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Title of the Invention

A DIELECTRIC, A MANUFACTURING METHOD THEREOF, AND SEMICONDUCTOR DEVICE

Background of the Invention

The present invention relates to a dielectric, a manufacturing method thereof, and a semiconductor device, especially to a dielectric with a low dielectric constant suitable for moderating wiring delay of signals and improving durability of semiconductor integrated circuits and the like.

In accordance with the conventional manufacturing process for semiconductor devices, a trial for moderating wiring delay of signals has been performed, and is as follows. The signals are transmitted through wiring and an organic film with a low dielectric constant used to insulate the wiring. However, the insulation of the wiring by the organic film is hardly used because of a problem with durability of the organic film.

Currently, to improve durability, forming methods for dielectric film composed of silicon, oxygen, and fluorine (called SiOF film hereinafter) have been developed. For instance, the method using silicon tetrafluoride (SiF_4) and oxygen as reacting gases, as disclosed in "Preparation of SiOF Films with Low Dielectric Constant by ECR Plasma Chemical Vapor Deposition" p158, Extended Abstract of the

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1993 Conference on Solid State Devices and Materials (1993). Further, another method adding gases from the fluorine group to the gases necessary for forming a silicon oxide film is disclosed in "Formation Mechanism of F-added SiO_2 Films using Plasma CVD" p.133, The 16th Proceedings of Symposium on Dry Process (1994).

In connection with the conventional SiOF films, fluctuation in the dielectric constant of films is so large that it is not possible to form a film with a low dielectric constant. The humidity resistance of the film is low.

The present invention has been developed with consideration of the above problems.

Summary of the Invention

The dielectric relating to the present invention comprises silicon oxide fluoride compounds, having covalent bonds of fluorine atoms and silicon atoms.

Further, in accordance with a method for manufacturing a dielectric relating to the present invention, SiOF film is formed by supplying an amount of energy which does not dissociate the covalent bonds of fluorine atoms and the silicon atoms of SiF_2X_2 to a gas which contains the SiF_2X_2.

Furthermore, in accordance with the semiconductor device relating to the present invention, dielectric bodies comprising silicon oxide fluoride compounds, having covalent

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bonds of fluorine atoms and silicon atoms, are provided between a plurality of wiring which are located on the substrate of the semiconductor device.

The dielectric constant of a substance is the sum of components based on orientation polarization, ionic polarization, and electronic polarization. The main component of a dielectric constant of non-orientated substance such as SiO_2 or SiOF film is almost the same as the dielectric constant based on electronic polarization. The dielectric constant based on the electronic polarization can be obtained from atomic refraction of constituent atoms, or electronic group refraction of bonds between the atoms.

FIG. 1 illustrates a molecular structure of SiOF film relating to the present invention, and FIGs. 2-8 illustrate molecular structures of conventionally known films of SiO, SiO_2, or SiOX (X = OF, H, OH, Cl). In said figures 2-8, specific dielectric constants ϵ are shown respectively calculated by the present inventor from their atomic refraction. The atomic fraction of F is calculated by subtracting the atomic refraction of C from the molecular refraction of CF_4. The atomic fraction of Si is calculated by subtracting the atomic refraction of F from the molecular refraction of SiF_4. The specific dielectric constant of the SiOF film is smaller than that of SiO and SiO_2 films as shown in said figures 2-8 and the specific dielectric constants ϵ. Furthermore, in accordance with

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investigation by the present inventor, the dielectric constant ϵ of a molecular structure of SiOF film having the covalent bond of Si and F is smaller than that of a molecular structure of SiOF film having the covalent bond of Si and O.

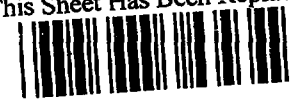
FIG. 9 indicates dissociation energies of various bonds. O-F bond is weaker than Si-F bond by approximately 1/3. Therefore, the SiOF film having Si-F bond has smaller ϵ and is chemically more stable than the SiOF film having O-F bond.

In order to form a SiOF film with a molecular structure having Si-F bond, SiF_2X_2 molecules are used. These molecules have at least two Si-F bonds and another two Si-X bonds, X is an atom or an atomic group. The Si-F bonds have smaller bond energy than Si-F bond energy. As shown in FIG. 9, bond energies of Si-H, Si-Cl, Si-O bonds are smaller than the bond energy of Si-F bond. Accordingly, molecules of Si-X wherein X is any of H, Cl, OCH_3, OC_2H_5, OC_3H_7, and the like are preferable.

When using a molecule wherein the bond energy of Si-X bond is smaller than the bond energy of Si-F bond, a condition of SiF_2X_2 molecules can be generated, wherein the Si-F bond keeps bonding but the Si-X bond dissociates.

In practice, a reaction temperature of thermal CVD apparatus or an input power of plasma treating apparatus are controlled so as to add 541 kJ per one mole of SiF_2X_2 molecule, which does not dissociate Si-F bond. In the above

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case, oxygen is combined with Si atom which has two Si-F bonds and dissociates X atoms. Furthermore, residual uncombined oxygen valence forms a bond with a similar Si in another SiF_2X_2 molecule. Accordingly, the SiOF film having a molecular structure wherein F is combined with Si as shown in FIG. 1 can be formed.

As shown in FIG. 9, the bond energy of Si-H bond is smaller than the bond energies of Si-Cl, and Si-O bonds. Therefore, using a molecule of Si-X wherein the X is H, margins of the operating conditions can be broadened.

Brief Description of the Drawings

FIG. 1 illustrates schematically a molecular structure of SiOF film of the present invention,

FIG. 2 illustrates schematically a molecular structure of conventional SiO (OF) film,

FIG. 3 illustrates schematically a molecular structure of conventional SiO_2 film,

FIG. 4 illustrates schematically a molecular structure of conventional SiOCl film,

FIG. 5 illustrates schematically a molecular structure of conventional SiO film,

FIG. 6 illustrates schematically a molecular structure of conventional SiOH film,

FIG. 7 illustrates schematically a molecular structure of conventional SiOF film,

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FIG. 8 illustrates schematically a molecular structure of conventional SiO(OH) film,

FIG. 9 indicates dissociation energies of various bonds,

FIG. 10 is a schematic cross section of an ECR-CVD apparatus in the present invention for forming SiOF film,

FIG. 11 is an infrared absorption spectrum of the SiOF film in the present invention,

FIG. 12 is a schematic cross section of a parallel plate type RF-CVD apparatus in the present invention for forming SiOF film,

FIG. 13 is a schematic cross section of an ICP-CVD apparatus in the present invention for forming SiOF film,

FIG. 14 schematically indicates a condition in the present invention, wherein wires on a semiconductor substrate are covered with the SiOF film,

FIG. 15 schematically indicates a condition in the present invention, wherein wires on a semiconductor substrate are covered with the SiOF films, which are formed by overlapped spattering,

FIG. 16 schematically indicates a condition in the present invention, wherein wires on a semiconductor substrate are covered with the planarized SiOF film,

FIG. 17 is a graph indicating a relationship between the dielectric constant and HWHH (A Half Width at Half Height) of the SiOF film in the present invention,

FIG. 18 is a graph indicating a relationship between

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the specific dielectric constant and the density of the SiOF film in the present invention,

FIG. 19 is a graph indicating a relationship between the density and dielectric breakdown electric field of the SiOF film in the present invention,

FIG. 20 is a graph indicating a relationship between the specific dielectric constant and the desorption amount in the present invention,

FIG. 21 is a schematic cross section of a SRAM in the present invention, wherein the SiOF film is used,

FIG. 22 is a schematic cross section of a DRAM in the present invention, wherein the SiOF film is used, and

FIG. 23 is a plan view of a memory cell of the DRAM shown in FIG. 22.

Description of the Preferred Embodiments

The present invention is explained in detail referring to the figures hereinafter.

(Embodiment 1)

FIG. 10 is a schematic cross section of an Electron Cyclotron Resonance (ECR)-CVD apparatus, which is one of CVD apparatus used for forming SiOF film. The apparatus comprises a plasma generating chamber 2 having a microwave introducing window 1, a reaction chamber 3, a magnetic field generating coil 4, reaction gas inlets 5 and 6, a holder 8

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holding a substrate 7, and a high frequency power source for supplying high frequency waves to the substrate 7.

First, a process for forming SiOF film using silicon tetrafluoride (SiF_4) and oxygen (O_2) gas in the present invention is explained. From the reaction gas inlets 5 and 6, O_2 by 200 (ml/min) and SiF_4 by 40 (ml/min) are introduced respectively into the reaction chamber 3. The pressure in the reaction chamber 3 is adjusted at 0.2 (Pa) by controlling an amount of exhaust gas. An exhaust gas system is not shown in FIG. 10. A magnetic field of 0.0875 (T) is generated in the plasma generating chamber 2 by the magnetic field generating coil 4, and ECR plasma is generated by introducing microwaves of 2.45 (GHz) so that said SiOF film is formed on the surface of the substrate because of reaction between O_2 and SiF_4. In this case, a p-type Si substrate 126 mm in diameter is used as the substrate. The introduced microwave power (Pμ) is 600 (W).

A film depositing rate (D.R.) increases in proportion to the introduced microwave power (Pμ), for instance, D.R. is 0.2 (μm/min) at 600 (W) of Pμ. The specific dielectric constant ε of the formed film is approximately 3.5. Bonding condition of the formed film is such that Si-Si bond is 10 % of O-Si-O bond, and Si-O-F bond is 30 % of Si-F bond. The specific dielectric constant ε can be measured by the formation of an aluminum electrode on the formed film. The bonding condition of the formed film can be measured by fluorescent X ray (XPS) analysis or nuclear magnetic

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resonance (NMR) analysis.

Next, a method for forming SiOF film by introducing silane difluoride (SiH_2F_2), as an embodiment of the present invention, is explained. Conditions for forming SiOF film are the same as those above process which uses SiF_4. The film deposition rate does not depend on the introduced microwave power, but increases in proportion to the amount of introduced SiH_2F_2 gas. When the SiH_2F_2 gas is introduced at a rate of 40 (ml/min), the film deposition rate (D.R.) is equal to 0.38 (μm/min), approximately twice of the rate when SiF_4 is used. The reason why the film deposition rate increases when using SiH_2F_2 gas is because dissociation energy of SiH_2F_2 is lower than that of SiF_4.

FIG. 11 indicates infrared absorption spectra of SiOF films formed by SiH_2F_2 and SiF_4, respectively. In a case of SiF_4 (hereinafter case: B), the center of Si-O vibration is 1065 (cm^{-1}), and with said half width at half height (HWHH) at a lower wave number side is 33 (cm^{-1}), although slight moisture (O-H) can be observed.

On the other hand, in a case of SiH_2F_2 (case:A), the center of Si-O vibration is 1080 (cm^{-1}), and with said half width at half height (HWHH) at a lower wave number side is 24 (cm^{-1}). A larger wave number indicates a stronger bond of Si-O, and a smaller WHWW indicates a simpler network with fewer kind of the bonds.

When the bonding condition is measured by fluorescent X ray (XPS) analysis and nuclear magnetic resonance (NMR)

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analysis, no Si-Si bond and Si-O-F bond can be observed. Accordingly, the structure of the film is mostly composed of Si-O bond and Si-F bond as shown in FIG. 1. The reason why O-H bond is not observed in the infrared spectrum is because the structure does not contain weak bond of Si-O-F.

The ϵ of the formed film is approximately 3.2. The ϵ is a value obtained by multiplying an estimated ϵ (= 1.88) of SiOF film shown in FIG. 1 by a conversion ratio η (= 1.76) of ϵ of SiO_2 film (= 2.27), estimated from atomic refraction and ϵ of observed glassy SiO_2 (= 4.0).

