wherein the film formation method further comprises: forming the self-assembled monolayer in the second region, the third

region, and the fourth region by selectively adsorbing the organic compound to the second region, the third region, and the fourth region, among the first region, the second region, the third region, and the fourth region; and forming the second insulating film in the first region while formation of the second insulating film in the second region, the third region, and the fourth region is inhibited by the self-assembled monolayer.

12. The film formation method of claim 2, wherein a second metal film made of a metal different from the first metal film is buried inside the recess, and wherein the first metal film is a cap film that covers the second metal film.

13. The film formation method of claim 2, wherein the first metal film is a Cu film or a W film.

14. The film formation method of claim 2, wherein the first insulating film is a SiN film, a SiO film, a SiOC film, a SiON film, or a SiOCN film.

15. The film formation method of claim 1, further comprising supplying the organic compound in a gaseous state to the surface of the substrate.

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