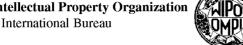
(19) World Intellectual Property Organization





(43) International Publication Date 29 January 2009 (29.01.2009)

(10) International Publication Number WO 2009/014741 A2

(51) International Patent Classification: C23C 16/50 (2006.01) H01L 21/20 (2006.01)

(21) International Application Number:

PCT/US2008/009021

(22) International Filing Date: 24 July 2008 (24.07.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/961.877 24 July 2007 (24.07.2007) US 12/005,683 28 December 2007 (28.12.2007)

(71) Applicant (for all designated States except US): TOKYO ELECTRON LIMITED [—/JP]; 3-1, Akasaka 5-chome, Minato-ku, Tokyo 107-6325 (JP).

(72) Inventors; and

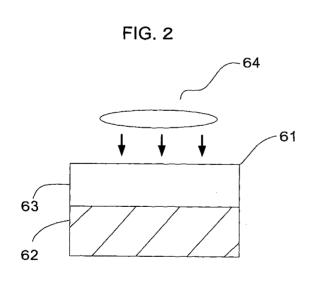
(75) Inventors/Applicants (for US only): MIYATANI, Kotaro [JP/JP]; c/o Tokyo Electron Technology Development Institute, Inc. 650, Mitsuzawa, Hosaka-cho, Nirasaki-shi, Yamanashi 407-0192 (JP). KAWAMURA, Kohei [JP/US]; c/o Tokyo Electron America. Inc., Suite 8, 1800 NE 25th Avenue, Hillsboro, OR 97124 (US). NOZAWA, Toshihisa [JP/JP]; c/o Tokyo Electron Technology Development Institut, e, Inc., 1-8, Fuso-cho, Amagasaki-shi, Hyogo 660-0891 (JP). MATSUOKA, Takaaki [JP/JP]; c/o Tokyo Electron Limited, 3-1, Akasaka 5-chome, Minato-ku, Tokyo 107-6325 (JP).

(74) Agent: MARTINEZ, Peter, R.; Masuvalley and Partners, 8765 Aero Drive, Suite 312, San Diego, CA 92123 (US).

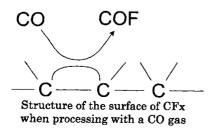
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ,

[Continued on next page]

(54) Title: A PLASMA PROCESSING METHOD FOR FORMING A FILM AND AN ELECTRONIC COMPONENT MANU-FACTURED BY THE METHOD



(57) Abstract: The present invention is a semiconductor device manufacturing method including the steps of forming a fluorinated insulating film, depositing a first Si_xC_vN_z film on the fluorinated insulating film by reacting a mono-methylsilane and depositing a second Si_xC_yN_z film on the first Si_xC_yN_z film by reacting a tri-methylsilane. The present invention is also a semiconductor device including a fluorinated insulating film, a first Si_xC_yN_z film deposited on the fluorinated insulating film by reacting a mono-methylsilane and a second Si_xC_vN_z film deposited on the first Si_xC_vN_z film by reacting a tri-methylsilane.



TM,TN,TR,TT,TZ,UA,UG,US,UZ,VC,VN,ZA,ZM,ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL,

NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

 as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

Published:

 without international search report and to be republished upon receipt of that report

A PLASMA PROCESSING METHOD FOR FORMING A FILM AND AN ELECTRONIC COMPONENT MANUFACTURED BY THE METHOD

[0001]

[**

This application claims priority to U.S. Provisional Application Serial No. 60/961,877, filed on July 24, 2007, entitled "Manufacturing Method for Semiconductor Device", which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

10

15

20

25

5

[0002]

The present invention relates to a method for forming a film on a substrate using plasma in an electronic component applicable to a semiconductor device, a liquid crystal display device and an organic EL element, and also relates to the electronic component manufactured by the method.

BACKGROUND OF THE INVENTION

[0003]

In a manufacturing process for electronic devices, such as semiconductor devices, liquid crystal display devices, and organic electro-luminescent (EL) elements, a film forming process is performed to form a conductive film or an insulating film on the surface of a substrate. A plasma film forming process for forming a film on a substrate using plasma is employed in this film forming process. In a case when forming a CF film on a substrate, and further forming an insulating film on the CF film in the film forming process, there has been a problem that the fluorine atom in the CF film diffuses in the insulating film, thereby the contactablity of the CF film and the insulating film decreases. Also, there has been a problem that the insulation film may peel off due to corrosion of the insulating film by the fluorine atom diffused in the insulating film when the CF film and the insulating film are heat treated at a subsequent film forming process.

30

[0004]

By the way, the above plasma film forming process is normally performed by a plasma film forming device. In recent years, a microwave plasma film forming device, which forms a film by generating plasma by a microwave field, has been attracting

attention as a type of plasma film forming device. According to this microwave plasma film forming device, high-density plasma compared to the conventional film forming devices can be obtained, thereby the film forming process to the substrate can be performed effectively in a short time.

5

[0005]

The microwave plasma film forming device described above is provided with, for example, a placing base to place a substrate inside a treatment vessel. And on the upper portion of the treatment vessel, provided are radial line slot antennas, and a shower plate to pass through the microwave from the radial line antennas and to supply plasma. Further, the microwave plasma film forming device is configured to a supply material gas for film from the wall surface of the treatment vessel.