As explained above, when the SiOF film is formed by introducing silane difluoride (SiH_2F_2), the deposition rate of the film increases, and the dielectric film having preferable chemical stability such as moisture-resistance and a low dielectric constant can be formed because the formed SiOF film is mostly composed of Si-O bonds and Si-F bonds.

(Embodiment 2)

When a film is formed by the same condition as the above embodiment 1 except introducing silicon dichloride difluoride (SiF_2Cl_2) instead of SiH_2F_2, a SiOF film can be formed, wherein no Cl is observed. The deposition rate of the film is almost same as the rate when SiH_2F_2 is used, and when D.R. = 0.36 (μm/min). The ϵ is approximately 3.3, slightly higher than that of the case using SiH_2F_2. That means, when SiF_2Cl_2 is used, an insulator film having a lower dielectric constant than that of the insulator film

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obtained by using SiH_2F_2 can be formed.

Furthermore, when a film is formed under the same condition as the embodiment 1 except introducing silicon dibromide difluoride (SiF_2Br_2) instead of SiH_2F_2, a SiOF film, wherein no Br is observed, can be formed. The deposition rate of the film is almost same as the rate in the case using SiH_2Cl_2, and D.R. = 0.36 (μm/min). Therefore, a dielectric film having a low dielectric constant ϵ such as approximately 3.3 can be formed.

(Embodiment 3)

When a film is formed under the same condition as the embodiment 1 except introducing dimethoxy silicon difluoride ($SiF_2(OCH_3)_2$) instead of SiH_2F_2, a SiOF film, wherein no C is observed, can be formed. The deposition rate of the film is approximately same as the rate in the case using SiH_2F_2, and D.R. = 0.36 (μm/min). The ϵ is slightly higher than the case using SiH_2F_2 and is approximately 3.3.

When a film is formed by the same condition as the embodiment 1 except introducing diethoxy silicon difluoride ($SiF_2(OC_2H_5)_2$) instead of SiH_2F_2, a SiOF film, wherein C is hardly observed, can be formed. The deposition rate of the film D.R. is 0.36 (μm/min), and is slower than that in the case using SiH_2F_2. The reason of the slower R.D. is because $SiF_2(OC_2H_5)_2$ has a lower vapor pressure at room temperature than SiH_2F_2. Therefore, if temperature of the source vessel and the piping are elevated so as to make it possible to

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introduce necessary amount of $SiF_2(OC_2H_5)_2$, 40 (ml/min), the D.R. increases to 0.36 (μm/min). The ϵ is approximately 3.3.

When a film is formed by the same condition as the embodiment 1 except introducing dipropoxy silicon difluoride ($SiF_2(OC_3H_7)_2$) instead of SiH_2F_2, a SiOF film can also be formed. However, the temperature of the source vessel and the piping must be elevated so as to make it possible to introduce necessary amount of $SiF_2(OC_3H_7)_2$, 40 (ml/min). In this case, the D.R. is 0.36 (μm/min), and the ϵ is approximately 3.3.

In accordance with the study by the present inventors, a coating condition of substrate surface when the SiOF film is formed on the substrate having uneven surface becomes more preferable depending on using source materials in the order of $SiF_2(OC_3H_7)_2$, $SiF_2(OC_2H_5)_2$, ($SiF_2(OCH_3)_2$), and SiH_2F_2.

(Embodiment 4)

FIG. 12 illustrates schematically a cross section of a parallel plate type RF (RF: radio frequency)-CVD apparatus for forming SiOF film. The apparatus comprises a reaction chamber 11, reaction gas inlets 5 and 6, a holder 12 for holding and heating a substrate 7., and a frequency power source 13 for supplying high frequency waves for plasma generation.

First, a process for forming SiOF film from SiH_2F_2 and nitrogen monoxide (N_2O) gas using the present apparatus is explained hereinafter.

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The film is formed by introducing N_2O gas by 800 (ml/min) and SiH_2F_2 by 200 (ml/min) through the reaction gas inlets 5 and 6, respectively. The pressure in the reaction chamber 3 is adjusted at 200 (Pa) by controlling the amount of the exhaust gas (the exhaust gas system is not shown in the figure). The SiOF film is formed on a substrate by generating plasma by supplying high frequency waves 400 (W) of 13.6 (MHz) to the upper electrode 14, and reacting N_2O with SiH_2F_2. The temperature of the substrate is kept at 350 ℃.

When SiF_4 is used, the film is scarcely formed. However, when SiH_2F_2 is used, the film can be formed with a deposition rate D.R. of 0.20 (μm/min). When O_2 is used instead of N_2O with SiH_2F_2, SiOF film can be formed, but deposition rate D.R. is less than 0.1 (μm/min). The film is scarcely formed when SiF_4 is used, because bond energy of Si-F is large. However, SiOF film can be formed by RF plasma using SiH_2F_2, because SiH_2F_2 has Si-H bond of weak bond energy.

As explained above, the deposition rate increases by using N_2O instead of O_2, because N_2O has lower generation energy of active oxygen than that of O_2. The dielectric constant ϵ of the formed SiOF film is approximately 3.2.

As described above, the SiOF film having a low dielectric constant can be formed by RF plasma when SiH_2F_2 is used.

(Embodiment 5)

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FIG. 13 illustrates schematically a cross section of an ICP (ICP: Inductively Coupled Plasma)-CVD apparatus for forming SiOF film. The apparatus comprises a reaction chamber 15 made of quartz, reaction gas inlets 5, 6, a holder 16 for holding a substrate 7, and a coil 17 for supplying high frequency waves for plasma generation.

First, in order to compare with the present invention, a process for forming SiOF film using SiF_4 and oxygen gas is explained hereinafter. From the reaction gas inlets 5 and 6, O_2 by 200 (ml/min) and SiF_4 by 40 (ml/min) are respectively introduced into the reaction chamber 15. The pressure in the reaction chamber 15 is adjusted at 0.2 (Pa) by controlling the amount of exhaust gas (the exhaust gas system is not shown in the figure). Plasma is generated by supplying 1 (kW) high frequency waves of 13.6 (MHz) to the coil 17 so that the SiOF film is formed on the surface of the substrate by reacting the O_2 and SiF_4. The film depositing rate (D.R.) is 0.2 (μm/min), and the specific dielectric constant ϵ of the formed film is approximately 3.5. Bonding condition of the formed film is such that Si-Si bond is 10 % of O-Si-O bond, and Si-O-F bond is 30 % of Si-F bond.

Next, a method for forming SiOF film by introducing silane difluoride (SiH_2F_2), an embodiment of the present invention, is explained hereinafter. Other conditions for forming the film than the introducing gas are same as the above explained process which uses SiF_4. The film deposition rate D.R. is 0.38 (μm/min), and is approximately twice of the

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case using SiF_4. The increase of the film deposition rate is by the reason that the dissociation energy of the SiH_2F_2 is lower than that of the SiF_4.

Regarding to the infrared absorption spectra of SiOF films formed by SiH_2F_2 and SiF_4, in a case of SiF_4 as same as the ECR plasma, the center of Si-O vibration is 1065 (cm^{-1}), and the half width at half height (HWHH) at a lower wave number side is 33 (cm^{-1}). Although slightly, moisture (O-H) can be observed. On the other hand, in a case of SiH_2F_2 (case:A), the center of Si-O vibration is 1080 (cm^{-1}), and the half width at half height (HWHH) at a lower wave number side is 24 (cm^{-1}).

Furthermore, any Si-Si bond and Si-O-F bond can not be observed in the film formed by SiH_2F_2. Accordingly, the structure of the film is mostly composed of Si-O bond and Si-F bond. The reason why O-H bond is not observed in the infrared spectrum is because the structure does not contain weak bond of Si-O-F. Further, the ϵ is approximately 3.2 as same as the embodiment 4, and the film having a low dielectric constant can be formed. Furthermore, the film formed in the present embodiment has preferable chemical stability.

As explained above, the SiOF film having a low dielectric constant can be formed by ICP plasma if silane difluoride (SiH_2F_2) is used.

(Embodiment 6)

In the above described respective embodiments, when

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wiring 18 provided on the surface of the semiconductor substrate of the semiconductor device is coated with the SiOF film 19 as shown i FIG. 14, the width of concave portion on the surface of the formed film becomes narrower than the width of the interval between the wiring. Therefore, when a second wiring is formed on the film for multilayers wiring, breaking fraction of wire of the second wiring increases and accordingly, production yield of the semiconductor device decreases. In order to prevent the above decrease of the production yield, the spattering must be overlapped in forming the SiOF film using SiH_4 and O_2.

As a reference example for forming the film by overlapping the spattering, a case of forming SiO_2 film with SiH_4 in stead of SiF_4 by the apparatus shown in FIG. 10 is explained hereinafter. However, in the above case, high frequency waves 400 (kHz) of 400 (W) are supplied to the substrate from a high frequency power source 9, and other conditions are made as same as the embodiment 1.

The film deposition rate (D.R.) is 0.38 (μm/min) when the spattering is not overlapped, and the film deposition rate when the spattering are overlapped is 0.27 (μm/min), 30 % reduction. The reduced amount of the film deposition is a spattering rate (S.R.), and, in the above case, the S.R. is 0.11 (μm/min). The film forming condition in the above case is shown in FIG. 15. The film forming condition is determined by the ratio of D.R. and S.R. The D.R. can be increased by increasing the amount of introducing SiH_4, but

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the S.R. can not be increased even if the amount of O_2 is increased. The specific dielectric constant ϵ of the formed film is approximately 4.0.

On the other hand, when SiOF film is formed with SiH_2F_2 and O_2, an embodiment of the present invention, the film deposition rate (D.R.) when the spattering are not overlapped is 0.38 (μm/min), and the D.R. when the spattering are overlapped is 0.19 (μm/min), 50 % reduction. The reduced amount of 0.19 (μm/min) is S.R., and is larger than the S.R. in the case when SiH_4 is used. The remarkable increase in the spattering rate (S.R.) when the spattering are overlapped is caused by etching of the film by F of SiH_2F_2. Therefore, D.R. can be increased by increasing the introducing amount of SiH_2F_2 as much as the increasing amount of the S.R. In accordance with the method explained above, wherein the amount of introducing SiH_2F_2 is controlled so as to obtain D.R. of 0.66 (μm/min), a film is formed on the surface of the wiring, i.e. when a film is formed on the surface of the wiring with an effective deposition rate of 0.66 (μm/min), the film is formed in a condition as shown in FIG. 15. In the above case, the specific dielectric constant ϵ of the formed film is approximately 3.2.

As explained above, if a film is formed with SiH_2F_2 by overlapping the spattering, not only a film having a low specific dielectric constant can be formed, but also the effective film deposition rate can be increased without

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increasing power source of the apparatus and others.

Furthermore, in order to decrease the breaking fraction of wire of the second wiring and improve the production yield, a film structure shown in FIG. 16 may be formed by applying a flattening film, or eliminating extra protrusion of the film by etching back, after forming the film shaped as shown in FIG. 15. In stead of the etching back, mechanical-chemical polishing (CMP) can be used.

(Embodiment 7)

FIG. 17 is a graph indicating a result of the investigation performed by the present inventor. A relationship between dielectric constant ϵ of SiOF film formed under various forming conditions and the half width at half height (HWHH) at a lower wave number side of Si-O peak in infrared spectrum. The result reveals that there is a strong correlation between the ϵ and the HWHH. In order to form a SiOF film having a low dielectric constant, a film having the half width at half height (HWHH) at a lower wave number side of Si-O peak in infrared spectrum of less than 30 cm^{-1} must be formed.

(Embodiment 8)

Breakdown voltage (B.V.) of the SiOF film formed with SiF_4 in embodiment 1 is approximately 5 (MV/cm). Generally, the breakdown voltage (B.V.) of conventional SiOF film is 9 (MV/cm). The breakdown voltage can be improved by forming a film having intermediate composition between the above described SiOF film and the conventional SiO_2 film.

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As a reference example, there is a film forming method using SiH_4, 20 (ml/min), and SiF_4, 20 (ml/min), instead of SiF_4, 40 (ml/min), in embodiment 1. In this case, film deposition rate (D.R.) of the film is 0.19 (μm/min). If composition of the formed film is in a range between the SiOF film and the conventional SiO_2 film, the specific dielectric constant ∈ of the film is a value approximately 3.75. However, ∈ of the SiOF film formed with SiF_4 is approximately 3.9. That means, fluorine doping hardly be achieved even if SiF_4 is used as doping gas of fluorine, F. Because bond energy of Si-F bond in SiF_4 is significantly larger than the bond energy of Si-H bond in SiH_4, and the energy introduced into plasma is hardly used for dissociation of SiF_4, but used for dissociation of SiH_4.

On the other hand, there is a film forming method wherein SiH_4, 20 (ml/min), and SiH_2F_2, 20 (ml/min), are used instead of SiF_4, 40 (ml/min), in embodiment 1 of the present invention. In this case, film deposition rate (D.R.) of the film is 0.38 (μm/min). The specific dielectric constant of the formed film was approximately 3.75. That means, the composition of the formed film is in an intermediate of the SiOF film and the conventional SiO_2 film. Because, bond energy of Si-H bond in SiH_2F_2 is almost similar with the Si-F bond in SiF_4, and the energy introduced into plasma is used evenly for dissociation of both SiH_2F_2 and SiH_4. The specific dielectric constant ∈ in a range of 3.2 -4.0 varies as a primary function of flow rate ratio (SiH_2F_2 /SiH_4).

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Therefore, the specific dielectric constant can be controlled readily.

As explained above, SiH_2F_2 is further preferable for doping of fluorine.

(Embodiment 9)

FIG. 21 illustrates schematically a cross sectional view of a SRAM using an insulator film manufactured by the present invention. The SRAM is manufactured by the following process.

After forming a field oxide film 2 on a p-type silicon substrate 1 by a selective oxide method (LOCOS), a first transistor having a gate 7 and n-type diffused layer 4, 5, and a second transistor adjacent to the first transistor holding the field oxide film 2 between are formed at predetermined locations. Subsequently, a titanium silicide ($TiSi_2$) film 24 which composes local wiring is formed on the diffused layer 4, 5. Unnecessary portion of the titanium silicide film 24 is eliminated by photolithography and etching. Then, an insulator film such as silicon oxide film (BSPG) containing phosphorus and boron is formed on whole surface of the substrate. A step difference of the insulator film is made gentle by re-flow at 750 ℃. Subsequently, a SiO_2 film is formed at 450 ℃ by a plasma CVD method. A planarized passivation insulator film 9 is composed of a BPSG film on the silicon substrate and a SiO_2 film on the BPSG film. The insulator film 9 formed with chemical mechanical polishing (CMP) process. Further,

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contact holes are formed on the titanium silicide ($TiSi_2$) film 24 by photolithography and etching. Bit lines made of tungsten and connecting plugs of wiring layer are formed in the contact holes. Next, a pad for connecting lead wire and a first layer of the wiring layer 11 are formed.

After forming the wiring layer 11, a SiOF film (specific dielectric constant is 3.3) is formed on the whole surface of the substrate by a plasma CVD method using SiH_2F_2. The first layer of the planarized insulator film 12 is formed by treating the SiOF film with a chemical mechanical polishing (CMP) process. The contact holes are formed on the planarized insulator film 12, and plugs 16, 17 made of tungsten are formed in the contact holes. Subsequently, after forming a second layer of the wiring layer 14 is formed, an insulator film 15 composed of the SiOF film is formed using SiH_2F_2. Through holes and the plugs 16, 17 made of tungsten are formed on the insulator film 15.

Consecutively, by the same process as the above, a third layer of the wiring layer 20, a third layer of the planarized insulator film 19, plugs 21, a fourth layer of the wiring layer 22, and a fourth layer of the planarized insulator film 23 are formed, respectively.

In accordance with an investigation by the present inventor, a signal delay time of the above SRAM is 22 ps. On the contrary, the signal delay time of the insulator film composed of the SiO_2 film which is formed with SiH_4 is 28 ps, and the signal delay time of the insulator film

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composed of the SiOF film which is formed with SiF_4 is 25 ps. In an accelerated test equivalent to 100,000 hours, the signal delay time of conventional SRAM fluctuates significantly in a range of 22-36 ps, but the signal delay time of the SRAM of the present invention scarcely change. Accordingly, signal delay of the SRAM can be decreased and reliability of the SRAM can be improved by using the SiOF film formed with SiH_2F_2 as the insulator film among wiring. The above advantage becomes more significant when integration of the SRAM increases and a distance between wires becomes finer.

FIG. 22 illustrates schematically a cross sectional view of a DRAM using an insulator film manufactured by the present invention. FIG. 23 is a plan view of a memory cell of the DRAM. In these figures, BL and WL indicate respectively a bit line and a word line. Furthermore, SN cont., and BL cont. indicate respectively a connecting portion to a storage node and a connecting portion to the bit line. SA indicates the memory cell and its shadow area, and X and Y indicate sizes of the memory cell. In a case of 256 Mbit DRAM, x and y are respectively 0.85 μm and 0.65 μm. The DRAM is manufactured by the following process.

After forming a field oxide film 2 on a p-type silicon substrate 1 by a selective oxide method (LOCOS), a first transistor having a gate 7 and n-type diffused layer 4, 5, and a second transistor adjacent to the first transistor holding the field oxide film 2 between are formed at

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predetermined locations. Subsequently, an insulator film such as silicon oxide film (BSPG) containing phosphorus and boron is formed on whole surface of the substrate. Then, a SiO_2 film is formed by a plasma CVD method. A planarized passivation insulator film 9 is formed by treating a multilayer body composed of the SiO_2 film and the insulator film with a chemical mechanical polishing (CMP) process. Further, contact holes are formed on the planarized passivation insulator film 9. A connecting plug made of phosphorus doped silicon for being connected to the bit line BL, the storage node SN, and the first layer of the wiring layer is formed in the contact holes. Next, a pad for being connected to the bit line BL and the storage node SN and the wiring layer 11 are formed. Both the pad and the wiring layer have a multilayer structure of TiN/Al/TiN, and are formed simultaneously.

After forming the wiring layer 11, a SiOF film is formed on the whole surface of the substrate by a plasma CVD method using SiH_2F_2. The first layer of the planarized insulator film 12 is formed by treating the SiOF film with a chemical mechanical polishing (CMP) process. The contact holes are formed on the planarized insulator film 12, and plugs 13, 14 made of tungsten are formed in the contact holes.

Subsequently, a capacitor is formed. Size of projected area of the capacitor formed portion is 0.65 μm X 0.65 μm. The capacitor has a cylindrical structure of 0.5 μm high in

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order to increase charge storage capacity. The capacitor is formed by the following process.

A lower electrode of the storage node SN is formed from tungsten film of 0.5 μm thick, which is formed by a CVD method, by manufacturing with photolithography and dry etching. Next, in order to form side electrode of the storage node SN, a SiO_2 film of 0.3 μm thick is deposited. The SiO_2 film is manufactured to a columnar block of 0.4 μm X 0.4 μm by photolithography and dry etching. A tungsten film of 0.2 μm thick is formed on the columnar block by a CVD method. The tungsten film is manufactured to side walls of the storage node SN by etching back. Unnecessary columnar block is eliminated by wet etching. Subsequently, a tantalum pentaoxide (Ta_2O_5) film is formed by a CVD method, and unnecessary portion of the tantalum pentaoxide film is eliminated by photolithography and dry etching. Next, a titanium nitride (TiN) film of 0.2 μm thick is formed on whole surface. A plate electrode PL is formed by etching back after a plate electrode PL lead out portion of the titanium nitride film is coated with resist by photolithography. At this time, a capacitor of 0.5 μm X 0.5 μm is formed on the plug 14. Next, after forming a TiN film, an Al film, and a TiN film orderly, a wiring layer of periphery circuit is formed by manufacturing the multilayer body with photolithography and dry etching.

Subsequently, an insulator film is formed in order to

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protect the capacitor and to insulate the second layer of the wiring layer. The insulator film is composed of an oxide film formed with organic silane. Next, through holes and the plugs 16, 17 made of tungsten are formed. By a method using selective growing of tungsten, it becomes possible to form the plugs 16, 17 having respectively different height as shown in FIG. 22.

Next, the third layer of the wiring layer 18 and the pad 19 are formed. Further, the third layer of the planarized SiOF insulator film 20 is formed by the method previously described. Subsequently, in accordance with the above described steps, the plug 21, the fourth layer of the wiring layer 22, and the fourth planarized insulator layer 23 are formed.

According to an investigation by the present inventor, a fraction defective in 200 hours' pressure cooker test of the above described DRAM relating to the present invention is 3 %. On the contrary, when the insulator film is the SiOF film formed with SiH_4, the fraction defective is approximately 38 %, and when the insulator film is the SiOF film formed with SiF_4, the fraction defective is approximately 62 %. Accordingly, the reliability of the DRAM can be increased by using the SiOF film formed with SiH_2F_2 as the insulator film.

Furthermore, the present inventor examined TFT characteristics of a TFT using the SiOF film formed with SiH_2F_2 as a gate insulator film of a TFT-LCD, and of a TFT

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using the SiO_2 film formed with conventional SiH_4. In accordance with the result, the mobility μ in the case using SiOF film is approximately 0.6 ($cm^2/v.s$), and the mobility μ in the case using SiO_2 film is approximately 0.4 ($cm^2/v.s$). The difference in μ as above described is caused by fluorine isolated in plasma when SiH_2F_2 is used, which flattens the surface of the formed film.

The SiOF film is preferable as a passivation film for LSI, power transistor, and TFT, because it is hydrophobic.

(Embodiment 10)

The present inventor investigated the SiOF film manufactured by the same apparatus and method as embodiment 1 under various reaction pressure, input power, and gas flow rate. Results of the investigation are explained hereinafter.

FIG. 18 is a graph indicating a relationship between specific dielectric constant and density of the formed film. The specific dielectric constant depends on the density, and especially, the specific dielectric constant can be expressed approximately by a primary function of the density when the density is in a range of 1.8-2.4 (g/cm^3). That means, the dielectric constant can be decreased by lowering the density.

FIG. 19 is a graph indicating a relationship between breakdown voltage and density of the formed film. The film has a sufficient breakdown voltage as an insulator film between wires in a region where the density is larger than

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1.8 (g/^{c}).

As explained above, the SiOF film having a density in a range of 1.8-2.4 (g/^{c}) is preferable as an insulator film of low dielectric constant.

(Embodiment 11)

A result of investigation by the present inventor on desorption amount of the SiOF film in embodiment 10 is explained hereinafter.

FIG. 20 indicates a relationship between the specific dielectric constant of the formed film and the desorption amount of the film when the film is heated at 600 ℃. The value of the desorption amount is normalized with the specific dielectric constant of the film formed with SiH_2F_2 in embodiment 1. As FIG. 20 indicates, when the specific dielectric constant is in a range of 2.8-3.2, the desorption amount is a constant. However, when the specific dielectric constant is less than 2.8 or larger than 3.2, the desorption amount increases. When the specific dielectric constant is less than 2.8, coarse portions of the film material is generated in the formed film because of low density, and moisture in air is taken into the coarse portions. Consequently, the desorption amount increases. When the specific dielectric constant is larger than 3.2, moisture in air or hydroxide group in moisture is readily taken into the film because of existing O-F bond Si-Si bond. Consequently, the desorption amount increases.