[0006]

15

10

As plasma processing method for forming a film using the microwave plasma film forming device, for example, the following has been known. For example, Japanese Published Unexamined Patent Application No. 2005-093737 discloses a plasma processing method for forming a film on a substrate which is capable of forming a high quality film with a low temperature in a short time by optimizing the amounts of radicals and ions supplied to the substrate. Also, Japanese Published Unexamined Application No. 2006-324023 discloses a plasma film forming device capable of minimizing deformation or distortion of the shower plate by maintaining the temperature of the shower plate to a desired temperature, and improving the uniformity of an in-plane temperature of the shower plate.

25

30

20

[0007]

Also, Japanese Published Unexamined Patent Application No. 2005-150612 discloses a plasma film forming device which prevents the gas for plasma excitation from plasmanizing before it is supplied to the treatment vessel, and appropriately generates plasma within the area of a high-frequency wave supplying side, that is, plasma generating area. Further, International Published Unexamined Patent Application No. 2000-74127 discloses a plasma process device capable of maintaining the stability of the plasma regardless of the type of gas used for the process because there is no film attachment on

the surface of the dielectric shower plate of the microwave introduction part due to dissociation or binding of the gas for processing.

[8000]

5

However, it is difficult to prevent the fluorine atom in the CF film formed on the substrate from diffusing in the insulating film, and also to prevent the contactablity of the CF film and the insulating film from deteriorating by using any of the methods described in the documents above.

10

15

20

25

SUMMARY OF THE INVENTION

[0009]

One aspect of the present invention may be a semiconductor device manufacturing method including the steps of forming a fluorinated insulating film, depositing a first $Si_xC_yN_z$ film on the fluorinated insulating film by reacting a mono-methylsilane and depositing a second $Si_xC_yN_z$ film on the first $Si_xC_yN_z$ film by reacting a tri-methylsilane.

[0010]

The surface of the fluorinated insulating film may be treated with a CO plasma. The method may include the step of depositing the first $Si_xC_yN_z$ film by treating the monomethylsilane with a microwave plasma processing apparatus. The method may include the step of depositing the second $Si_xC_yN_z$ film by treating the tri-methylsilane with a microwave plasma processing apparatus. The first $Si_xC_yN_z$ film may satisfys an equation "y < z". The second $Si_xC_yN_z$ film may satisfy an equation "y > z". The fluorinated insulating film may be made of a material gas selected from a group including a C_4F_6 gas, a C_5F_8 gas and a C_3F_4 gas.

[0011]

30 fluoring by reac

Another aspect of the present invention may be a semiconductor device including a fluorinated insulating film, a first $\mathrm{Si_xC_yN_z}$ film deposited on the fluorinated insulating film by reacting a mono-methylsilane and a second $\mathrm{Si_xC_yN_z}$ film deposited on the first $\mathrm{Si_xC_yN_z}$ film by reacting a tri-methylsilane.

[0012]

The surface of the fluorinated insulating film may be treated with a CO plasma. The mono-methylsilane may be treated with a microwave plasma processing apparatus. The tri-methylsilane may be treated with a microwave plasma processing apparatus. The first $Si_xC_yN_z$ film may satisfys an equation "y < z". The second $Si_xC_yN_z$ film may satisfy an equation "y > z". The fluorinated insulating film may be made of a material gas selected from a group including a C_4F_6 gas, a C_5F_8 gas and a C_3F_4 gas.

[0013]

5

10

15

20

25

30

In a case when processing the CF film with plasma before forming the insulating film on the CF film, the diffusion of the fluorine in the insulating film may be decreased because the fluorine existing on the surface of the CF film can be reduced and removed. Further, by processing the CF film with the plasma, the corrosion of the insulating film can be prevented when heat treating the insulating film. In this way, the contactability of the CF film and the insulating film can be improved.

[0014]

In a case when forming the SiCN film, which has a higher nitrogen content than a methyl content, on the CF film, the diffusion of the fluorine atom from the CF film to the SiCN film may be decreased because the barrier characteristic of the SiCN film against the fluorine increases. As a result, the contactability of the CF film and the SiCN film can be improved.

[0015]

In a case when forming the SiCN film, which has a higher methyl content than a nitrogen content, the hydrogen plasma damage to the CF film and the SiCN film may be decreased due to the low hydrogen content of the SiCN film. In this way, the contactability of the CF film and the SiCN film can be improved.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016]

Figure 1 illustrates an electronic component forming a CF film on a substrate.

Figure 2 illustrates a condition of processing the surface of a CF film formed on a substrate with gas processed with plasma.

Figure 3 illustrates an electronic component after removing a fluorine end group on the surface of the CF film

Figure 4 illustrates an electronic component forming an insulating film on a CF film using a material gas processed with plasma.

Figure 5 illustrates an electronic component forming a SiCN film on the surface of a CF film using mono-methilsilane (1MS) and nitrogen (N₂), or ammonia (NH₃).

Figure 6 illustrates an electronic component further forming a SiCN film on the SiCN film formed in figure 5.

Figure 7 and 8 are diagrams showing a structure of a microwave plasma processing apparatus according to a first embodiment of the present invention.

Figure 9 is a perspective view showing a structure of a process gas supply mechanism of the microwave plasma processing apparatus of Figure 7 and 8.

Figure 10 is a bottom view showing a disk-like conductive body constituting a portion of the process gas supply mechanism in Figure 9.

Figure 11 illustrates a measurement of contactablity of a CF film and an insulating film of an electronic component manufactured without CO plasma process on the CF film.

Figure 12 illustrates a measurement of contactablity of a CF film and an insulating film of an electronic component manufactured with CO plasma process on the CF film.