As explained above, in order to decrease moisture

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content of the film, use of the film having the specific dielectric constant in a range of 2.8-3.2 is preferable. By using such a film as described above, reliability of semiconductor devices such as LSI and the like can be improved.

SiNF film can be formed by using nitration gas such as N_2, or NH_3 instead of oxidation gas. When a SiN film formed with SiH_2F_2 and nitration gas such as N_2, or NH_3 is used as a TFT gate film, more preferable characteristics can be obtained than a TFT using a SiN film formed with SiH_4 as a gate film. As explained above, SiH_2F_2 is preferable for forming a gate insulator film of semiconductor.

In accordance with the present invention, a dielectric film having a low dielectric constant and high reliability can be formed, and consequently, a semiconductor device of less wiring delay of signal and a semiconductor device having preferable characteristics can be manufactured. Because the dielectric film having a low dielectric constant and high reliability can be formed effectively, such an advantage as reducing manufacturing cost of the semiconductor devices can be realized.

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What is claimed is;

1. A dielectric comprising a silicon oxide fluoride compound having a covalent bond between a fluorine atom and a silicon atom.

2. A dielectric as claimed in claim 1, wherein

said silicon oxide fluoride compound has an additional covalent bond between a silicon atom and an oxygen atom.

3. A dielectric comprising a silicon oxide fluoride compound, which has a half width at half height of equal to or less than 30 cm^{-1} at a region in the infrared spectrum with low frequency waves.

4. A dielectric comprising a silicon oxide fluoride compound, which has a density in a range of 1.8-2.4 $g/^{c}$.

5. A dielectric comprising a silicon oxide fluoride compound, which has a specific dielectric constant in a range of 2.8-3.2.

6. A method for manufacturing a dielectric comprising the steps of;

introducing a gas containing SiF_2X_2 gas onto a substrate, and

supplying an energy which does not dissociate the covalent bond between a fluorine atom and a silicon atom in

said SiF_2X_2 gas to said gas containing SiF_2X_2 gas.

7. A method for manufacturing a dielectric as claimed in claim 6, wherein

said X is any one selected from a group consisting of H, Cl, Br, OCH_3, OC_2H_5, and OC_3H_5.

8. A method for manufacturing a dielectric as claimed in claim 6, wherein

said energy is less than 541 kJ per 1 mol of SiF_2X_2.

9. A method for manufacturing a dielectric as claimed in claim 6, wherein

said energy is supplied by a CVD apparatus.

10. A method for manufacturing a dielectric as claimed in claim 6, wherein

said energy is supplied by a plasma treating apparatus.

11. A method for manufacturing a dielectric as claimed in claim 9, wherein

spattering processes are overlapped.

12. A method for manufacturing a dielectric as claimed in claim 10, wherein

said plasma is generated by radio waves.

13. A semiconductor device comprising

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* C L M S *

a plurality of wiring located on the surface of a semiconductor substrate, and

a dielectric comprising a silicon oxide fluoride compound having a covalent bond between a fluorine atom and a silicon atom located at intervals between said plurality of wiring.

14. A semiconductor device comprising

a plurality of wiring located on the surface of a semiconductor substrate, and

a dielectric comprising a silicon oxide fluoride compound, which has a half width at half height of equal to or less than 30 cm^{-1} at a region in the infrared spectrum with low frequency waves.

15. A semiconductor device comprising

a plurality of wiring located on the surface of a semiconductor substrate, and

a dielectric comprising a silicon oxide fluoride compound, which has a density in a range of 1.8-2.4 g/^{c}.

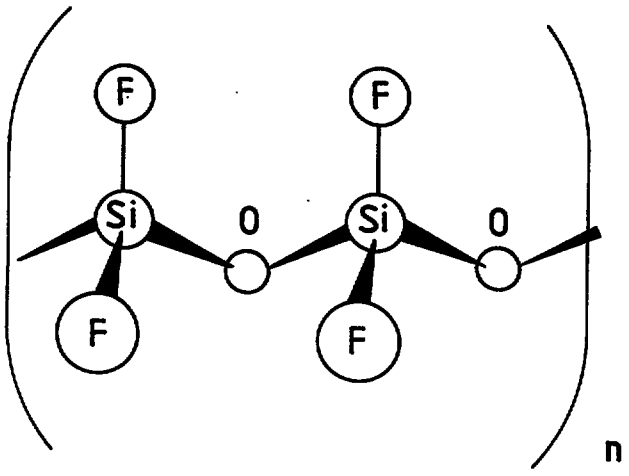
16. A semiconductor device comprising

a plurality of wiring located on the surface of a semiconductor substrate, and

a dielectric comprising a silicon oxide fluoride compound, which has a specific dielectric constant in a range of 2.8-3.2.

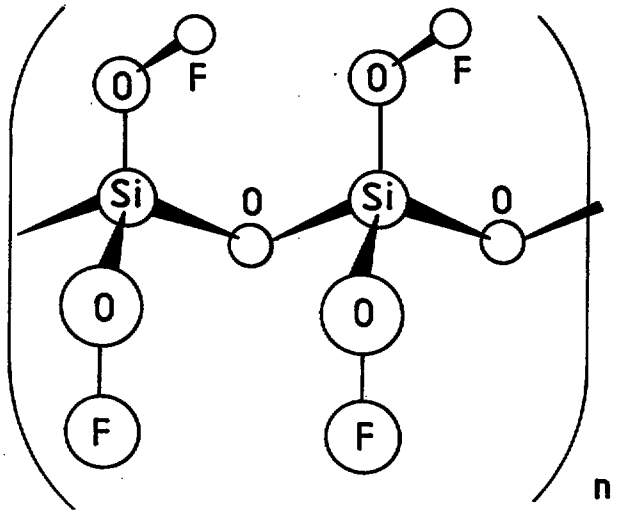
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FIG. 1



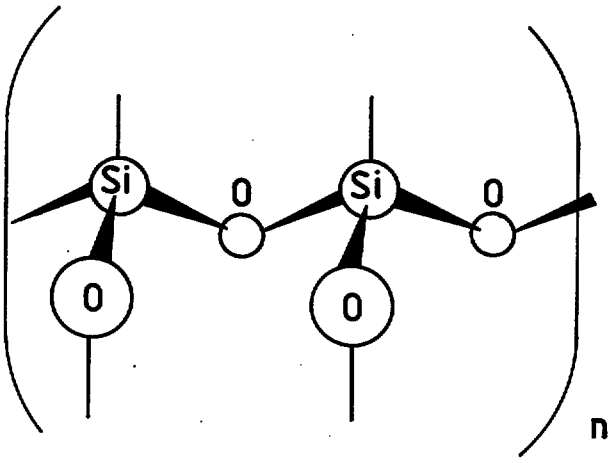
$\varepsilon = 1.88$

FIG. 2



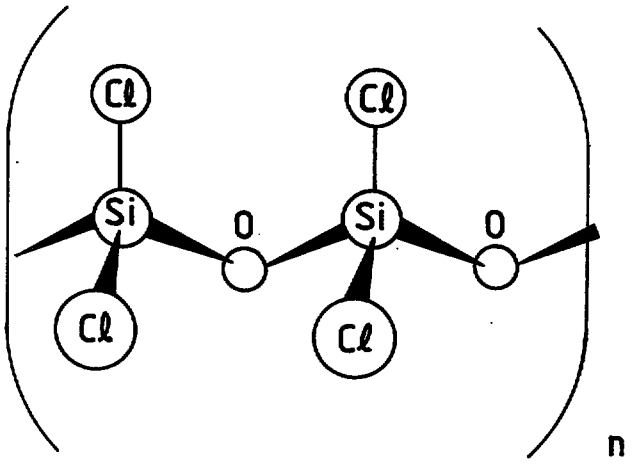
$\varepsilon = 2.00$

FIG. 3



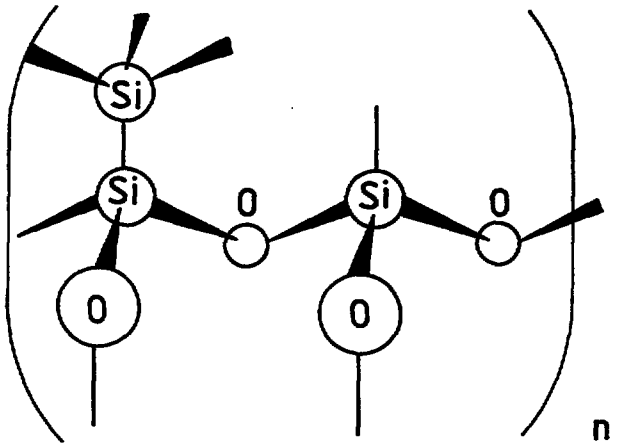
$\varepsilon = 2.27$

FIG. 4



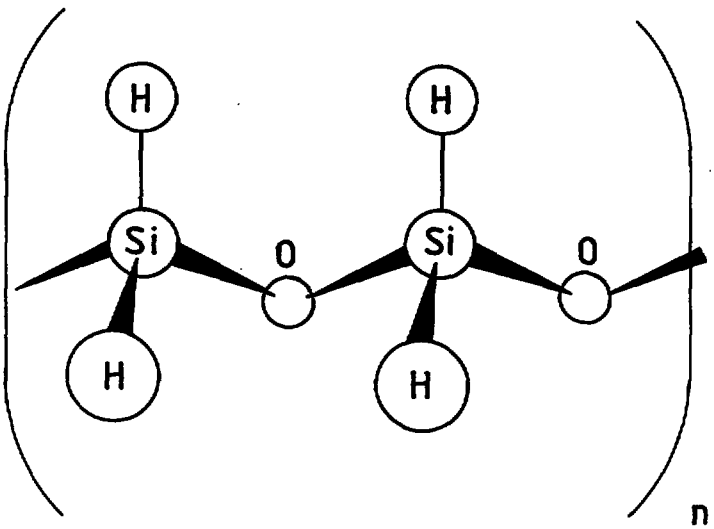
$\varepsilon = 2.90$

FIG. 5



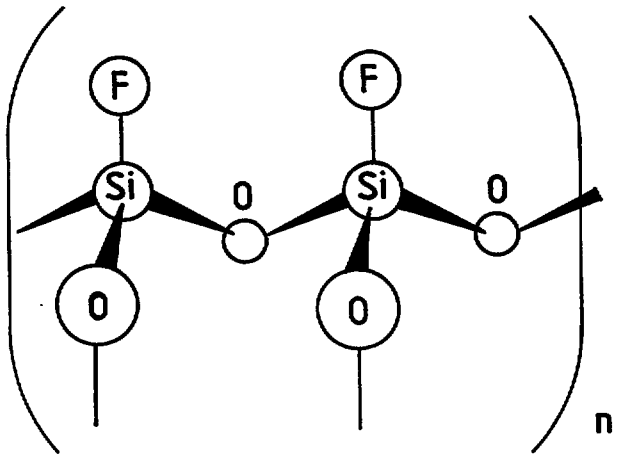
ε=2.35

FIG. 6



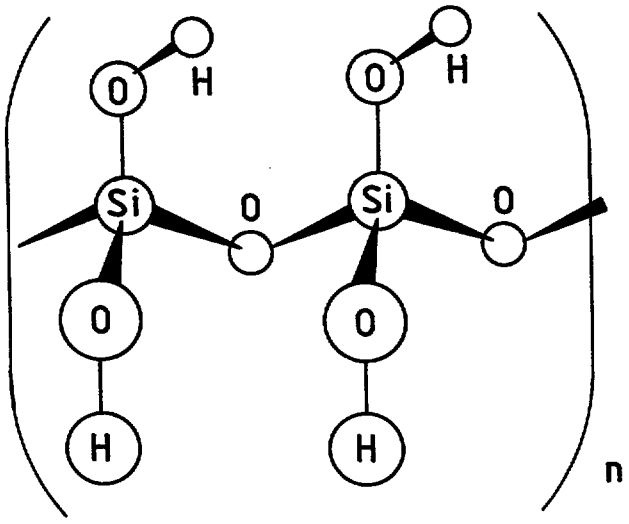
ε=2.19

FIG. 7



ε=2.09

FIG. 8



ε=2.61

FIG. 9

BOND	ENERGY (KJ/mol)	BOND	ENERGY (KJ/mol)
Si－F	541.0	Si－H	294.6
C－H	413.4	O－F	184.9
Si－O	369.0	Si－Si	176.6
Si－Cl	358.6	F－F	153.0
C－O	351.5	O－O	1386
$O_2 \rightarrow O^*$	351.5	$N_2O \rightarrow O^*$	305.4