DETAILED DESCRIPTION OF INVENTION

25 [0017]

5

10

15

20

30

One aspect of the present invention is a plasma processing method for forming a film on a substrate with gas processed with plasma, the plasma processing method for forming a film including the steps of forming a CF film on the substrate by using C_aF_b gas (here, a is a counting number, and b is a counting number which satisfying an equation of "b=2 X a-2".), processing the CF film with the gas processed by plasma and forming an insulating film on the CF film processed by using an insulating material processed with plasma.

[0018]

First, a CF film is formed on a substrate in the plasma processing method for forming a film. Figure 1 illustrates an electronic component 61 forming a CF film 63 on a substrate 62. The surface of the CF film on the substrate has a structure, for example, shown on the lower portion of Figure 1. With respect to the C_aF_b gas according to the present invention, a is a counting number, and b is a counting number which satisfies an equation of "b=2 X a-2". Particularly, C_4F_6 gas, C_5F_8 gas, C_3F_4 gas, C_6F_{10} gas, C_7F_{12} gas, or C_2F_2 gas may be utilized as the C_aF_b gas. Further, a plurality of CF films may be formed on the substrate according to the present invention.

[0019]

5

10

15

25

30

After forming the CF film on the substrate, process the formed CF film with gas processed by plasma. Figure 2 illustrates a condition of processing the surface of the CF film 63 formed on the substrate 62 with gas 64 processed with plasma. With respect to the gas processed by plasma (hereinafter also referred as plasma), a CO based plasma may be utilized. For example, CO plasma (carbon monoxide plasma), HCO plasma, and CH₃CO plasma may be utilized as CO based plasma. In a case when processing the surface of the CF film 63 with the CO plasma, the CO plasma and a fluorine atom, which exists in the surface of the CF film 63, react and generate COF plasma as shown in the lower portion of Figure 2. That is, the fluorine end group on the surface of the CF film is removed.

[0020]

Figure 3 illustrates an electronic component 61 after removing the fluorine end group on the surface of the CF film 65. The CF film reacts with a carbon atom derived CO, terminating the carbon atom bond with a carbon atom after removing the fluorine, and forming a cross-linked structure of carbon-carbon coupling. The result is a CF film processed with the CO plasma, for example, a chemical structure shown in the lower portion of Figure 3.

[0021]

Next, form an insulating film, which may act as a hard mask or a barrier layer, on the CF film processed with plasma. The insulating film is formed on the CF film by using a material gas processed with plasma. Figure 4 illustrates an electronic component 61, in which an insulating film 66 is formed on a CF film 65 by using a material gas processed with plasma. Here, for example, SiC film, SiCN film, SiCO film, SiCN film, SiCN film may

be utilized as an insulating film. A plurality of insulating films may be formed on the CF film 65.

[0022]

5

10

Further, for example, methane and, silane, mono-methylsilane (1MS), dimethylsilane (2MS), tri-methylsilane (3MS), tetra-methylsilane (4MS), and silazane may be utilized as the material gas. As a silazane, for example, methylsilazane, and ethylsilazane may be utilized. These material gases may be mixed to form the insulating film. Additional gasses may be utilized to form the insulating film as needed. For example, nitrogen (N₂) and ammonia (NH₃) may be utilized as an additional gas. Further, these gases may be mixed to form the insulating film. In a case when methylsilazane is used as a material gas to form a SiCN film as an insulating film, the SiCN film may be formed without using the additional gas. In a case when nitrogen (N₂) or ammonia (NH₃) is used when using methylsilazane, the amount of nitrogen in the SiCN film to be formed may be increased. In this way, the additional gas may be used to adjust the concentration of nitrogen in the SiCN film.

[0023]

20

15

film on the CF film, diffusion of fluorine in the insulating film may be decreased because the fluorine existing on the surface of the CF film can be reduced and removed. Also, processing the CF film with plasma prevents the insulating film from corrosion when the insulating film is heat processed. In this way, the contactability of the CF film and the insulating film can be increased. In a case when the insulating film is formed on the CF film after processing with plasma, a cross-linked structure of the carbon-carbon coupling as shown in the lower portion of Figure 3 is formed on the substrate 62, and the electronic component 61 will have a chemical structure that the insulating film binds to the carbon-carbon coupling. At this time, the chemical structure between the CF film and the

In a case when processing the CF film with plasma before forming the insulating

30

25

[0024]

Next, a process to form an insulating film on a CF film is explained by referring to a specific example. Figure 5 illustrates an electronic component 61 forming a SiCN film 67 on the surface of a CF film 65 using mono-methylsilane (1MS), and nitrogen (N₂) or

insulating film may be, for example, as shown in the lower portion of Figure 4.

ammonia (NH₃) processed with plasma. In this embodiment, mono-methylsilane (1MS) is used as a material gas, thus the nitrogen content in the formed SiCN film 67 is larger than the methyl content. Namely, when indicating the SiCN film 67 formed in the process in a form of Si_xC_yN_z, it is Si_xC_yN_z film (here, x, y and z are conting numbers, and y and z satisfy y<z). At this time, the chemical structure between the CF film and the SiCN film is, for example, as shown in the lower portion of Figure 5. As it can be appreciated from the chemical structure shown in the lower portion of Figure 5, the SiCN film 67 is in a condition where the amount of nitrogen atoms is larger than the methyl group.

10 [0025]

5

15

20

25

In a case when forming the SiCN film which has a higher nitrogen content than a methyl content, on the CF film, the diffusion of fluorine atom from the CF film to SiCN film may be decreased because the barrier characteristics of the SiCN film against the fluorine increases. As a result, contactability of the CF film and SiCN film can be increased.

[0026]

Figure 6 illustrates an electronic component 61 further forming a SiCN film 68 on the SiCN film 67 formed in Figure 5. The SiCN film 68 is formed by using trimethylsilane (3MS), and nitrogen (N₂), or ammonia (NH₃) processed with plasma. Since the SiCN film 68 is formed by using tri-methylsilane (3MS), the methyl content is larger than the nitrogen content. Namely, when indicating the SiCN film 68 formed in the process in a form of Si_{x'}, C_{y'}, N_{z'}, it is a Si_{x'}C_{y'}N_{z'} film (here, x', y' and z' are counting numbers, and y' and z' satisfy y'>z'). At this time, the chemical structures between each film, the CF film 65, SiCN film 67 and SiCN film 68, are, for example, as shown in the lower portion of Figure 6. As it can be appreciated from the chemical structure shown in the lower portion of Figure 6, the SiCN film 68 is in a condition where the amount of nitrogen atoms is larger than the methyl group.

30 [0027]

Because the SiCN film 68 formed in the process illustrated in Figure 6 utilizes trymethylsilane as a material gas, which has low hydrogen content, the hydrogen plasma damage to the CF film and the SiCN film 67 can be decreased. In other words, since the hydrogen atom is small, the hydrogen atom goes through the SiCN film 67, gets into the

CF film 65 and gives some damage to the CF film 65. When the amount of the hydrogen atom is small in the material gas, the damage is small. This also improves contactability of the CF film 65, and the SiCN films 67.

5 [0028]

10

15

20

25

30

Next, a method for forming a film by generating plasma and a plasma processing method for forming a film according to the present invention is discussed. In this aspect of the present invention, the method for forming a film by generating plasma is not limited specifically, and any method may be used. A method for forming a film using a plasma film forming device is hereinafter explained.

[0029]

Next, a CVD device for generating plasma using RLSA is hereinafter explained. FIGS. 7 and 8 are diagrams showing a construction of a microwave plasma processing apparatus 10 according to a first embodiment of the present invention.

[0030]

Referring to FIG. 7, the microwave plasma processing apparatus 10 includes a processing vessel 11 and a stage 13 provided in the processing vessel 11 for holding a substrate 12 to be processed by an electrostatic chuck, wherein the stage 13 is preferably formed of AlN or Al₂O₃ by a hot isostatic pressing (HIP) process. In the processing vessel 11, there are formed at least two or preferably more than or equal to three evacuation ports 111A in a space 11A surrounding the stage 13 with an equal distance, and hence with an axial symmetry with respect to the substrate 12 on the stage 13. The processing vessel 11 is evacuated to a low pressure via the evacuation port 111A by a gradational lead screw pump to be explained later.

[0031]

The processing vessel 11 is preferably formed of an austenite stainless steel containing Al, and there is formed a protective film of aluminum oxide on the inner wall surface by an oxidizing process. Further, there is formed a disk-like shower plate 14 of dense Al₂O₃, formed by a HIP process, in the part of the outer wall of the processing vessel 11 corresponding to the substrate 12 as a part of the outer wall, wherein the shower plate 14 includes a large number of nozzle apertures 14A. The Al₂O₃ shower plate 14 thus formed

by a HIP process is formed by using an Y_2O_3 additive and has a porosity of 0.03% or less. This means that the Al_2O_3 shower plate is substantially free from pores or pinholes and has a very large, while not so large as that of AlN, thermal conductivity for a ceramic of 30 W/mK.

5

[0032]

The shower plate 14 is mounted on the processing vessel 11 via a seal ring 111S, and a cover plate 15 of dense Al₂O₃ formed also of an HIP process is provided on the shower plate 14 via a seal ring 111T. The shower plate 14 is formed with a depression 14B communicating with each of the nozzle apertures 14A and serving for the plasma passage, at the side thereof contacting with the cover plate 15, wherein the depression 14B also communicates with another plasma passage 14C formed in the interior of the shower plate 14 in communication with plasma inlet 111P formed on the outer wall of the processing vessel 11.

15

10

[0033]

The shower plate 14 is held by an extending part lip formed on the inner wall of the processing vessel 11, wherein the extending part 111B is formed with a round surface at the part holding the shower plate 14 so as to suppress an electric discharge.

20

[0034]

Thus, the plasma such as Ar or Kr supplied to the plasma inlet 111P is supplied to a space 11B right underneath the shower plate 14 uniformly via the apertures 14A after being passed through the passages 14C and 14B in the shower plate 14.

25

30

[0035]

On the cover plate 15, there is provided a radial line slot antenna 20 formed of a disk-like slot plate 16 formed with a number of slots 16A and 16B shown in FIG. 8 in intimate contact with the cover plate 15, a disk-like antenna body 17 holding the slot plate 16, and a retardation plate 18 of a dielectric material of low loss such as Al₂O₃, SiO₂ or Si₃N₄ sandwiched between the slot plate 16 and the antenna body 17. The radial line slot antenna 20 is mounted on the processing vessel 11 by way of a seal ring 111U, and a microwave of 2.45 GHz or 8.3 GHz frequency is fed to the radial line slot antenna 20 from an external microwave source (not shown) via a coaxial waveguide 21. The microwave thus supplied

is radiated into the interior of the processing vessel from the slots 16A and 16B on the slot plate 16 via the cover plate 15 and the shower plate 14. Thereby, the microwave causes excitation of plasma in the plasma supplied from the apertures 14A in the space 11B right underneath the shower plate 14. It should be noted that the cover plate 15 and the shower plate 14 are formed of Al₂O₃ and function as an efficient microwave-transmitting window. In order to avoid plasma excitation in the plasma passages 14A-14C, the plasma is held at the pressure of about 6666 Pa-13332 Pa (about 50-100 Torr) in the foregoing passages 14A-14C.