FIG. 10

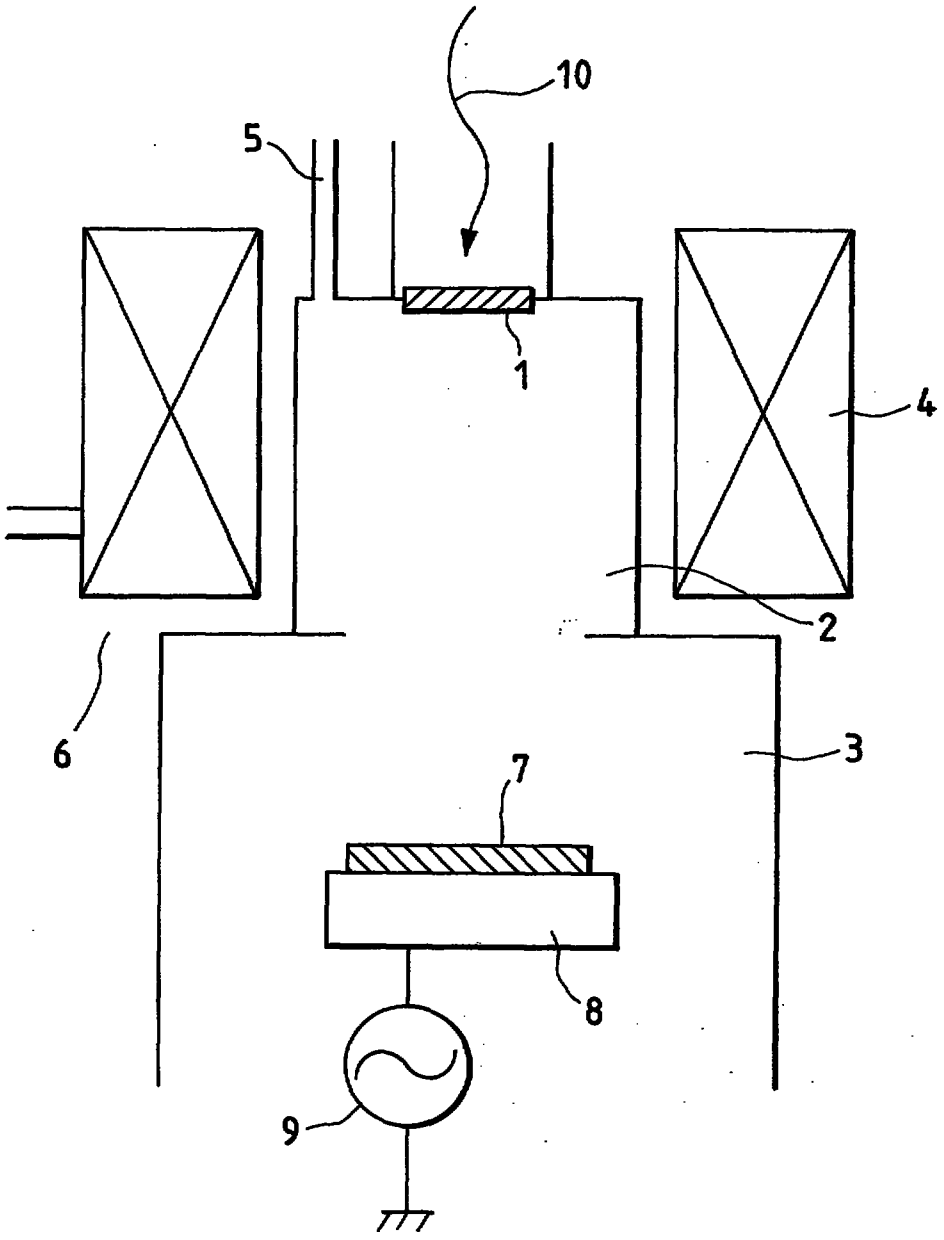


FIG. 11

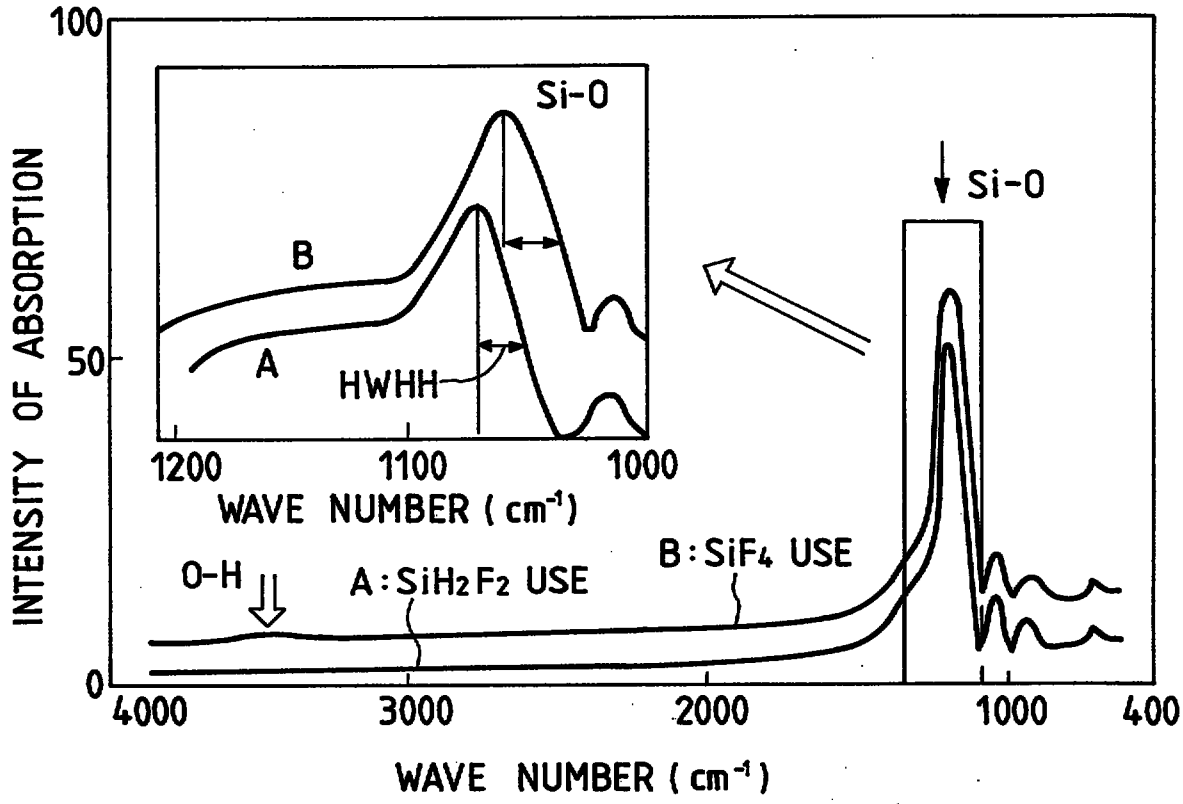

100
50
0
INTENSITY OF ABSORPTION
Si-O
B
A
HWHH
1200
1100
1000
WAVE NUMBER (cm⁻¹)
Si-O
O-H
A : SiH2F2 USE
B : SiF4 USE
4000
3000
2000
1000
400
WAVE NUMBER (cm⁻¹)