10 [0036]

5

15

20

25

30

In order to improve intimate contact between the radial line slot antenna 20 and the cover plate 15, the microwave plasma processing apparatus 10 of the present embodiment has a ring-shaped groove on a part of the processing vessel 11 so as to engage with the slot plate 16. By evacuating the groove via an evacuation port 11G communicating therewith, the pressure in the gap formed between the slot plate 16 and the cover plate 15 is reduced and the radial line slot antenna 20 is urged firmly upon the cover plate 15 by the atmospheric pressure. It should be noted that such a gap includes not only the slots 16A and 16B formed in the slot plate 16 but also a gap formed by other various reasons. It should be noted further that such a gap is sealed by the seal ring 111U provided between the radial line slot antenna 20 and the processing vessel 11.

[0037]

By filling the gap between the slot plate 16 and the cover plate 15 with inert gas of a small molecular weight via the evacuation port 11G and the groove 111G, heat transfer from the cover plate 15 to the slot plate 16 is facilitated. Thereby, it is preferable to use He for such inert gas in view of the large thermal conductivity and large ionization energy. In the case where the gap is filled with He, it is preferable to set the pressure to about 0.8 atm. In the construction of FIG. 7, there is provided a valve 11V on the evacuation port 11G for the evacuation of the groove 111G and filling of the inert gas into the groove 111G.

[0038]

It should be noted that an outer waveguide tube of the coaxial waveguide 21A is connected to the disk-like antenna body 17 while a central conductor 21B is connected to the slot plate 16 via an opening formed in the retardation plate 18. Thus, the microwave fed to the

coaxial waveguide 21A is propagated in the radial direction between the antenna body 17 and the slot plate 16 and is emitted from the slots 16A and 16B.

[0039]

FIG. 8 shows the slots 16A and 16B formed on the slot plate 16. Referring to FIG. 8, the slots 16A are arranged in a concentric manner such that there is provided a slot 16B for each slot 16A such that the slot 16B crosses the slot 16A perpendicularly and such that the slot 16B is aligned concentrically with the slot 16A. The slots 16A and 16B are formed with an interval corresponding to the wavelength of the microwave compressed by the radiation plate 18 in the radial direction of the slot plate 16, and as a result, the microwave is radiated from the slot plate 16 in the form of a near plane wave. Because the slots 16A and the slots 16B are formed in a mutually perpendicular relationship, the microwave thus radiated forms a circularly polarized wave including two perpendicular polarization components.

15

20

25

30

[0040]

5

10

In the plasma processing apparatus 10 of FIG. 7, there is provided a coolant block 19 formed with a coolant water passage 19A on the antenna body 17, and the heat accumulated in the shower plate 14 is absorbed via the radial line slot antenna 20 by cooling the coolant block 19 by the coolant water in the coolant water passage 19A. The coolant water passage 19A is formed on the coolant block 19 in a spiral form, and coolant water having a controlled oxidation-reduction potential is supplied thereto, wherein the control of the oxidation reduction potential is achieved by eliminating oxygen dissolved in the coolant water by way of bubbling of H₂ gas.

[0041]

In the microwave plasma processing apparatus 10 of FIG. 7, there is further provided a process gas supply mechanism 31 in the processing vessel 11 between the shower plate 14 and the substrate 12 on the stage 13, wherein the process gas supply mechanism 31 has gas passages 31A arranged in a lattice shape and releases process gas supplied from the process gas inlet port 111R provided on the outer wall of the processing vessel 11 through a large number of process gas nozzle apertures. Thereby, a desired uniform substrate processing is achieved in a space 11C between the process gas supply structure 31 and the substrate 12. Such substrate processing includes plasma oxidation processing, plasma

nitridation processing, plasma oxynitridation processing, and plasma CVD processing. Further, it is possible to conduct a reactive ion etching of the substrate 12 by supplying readily decomposing fluorocarbon gas such as C₄F₈, C₅F₈ or C₄F₆ or etching gas containing F or Cl and further by applying a high-frequency voltage to the stage 13 from a high-frequency power source 13A.

[0042]

5

10

In the microwave plasma processing apparatus 10 of the present embodiment, it is possible to avoid deposition of reaction byproducts on the inner wall of the processing vessel by heating the outer wall of the processing vessel 11 to a temperature of about 150°C. Thereby, the microwave plasma processing apparatus 10 can be operated constantly and with reliability, by merely conducing a dry cleaning process once a day or so.

[0043]

FIG. 9 is a bottom view showing a structure of the process gas supply mechanism 31 of FIG. 7. Referring to FIG. 9, the process gas supply mechanism 31 is formed in a stack of disk-like conductive members 311 and 312 such as an Al alloy containing Mg or a stainless steel added with Al. There is provided apertures 31A disposed in a matrix form to serve for plasma passage. For example, the aperture 31A has a size of 19 mm × 19 mm and is provided iteratively at a pitch of 24 mm both in the row direction and in the column direction. The process gas supply mechanism 31 has a total thickness of about 8.5 mm and is typically mounted with a separation of about 16 mm from the surface of the substrate 12.