FIG. 12

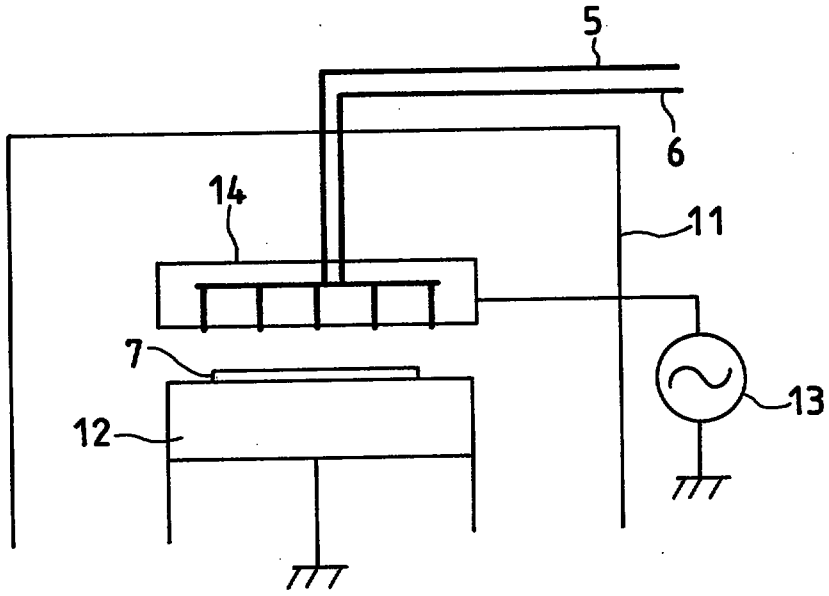


FIG. 13

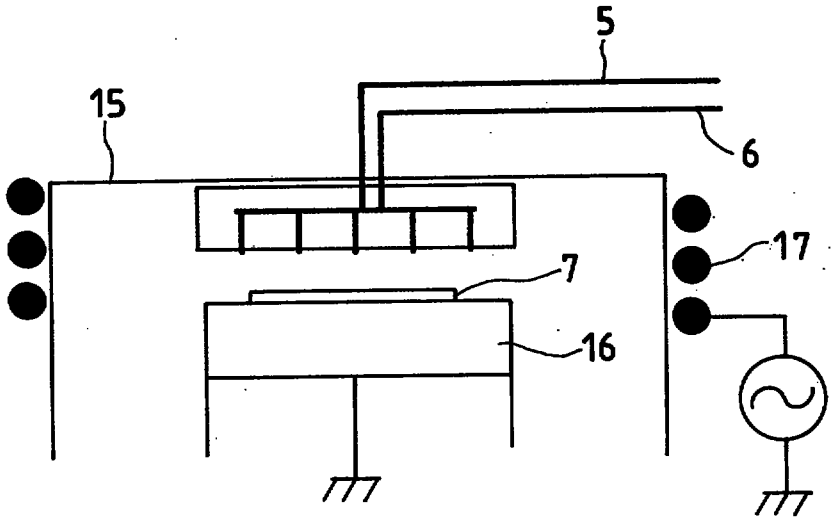


FIG. 14

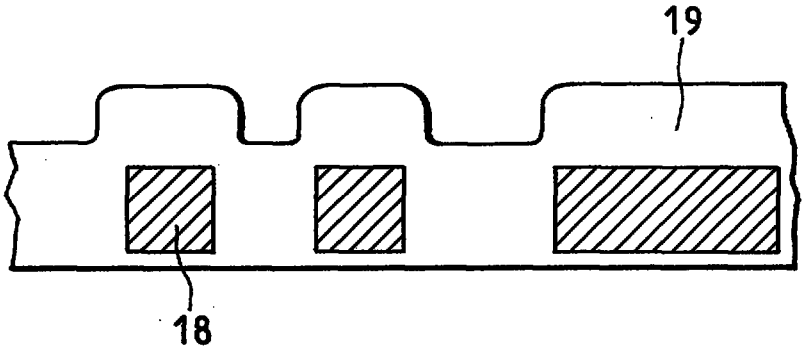


FIG. 15

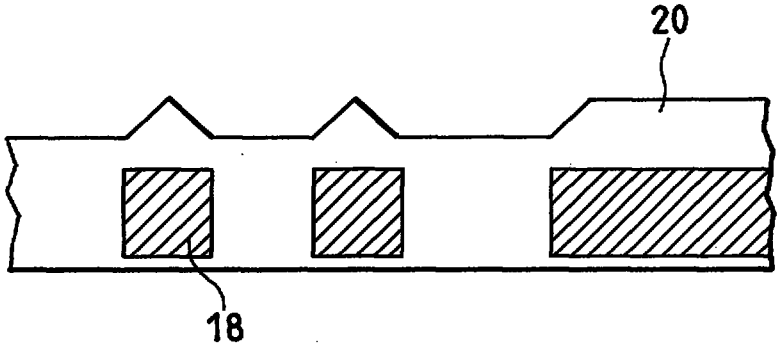


FIG. 16

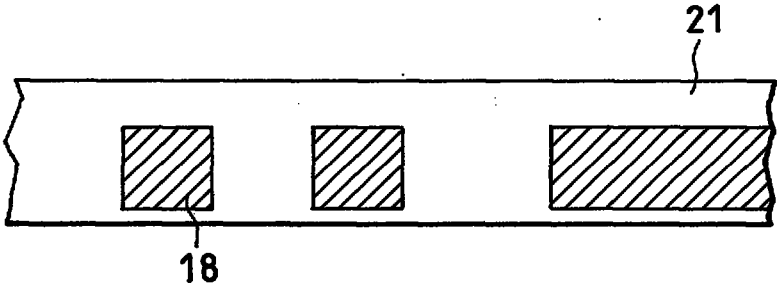


FIG. 17

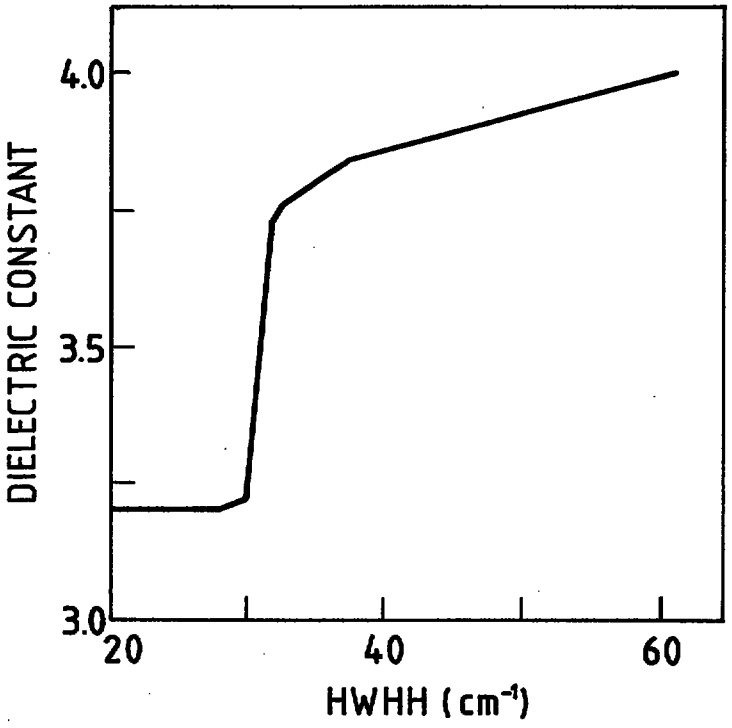

4.0
3.5
3.0
DIELECTRIC CONSTANT
20
40
60
HWHH (cm⁻¹)

FIG. 18

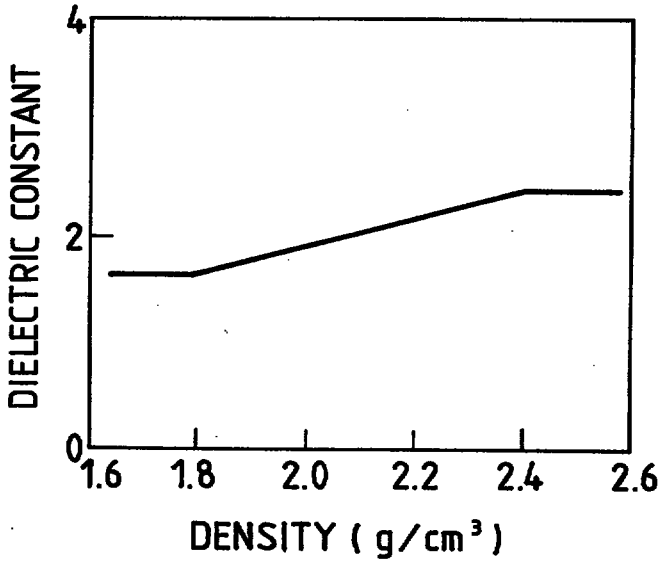

4
2
0
DIELECTRIC CONSTANT
1.6
1.8
2.0
2.2
2.4
2.6
DENSITY (g/cm³)

FIG. 19

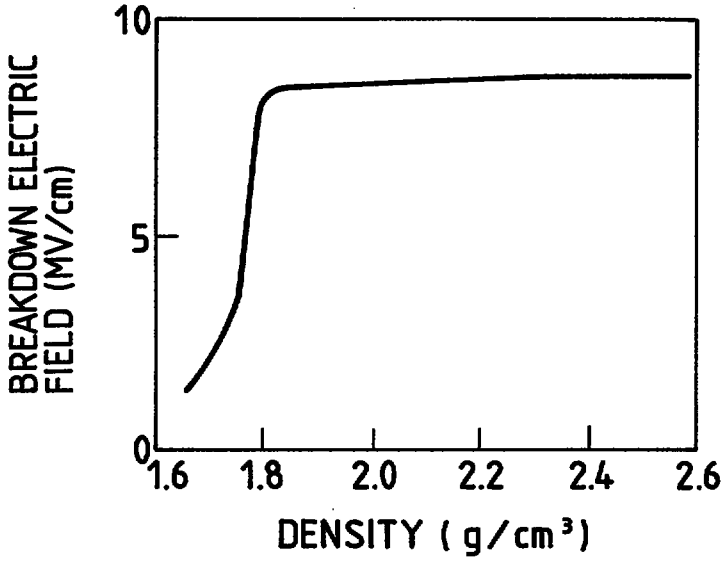

10
5
0
BREAKDOWN ELECTRIC FIELD (MV/cm)
1.6
1.8
2.0
2.2
2.4
2.6
DENSITY (g/cm³)

FIG. 20

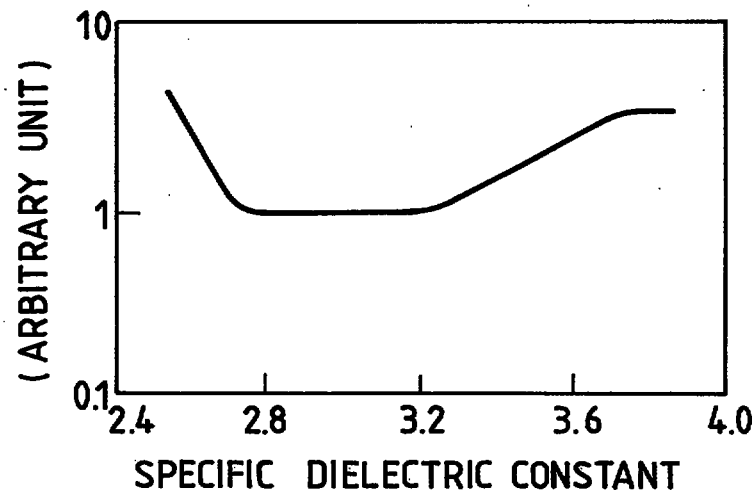

10
1
0.1
(ARBITRARY UNIT)
2.4
2.8
3.2
3.6
4.0
SPECIFIC DIELECTRIC CONSTANT

FIG. 21

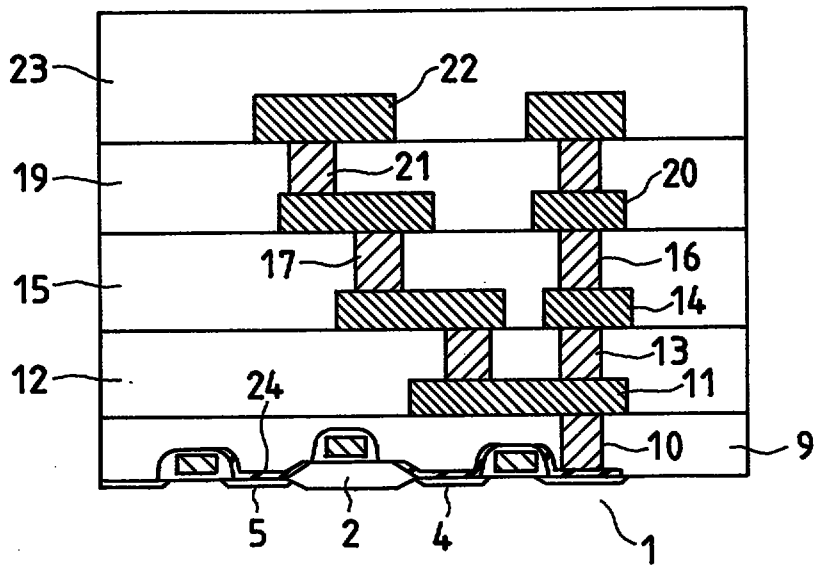


FIG. 22

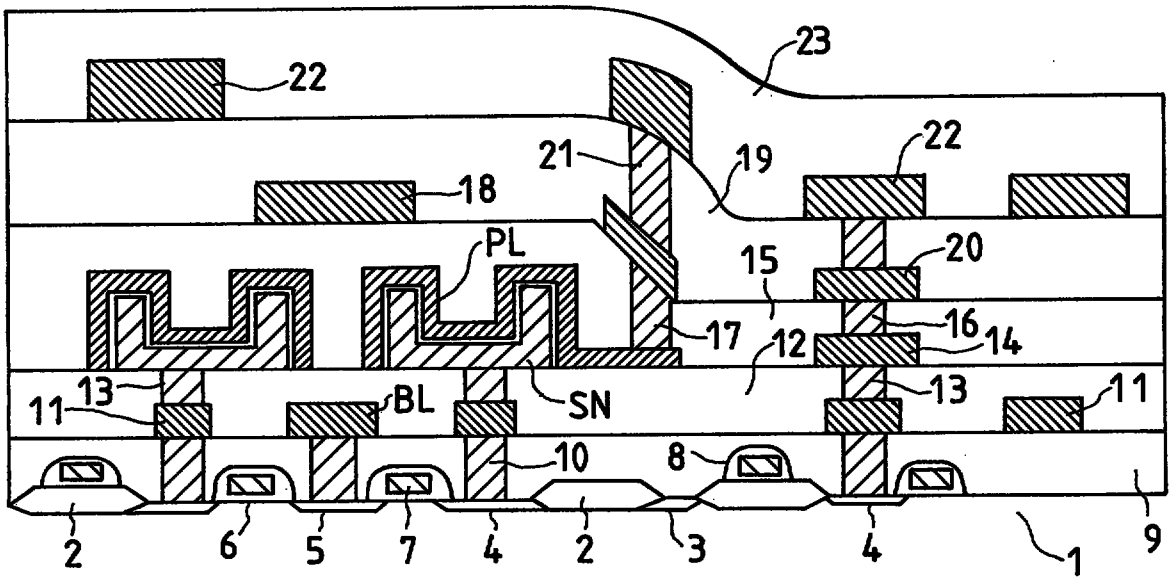
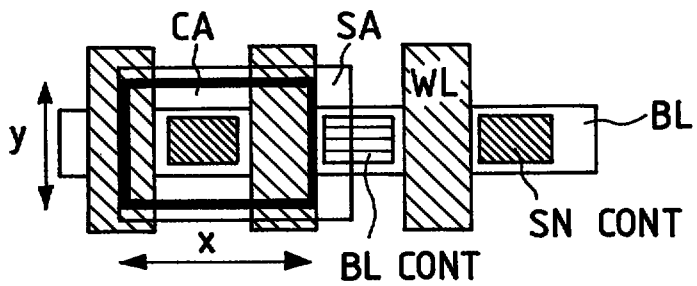


FIG. 23



Abstract of the Disclosure

A silicon oxide fluoride film having Si-F bonds and Si-O bonds is used for insulator wiring of a semiconductor device, and a dielectric film is formed using SiF_2X_2 gas (X = H, Cl, Br, OCH_3, OC_2H_5, and OC_3H_5) as a reactant.