[0044]

25

30

FIG. 10 is a bottom diagram showing a structure of the disk-like conductive member 311 in FIG. 9. Referring to FIG. 10, in the disk-like conductive member 311, there is provided a lattice-shaped process gas passage 31B in communication with the process gas supply passage 31C formed along an outer circumference of the disk-like conductive member 311 represented by a broken line in FIG. 10. The process gas supply passage 31C is connected to the process gas inlet port 111R. In the opposite surface of the disk-like conductive member 311, there are formed a large number of process gas nozzle apertures 31D in communication with the process gas passage 31B. The process gas is released from the process gas nozzle apertures 31D to the disk-like conductive member 312.

[0045]

5

10

15

20

25

30

Methylsilane (such as, mono-methylsilane, di-methylsilane, tri-methylsilane and tetra-methylsilane), or silazane (such as methylsilazane, and ethylsilazane) may be flowed into the space 11B from the plasma inlet 111P. Also, nitrogen gas, or ammonia gas may be flowed into the space 11B from the plasma inlet 111P. Further, a noble gas, such as, argon gas or hydrogen may be flowed into the space 11B from the plasma inlet 111P. In the microwave plasma processing apparatus 10, the flow rate of the gas may also be adjusted. The adjustment of the flow rate of the gas may be performed with time or by each step of forming a film, thereby allowing adjustment according to the characteristics or types of film desired.

[0046]

For example, methylsilane (such as, mono-methylsilane, di-methylsilane, tri-methylsilane and tetra-methylsilane), or silazane (such as methylsilazane, and ethylsilazane), may be flowed into the space 11C from the process gas inlet port 111R. Also, nitrogen gas, or ammonia gas may be flowed into the space 11C from the process gas inlet port 111R. Further, a noble gas, such as, argon gas or hydrogen may be flowed into the space 11C from the process gas inlet port 111R. In the microwave plasma processing apparatus 10, the flow rate of the gas may also be adjusted. The adjustment of the flow rate of the gas may be performed with time or by each film forming step, thereby allowing adjustment according to the characteristics or types of the film desired.

[0047]

Next explained is the contactability of a CF film and an insulating film for an electronic component according to the present invention referring to experimental data. Figure 11 shows the measurement of the contactability of the CF film and the insulating film by using a 4-Point Bending Method. In the 4-Point Bending Method, first, form a thin film on a substrate, thereafter, cut it into a strip as a sample, and place the sample horizontally. The method then applies a load in a perpendicular direction on both ends of the long side of the horizontally placed sample, and a measurement of the position where the film is peeled off, and the load when the film is peeled off is obtained.

[0048]

Figure 11 illustrates a measurement of the contactability of a CF film and an insulating film by applying the 4-Point Bending Method to the electronic component manufactured without the CO plasma process on the CF film. The horizontal axis in the Figure 11 indicates the amount of stroke when applying a load on a sample. The vertical axis in Figure 11 indicates the size of the load applied to the sample.

[0049]

5

10

15

20

25

30

It can be seen from Figure 11 that the amount of stroke increases as the load applied to the sample increases. That is, it can be seen that the load against the sample film is increasing. And, the amount of stroke sharply decreases as the load reaches at 2.80 lbs. This indicates a condition that the film is peeled off in a horizontal direction from the sample face because the sample film can not withstand the load, thereby the load is relived.

[0050]

Figure 12 illustrates a measurement of the contactability of a CF film and an insulating film by applying the 4-Point Bending Method to an electronic component manufactured by applying the CO plasma process to the CF film. The horizontal axis in Figure 12 indicates the amount of stroke when applying a load on a sample. The vertical axis in Figure 12 indicates the size of the load applied to the sample.

[0051]

It can be seen from Figure 12 that the amount of stroke increases as the load applied to the sample increases. That is, it can be seen that the load against the sample film is increasing. And, the amount of stroke sharply decreases as the load reaches 3.15 lbs. This indicates the condition that the film is peeled off in a horizontal direction from the sample face because the sample film can not withstand the load, thereby the load is relived.

[0052]

By comparing the experimental results of Figures 11 and 12, it can be seen that the electronic component, which has the insulating film formed after applying the CO plasma process on the CF film, has a higher contactability of the CF film and the insulating film than the electronic component without the CO plasma process.

[0053]

One embodiment of the present invention is explained above, however, the present invention is not limited to the above specific examples. For example, the insulating film is formed on the substrate in the embodiment described above, however, the plasma processing method for forming a film according to the present invention may be applied for forming other films, such as an electrode film. Also, other plasmas, such as xenon plasma, or krypton plasma, may be utilized as the plasma supplied from the shower plate 14. Further, the plasma processing method for forming a film according to the present invention can be applied not only to the substrate of the semiconductor device, but also, for example, to the substrates for manufacturing liquid crystal display devices or organic EL elements.

[0054]

5

10

15

20

The substrate processing related to the present invention includes, for example, plasma oxidation processing, plasma nitridation processing, plasma oxynitridation processing, plasma CVD processing, and the like. The microwave plasma processing apparatus 10 according to the present embodiment can avoid the deposition of the reaction byproducts and the like onto the inner wall of the above-described processing vessel 11 by heating the outer wall of the treatment vessel at a temperature of approximately 150 °C, and can be constantly stably operated by dry cleaning around once a day.

CLAIMS

What is claimed is:

1. A semiconductor device manufacturing method, comprising the steps of: forming a fluorinated insulating film;

depositing a first $Si_xC_yN_z$ film on the fluorinated insulating film by reacting a mono-methylsilane; and

depositing a second $Si_xC_yN_z$ film on the first $Si_xC_yN_z$ film by reacting a trimethylsilane.