A semiconductor device having a small wiring delay and high reliability can be manufactured, because the silicon oxide fluoride film having Si-F bonds and Si-O bonds has a smaller dielectric constant than a silicon oxide fluoride film having Si-Si bonds and O-F bonds.

REPLACEMENT SHEETS SG
☑ Description : paged 1 to paged 28
☐ Claim(s) : paged ... to paged ...
☐ Drawing(s) : paged ... to paged ...
☑ Abstract : paged ... to paged ...
DATE OF RECEIPT 12 NOV 1996

Title of the Invention

A DIELECTRIC, A MANUFACTURING METHOD THEREOF, AND SEMICONDUCTOR DEVICE

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☑ Description : paged 1 to paged 28
☐ Claim(s) : paged ... to paged ...
☐ Drawing(s) : paged ... to paged ...
☑ Abstract : paged ... to paged ...

Background of the Invention

The present invention relates to a dielectric, a manufacturing method thereof, and a semiconductor device, especially to a dielectric with a low dielectric constant suitable for moderating wiring delay of signals and improving durability of semiconductor integrated circuits and the like.

In accordance with the conventional manufacturing process for semiconductor devices, a trial for moderating wiring delay of signals has been performed, and is as follows. The signals are transmitted through wiring and an organic film with a low dielectric constant used to insulate the wiring. However, the insulation of the wiring by the organic film is hardly used because of a problem with durability of the organic film.

Currently, to improve durability, forming methods for dielectric film composed of silicon, oxygen, and fluorine (called SiOF film hereinafter) have been developed. For instance, the method using silicon tetrafluoride (SiF_4) and oxygen as reacting gases, as disclosed in "Preparation of SiOF Films with Low Dielectric Constant by ECR Plasma Chemical Vapor Deposition" p158, Extended Abstract of the

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1993 Conference on Solid State Devices and Materials (1993). Further, another method adding gases from the fluorine group to the gases necessary for forming a silicon oxide film is disclosed in "Formation Mechanism of F-added SiO_2 Films using Plasma CVD" p.133, The 16th Proceedings of Symposium on Dry Process (1994).

In connection with the conventional SiOF films, fluctuation in the dielectric constant of films is so large that it is not possible to form a film with a low dielectric constant. The humidity resistance of the film is low.

The present invention has been developed with consideration of the above problems.

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Summary of the Invention

The dielectric relating to the present invention comprises silicon oxide fluoride compounds, having covalent bonds of fluorine atoms and silicon atoms.

Further, in accordance with a method for manufacturing a dielectric relating to the present invention, SiOF film is formed by supplying an amount of energy which does not dissociate the covalent bonds of fluorine atoms and the silicon atoms of SiF_2X_2 to a gas which contains the SiF_2X_2.

Furthermore, in accordance with the semiconductor device relating to the present invention, dielectric bodies comprising silicon oxide fluoride compounds, having covalent

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bonds of fluorine atoms and silicon atoms, are provided between a plurality of wiring which are located on the substrate of the semiconductor device.

The dielectric constant of a substance is the sum of components based on orientation polarization, ionic polarization, and electronic polarization. The main component of a dielectric constant of non-orientated substance such as SiO_2 or SiOF film is almost the same as the dielectric constant based on electronic polarization. The dielectric constant based on the electronic polarization can be obtained from atomic refraction of constituent atoms, or electronic group refraction of bonds between the atoms.

FIG. 1 illustrates a molecular structure of SiOF film relating to the present invention, and FIGs. 2-8 illustrate molecular structures of conventionally known films of SiO, SiO_2, or SiOX (X = OF, H, OH, Cl). In said figures 2-8, specific dielectric constants ϵ are shown respectively calculated by the present inventor from their atomic refraction. The atomic fraction of F is calculated by subtracting the atomic refraction of C from the molecular refraction of CF_4. The atomic fraction of Si is calculated by subtracting the atomic refraction of F from the molecular refraction of SiF_4. The specific dielectric constant of the SiOF film is smaller than that of SiO and SiO_2 films as shown in said figures 2-8 and the specific dielectric constants ϵ. Furthermore, in accordance with

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investigation by the present inventor, the dielectric constant ϵ of a molecular structure of SiOF film having the covalent bond of Si and F is smaller than that of a molecular structure of SiOF film having the covalent bond of Si and O.

FIG. 9 indicates dissociation energies of various bonds. O-F bond is weaker than Si-F bond by approximately 1/3. Therefore, the SiOF film having Si-F bond has smaller ϵ and is chemically more stable than the SiOF film having O-F bond.

In order to form a SiOF film with a molecular structure having Si-F bond, SiF_2X_2 molecules are used. These molecules have at least two Si-F bonds and another two Si-X bonds, X is an atom or an atomic group. The Si-F bonds have smaller bond energy than Si-F bond energy. As shown in FIG. 9, bond energies of Si-H, Si-Cl, Si-O bonds are smaller than the bond energy of Si-F bond. Accordingly, molecules of Si-X wherein X is any of H, Cl, OCH_3, OC_2H_5, OC_3H_7, and the like are preferable.

When using a molecule wherein the bond energy of Si-X bond is smaller than the bond energy of Si-F bond, a condition of SiF_2X_2 molecules can be generated, wherein the Si-F bond keeps bonding but the Si-X bond dissociates.

In practice, a reaction temperature of thermal CVD apparatus or an input power of plasma treating apparatus are controlled so as to add 541 kJ per one mole of SiF_2X_2 molecule, which does not dissociate Si-F bond. In the above

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case, oxygen is combined with Si atom which has two Si-F bonds and dissociates X atoms. Furthermore, residual uncombined oxygen valence forms a bond with a similar Si in another SiF_2X_2 molecule. Accordingly, the SiOF film having a molecular structure wherein F is combined with Si as shown in FIG. 1 can be formed.

As shown in FIG. 9, the bond energy of Si-H bond is smaller than the bond energies of Si-Cl, and Si-O bonds. Therefore, using a molecule of Si-X wherein the X is H, margins of the operating conditions can be broadened.

Brief Description of the Drawings

FIG. 1 illustrates schematically a molecular structure of SiOF film of the present invention,

FIG. 2 illustrates schematically a molecular structure of conventional SiO (OF) film,

FIG. 3 illustrates schematically a molecular structure of conventional SiO_2 film,

FIG. 4 illustrates schematically a molecular structure of conventional SiOCl film,

FIG. 5 illustrates schematically a molecular structure of conventional SiO film,

FIG. 6 illustrates schematically a molecular structure of conventional SiOH film,

FIG. 7 illustrates schematically a molecular structure of conventional SiOF film,

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FIG. 8 illustrates schematically a molecular structure of conventional SiO(OH) film,

FIG. 9 indicates dissociation energies of various bonds,

FIG. 10 is a schematic cross section of an ECR-CVD apparatus in the present invention for forming SiOF film,

FIG. 11 is an infrared absorption spectrum of the SiOF film in the present invention,

FIG. 12 is a schematic cross section of a parallel plate type RF-CVD apparatus in the present invention for forming SiOF film,

FIG. 13 is a schematic cross section of an ICP-CVD apparatus in the present invention for forming SiOF film,

FIG. 14 schematically indicates a condition in the present invention, wherein wires on a semiconductor substrate are covered with the SiOF film,

FIG. 15 schematically indicates a condition in the present invention, wherein wires on a semiconductor substrate are covered with the SiOF films, which are formed by overlapped spattering,

FIG. 16 schematically indicates a condition in the present invention, wherein wires on a semiconductor substrate are covered with the planarized SiOF film,

FIG. 17 is a graph indicating a relationship between the dielectric constant and HWHH (A Half Width at Half Height) of the SiOF film in the present invention,

FIG. 18 is a graph indicating a relationship between

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the specific dielectric constant and the density of the SiOF film in the present invention,

FIG. 19 is a graph indicating a relationship between the density and dielectric breakdown electric field of the SiOF film in the present invention,

FIG. 20 is a graph indicating a relationship between the specific dielectric constant and the desorption amount in the present invention,

FIG. 21 is a schematic cross section of a SRAM in the present invention, wherein the SiOF film is used,

FIG. 22 is a schematic cross section of a DRAM in the present invention, wherein the SiOF film is used, and

FIG. 23 is a plan view of a memory cell of the DRAM shown in FIG. 22.

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Description of the Preferred Embodiments

The present invention is explained in detail referring to the figures hereinafter.

(Embodiment 1)

FIG. 10 is a schematic cross section of an Electron Cyclotron Resonance (ECR)-CVD apparatus, which is one of CVD apparatus used for forming SiOF film. The apparatus comprises a plasma generating chamber 2 having a microwave introducing window 1, a reaction chamber 3, a magnetic field generating coil 4, reaction gas inlets 5 and 6, a holder 8

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holding a substrate 7, and a high frequency power source for supplying high frequency waves to the substrate 7.

First, a process for forming SiOF film using silicon tetrafluoride (SiF_4) and oxygen (O_2) gas in the present invention is explained. From the reaction gas inlets 5 and 6, O_2 by 200 (ml/min) and SiF_4 by 40 (ml/min) are introduced respectively into the reaction chamber 3. The pressure in the reaction chamber 3 is adjusted at 0.2 (Pa) by controlling an amount of exhaust gas. An exhaust gas system is not shown in FIG. 10. A magnetic field of 0.0875 (T) is generated in the plasma generating chamber 2 by the magnetic field generating coil 4, and ECR plasma is generated by introducing microwaves of 2.45 (GHz) so that said SiOF film is formed on the surface of the substrate because of reaction between O_2 and SiF_4. In this case, a p-type Si substrate 126 mm in diameter is used as the substrate. The introduced microwave power (Pμ) is 600 (W).

A film depositing rate (D.R.) increases in proportion to the introduced microwave power (Pμ), for instance, D.R. is 0.2 (μm/min) at 600 (W) of Pμ. The specific dielectric constant ϵ of the formed film is approximately 3.5. Bonding condition of the formed film is such that Si-Si bond is 10 % of O-Si-O bond, and Si-O-F bond is 30 % of Si-F bond. The specific dielectric constant ϵ can be measured by the formation of an aluminum electrode on the formed film. The bonding condition of the formed film can be measured by fluorescent X ray (XPS) analysis or nuclear magnetic

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resonance (NMR) analysis.