10

15

20

30

5

- 2. The semiconductor device manufacturing method of claim 1, wherein the surface of the fluorinated insulating film is treated with a CO plasma.
- 3. The semiconductor device manufacturing method of claim 1, wherein the method includes the step of depositing the first Si_xC_yN_z film by treating the mono-methylsilane with a microwave plasma processing apparatus.
 - 4. The semiconductor device manufacturing method of claim 1, wherein the method includes the step of depositing the second $Si_xC_yN_z$ film by treating the tri-methylsilane with a microwave plasma processing apparatus.
 - 5. The semiconductor device manufacturing method of claim 1, wherein the first $Si_xC_yN_z$ film satisfys an equation "y < z".
- 25 6. The semiconductor device manufacturing method of claim 1, wherein the second $Si_xC_yN_z$ film satisfys an equation "y>z".
 - 7. The semiconductor device manufacturing method of claim 1, wherein the fluorinated insulating film is made of a material gas selected from a group including a C_4F_6 gas, a C_5F_8 gas and a C_3F_4 gas.
 - 8. A semiconductor device, comprising of: a fluorinated insulating film;

a first $Si_xC_yN_z$ film deposited on the fluorinated insulating film by reacting a mono-methylsilane; and

a second $Si_xC_yN_z$ film deposited on the first $Si_xC_yN_z$ film by reacting a trimethylsilane.

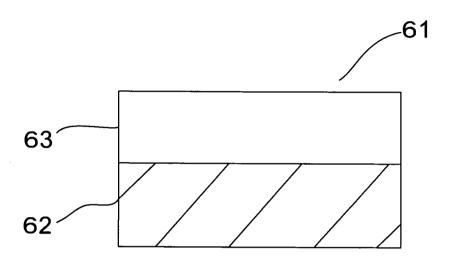
5

- 9. The semiconductor device of claim 8, wherein the surface of the fluorinated insulating film is treated with a CO plasma.
- 10. The semiconductor device of claim 8, wherein the mono-methylsilane is treated with a microwave plasma processing apparatus.
 - 11. The semiconductor device of claim 8, wherein the tri-methylsilane is treated with a microwave plasma processing apparatus.
- 15 12. The semiconductor device of claim 8, wherein the first $Si_xC_yN_z$ film satisfys an equation "y < z".
 - 13. The semiconductor device of claim 8, wherein the second $Si_xC_yN_z$ film satisfys an equation "y>z".

20

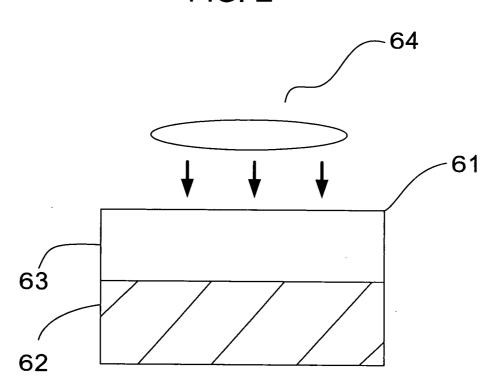
14. The semiconductor device of claim 8, wherein the fluorinated insulating film is made of a material gas selected from a group including a C_4F_6 gas, a C_5F_8 gas and a C_3F_4 gas.

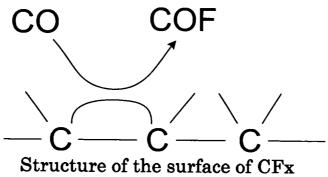
FIG. 1



Structural formula of the surface of CFx

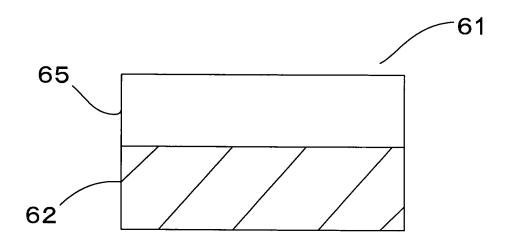
FIG. 2

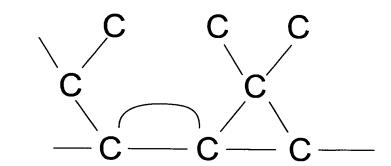




when processing with a CO gas

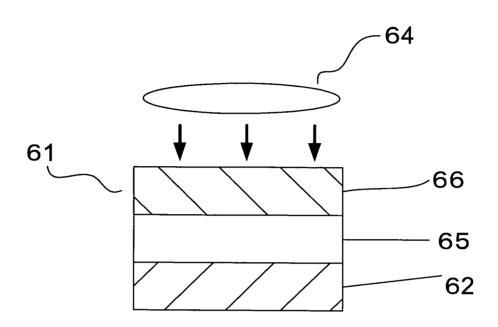
FIG. 3





Structural formula of the surface of CFx after processing with a CO gas

FIG. 4



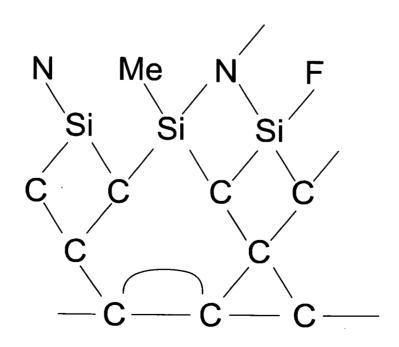
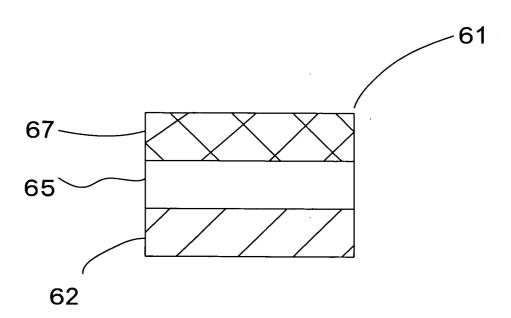
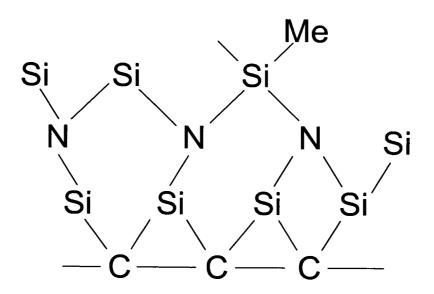
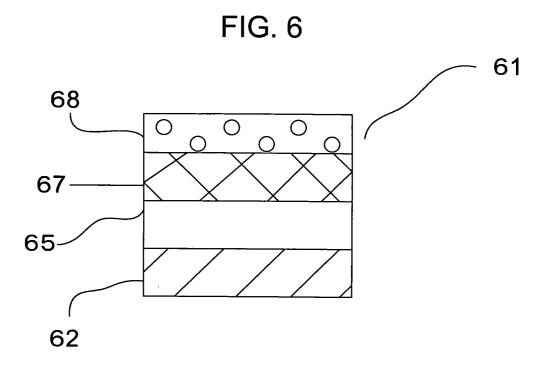
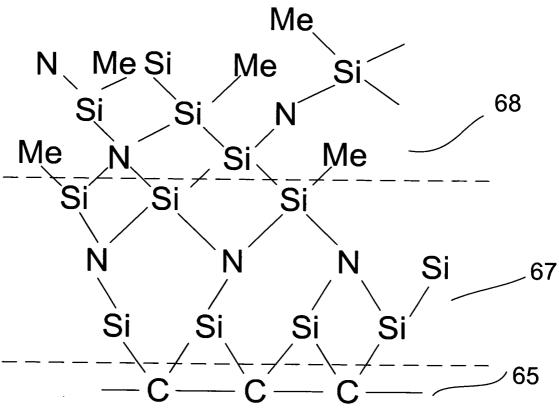


FIG. 5









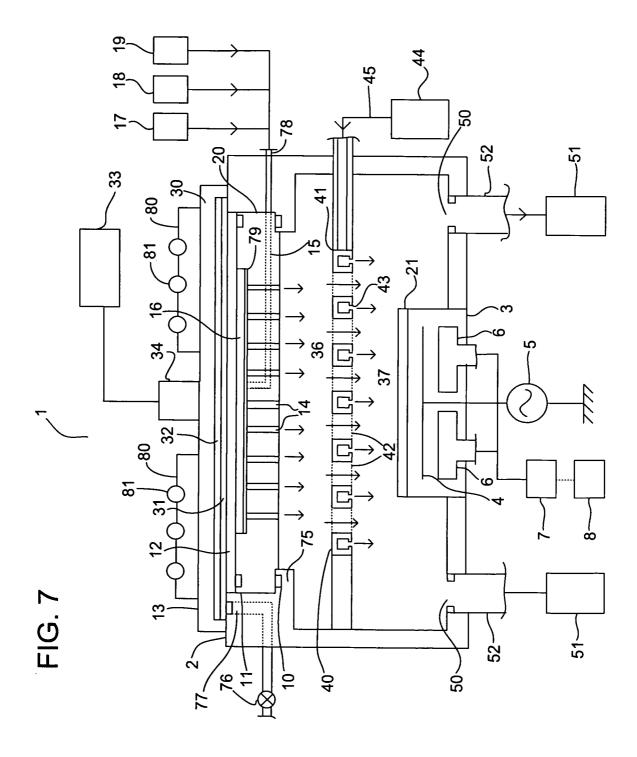


FIG. 8

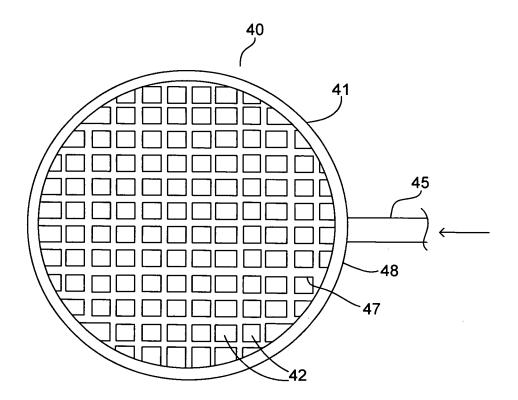


FIG. 9

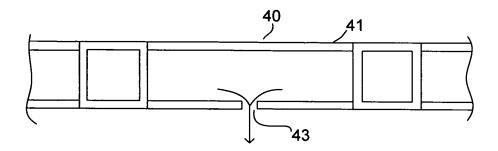


FIG. 10

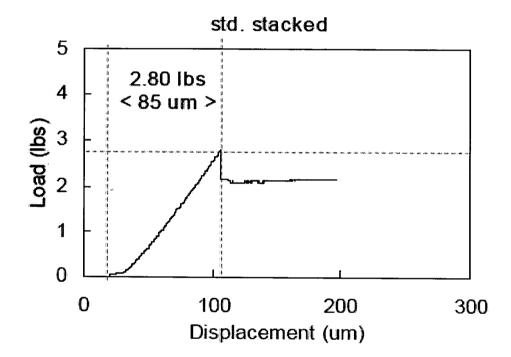


FIG. 11