Next, a method for forming SiOF film by introducing silane difluoride (SiH_2F_2), as an embodiment of the present invention, is explained. Conditions for forming SiOF film are the same as those above process which uses SiF_4. The film deposition rate does not depend on the introduced microwave power, but increases in proportion to the amount of introduced SiH_2F_2 gas. When the SiH_2F_2 gas is introduced at a rate of 40 (ml/min), the film deposition rate (D.R.) is equal to 0.38 (μm/min), approximately twice of the rate when SiF_4 is used. The reason why the film deposition rate increases when using SiH_2F_2 gas is because dissociation energy of SiH_2F_2 is lower than that of SiF_4.

FIG. 11 indicates infrared absorption spectra of SiOF films formed by SiH_2F_2 and SiF_4, respectively. In a case of SiF_4 (hereinafter case: B), the center of Si-O vibration is 1065 (cm^{-1}), and with said half width at half height (HWHH) at a lower wave number side is 33 (cm^{-1}), although slight moisture (O-H) can be observed.

On the other hand, in a case of SiH_2F_2 (case:A), the center of Si-O vibration is 1080 (cm^{-1}), and with said half width at half height (HWHH) at a lower wave number side is 24 (cm^{-1}). A larger wave number indicates a stronger bond of Si-O, and a smaller WHWW indicates a simpler network with fewer kind of the bonds.

When the bonding condition is measured by fluorescent X ray (XPS) analysis and nuclear magnetic resonance (NMR)

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analysis, no Si-Si bond and Si-O-F bond can be observed. Accordingly, the structure of the film is mostly composed of Si-O bond and Si-F bond as shown in FIG. 1. The reason why O-H bond is not observed in the infrared spectrum is because the structure does not contain weak bond of Si-O-F.

The ϵ of the formed film is approximately 3.2. The ϵ is a value obtained by multiplying an estimated ϵ (= 1.88) of SiOF film shown in FIG. 1 by a conversion ratio η (= 1.76) of ϵ of SiO_2 film (= 2.27), estimated from atomic refraction and ϵ of observed glassy SiO_2 (= 4.0).

As explained above, when the SiOF film is formed by introducing silane difluoride (SiH_2F_2), the deposition rate of the film increases, and the dielectric film having preferable chemical stability such as moisture-resistance and a low dielectric constant can be formed because the formed SiOF film is mostly composed of Si-O bonds and Si-F bonds.

(Embodiment 2)

When a film is formed by the same condition as the above embodiment 1 except introducing silicon dichloride difluoride (SiF_2Cl_2) instead of SiH_2F_2, a SiOF film can be formed, wherein no Cl is observed. The deposition rate of the film is almost same as the rate when SiH_2F_2 is used, and when D.R. = 0.36 (μm/min). The ϵ is approximately 3.3, slightly higher than that of the case using SiH_2F_2. That means, when SiF_2Cl_2 is used, an insulator film having a lower dielectric constant than that of the insulator film

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obtained by using SiH_2F_2 can be formed.

Furthermore, when a film is formed under the same condition as the embodiment 1 except introducing silicon dibromide difluoride (SiF_2Br_2) instead of SiH_2F_2, a SiOF film, wherein no Br is observed, can be formed. The deposition rate of the film is almost same as the rate in the case using SiH_2Cl_2, and D.R. = 0.36 (μm/min). Therefore, a dielectric film having a low dielectric constant ϵ such as approximately 3.3 can be formed.

(Embodiment 3)

When a film is formed under the same condition as the embodiment 1 except introducing dimethoxy silicon difluoride ($SiF_2(OCH_3)_2$) instead of SiH_2F_2, a SiOF film, wherein no C is observed, can be formed. The deposition rate of the film is approximately same as the rate in the case using SiH_2F_2, and D.R. = 0.36 (μm/min). The ϵ is slightly higher than the case using SiH_2F_2 and is approximately 3.3.

When a film is formed by the same condition as the embodiment 1 except introducing diethoxy silicon difluoride ($SiF_2(OC_2H_5)_2$) instead of SiH_2F_2, a SiOF film, wherein C is hardly observed, can be formed. The deposition rate of the film D.R. is 0.36 (μm/min), and is slower than that in the case using SiH_2F_2. The reason of the slower R.D. is because $SiF_2(OC_2H_5)_2$ has a lower vapor pressure at room temperature than SiH_2F_2. Therefore, if temperature of the source vessel and the piping are elevated so as to make it possible to

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introduce necessary amount of $SiF_2(OC_2H_5)_2$, 40 (ml/min), the D.R. increases to 0.36 (μm/min). The ϵ is approximately 3.3.

When a film is formed by the same condition as the embodiment 1 except introducing dipropoxy silicon difluoride ($SiF_2(OC_3H_7)_2$) instead of SiH_2F_2, a SiOF film can also be formed. However, the temperature of the source vessel and the piping must be elevated so as to make it possible to introduce necessary amount of $SiF_2(OC_3H_7)_2$, 40 (ml/min). In this case, the D.R. is 0.36 (μm/min), and the ϵ is approximately 3.3.

In accordance with the study by the present inventors, a coating condition of substrate surface when the SiOF film is formed on the substrate having uneven surface becomes more preferable depending on using source materials in the order of $SiF_2(OC_3H_7)_2$, $SiF_2(OC_2H_5)_2$, ($SiF_2(OCH_3)_2$), and SiH_2F_2.

(Embodiment 4)

FIG. 12 illustrates schematically a cross section of a parallel plate type RF (RF: radio frequency)-CVD apparatus for forming SiOF film. The apparatus comprises a reaction chamber 11, reaction gas inlets 5 and 6, a holder 12 for holding and heating a substrate 7., and a frequency power source 13 for supplying high frequency waves for plasma generation.

First, a process for forming SiOF film from SiH_2F_2 and nitrogen monoxide (N_2O) gas using the present apparatus is explained hereinafter.

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The film is formed by introducing N_2O gas by 800 (ml/min) and SiH_2F_2 by 200 (ml/min) through the reaction gas inlets 5 and 6, respectively. The pressure in the reaction chamber 3 is adjusted at 200 (Pa) by controlling the amount of the exhaust gas (the exhaust gas system is not shown in the figure). The SiOF film is formed on a substrate by generating plasma by supplying high frequency waves 400 (W) of 13.6 (MHz) to the upper electrode 14, and reacting N_2O with SiH_2F_2. The temperature of the substrate is kept at 350 ℃.

When SiF_4 is used, the film is scarcely formed. However, when SiH_2F_2 is used, the film can be formed with a deposition rate D.R. of 0.20 (μm/min). When O_2 is used instead of N_2O with SiH_2F_2, SiOF film can be formed, but deposition rate D.R. is less than 0.1 (μm/min). The film is scarcely formed when SiF_4 is used, because bond energy of Si-F is large. However, SiOF film can be formed by RF plasma using SiH_2F_2, because SiH_2F_2 has Si-H bond of weak bond energy.

As explained above, the deposition rate increases by using N_2O instead of O_2, because N_2O has lower generation energy of active oxygen than that of O_2. The dielectric constant ϵ of the formed SiOF film is approximately 3.2.

As described above, the SiOF film having a low dielectric constant can be formed by RF plasma when SiH_2F_2 is used.

(Embodiment 5)

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FIG. 13 illustrates schematically a cross section of an ICP (ICP: Inductively Coupled Plasma)-CVD apparatus for forming SiOF film. The apparatus comprises a reaction chamber 15 made of quartz, reaction gas inlets 5, 6, a holder 16 for holding a substrate 7, and a coil 17 for supplying high frequency waves for plasma generation.

First, in order to compare with the present invention, a process for forming SiOF film using SiF_4 and oxygen gas is explained hereinafter. From the reaction gas inlets 5 and 6, O_2 by 200 (ml/min) and SiF_4 by 40 (ml/min) are respectively introduced into the reaction chamber 15. The pressure in the reaction chamber 15 is adjusted at 0.2 (Pa) by controlling the amount of exhaust gas (the exhaust gas system is not shown in the figure). Plasma is generated by supplying 1 (kW) high frequency waves of 13.6 (MHz) to the coil 17 so that the SiOF film is formed on the surface of the substrate by reacting the O_2 and SiF_4. The film depositing rate (D.R.) is 0.2 (μm/min), and the specific dielectric constant ϵ of the formed film is approximately 3.5. Bonding condition of the formed film is such that Si-Si bond is 10 % of O-Si-O bond, and Si-O-F bond is 30 % of Si-F bond.

Next, a method for forming SiOF film by introducing silane difluoride (SiH_2F_2), an embodiment of the present invention, is explained hereinafter. Other conditions for forming the film than the introducing gas are same as the above explained process which uses SiF_4. The film deposition rate D.R. is 0.38 (μm/min), and is approximately twice of the

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case using SiF_4. The increase of the film deposition rate is by the reason that the dissociation energy of the SiH_2F_2 is lower than that of the SiF_4.

Regarding to the infrared absorption spectra of SiOF films formed by SiH_2F_2 and SiF_4, in a case of SiF_4 as same as the ECR plasma, the center of Si-O vibration is 1065 (cm^{-1}), and the half width at half height (HWHH) at a lower wave number side is 33 (cm^{-1}). Although slightly, moisture (O-H) can be observed. On the other hand, in a case of SiH_2F_2 (case:A), the center of Si-O vibration is 1080 (cm^{-1}), and the half width at half height (HWHH) at a lower wave number side is 24 (cm^{-1}).

Furthermore, any Si-Si bond and Si-O-F bond can not be observed in the film formed by SiH_2F_2. Accordingly, the structure of the film is mostly composed of Si-O bond and Si-F bond. The reason why O-H bond is not observed in the infrared spectrum is because the structure does not contain weak bond of Si-O-F. Further, the ϵ is approximately 3.2 as same as the embodiment 4, and the film having a low dielectric constant can be formed. Furthermore, the film formed in the present embodiment has preferable chemical stability.

As explained above, the SiOF film having a low dielectric constant can be formed by ICP plasma if silane difluoride (SiH_2F_2) is used.

(Embodiment 6)

In the above described respective embodiments, when

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wiring 18 provided on the surface of the semiconductor substrate of the semiconductor device is coated with the SiOF film 19 as shown i FIG. 14, the width of concave portion on the surface of the formed film becomes narrower than the width of the interval between the wiring. Therefore, when a second wiring is formed on the film for multilayers wiring, breaking fraction of wire of the second wiring increases and accordingly, production yield of the semiconductor device decreases. In order to prevent the above decrease of the production yield, the spattering must be overlapped in forming the SiOF film using SiH_4 and O_2.

As a reference example for forming the film by overlapping the spattering, a case of forming SiO_2 film with SiH_4 in stead of SiF_4 by the apparatus shown in FIG. 10 is explained hereinafter. However, in the above case, high frequency waves 400 (kHz) of 400 (W) are supplied to the substrate from a high frequency power source 9, and other conditions are made as same as the embodiment 1.

The film deposition rate (D.R.) is 0.38 (μm/min) when the spattering is not overlapped, and the film deposition rate when the spattering are overlapped is 0.27 (μm/min), 30 % reduction. The reduced amount of the film deposition is a spattering rate (S.R.), and, in the above case, the S.R. is 0.11 (μm/min). The film forming condition in the above case is shown in FIG. 15. The film forming condition is determined by the ratio of D.R. and S.R. The D.R. can be increased by increasing the amount of introducing SiH_4, but

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the S.R. can not be increased even if the amount of O_2 is increased. The specific dielectric constant ϵ of the formed film is approximately 4.0.

On the other hand, when SiOF film is formed with SiH_2F_2 and O_2, an embodiment of the present invention, the film deposition rate (D.R.) when the spattering are not overlapped is 0.38 (μm/min), and the D.R. when the spattering are overlapped is 0.19 (μm/min), 50 % reduction. The reduced amount of 0.19 (μm/min) is S.R., and is larger than the S.R. in the case when SiH_4 is used. The remarkable increase in the spattering rate (S.R.) when the spattering are overlapped is caused by etching of the film by F of SiH_2F_2. Therefore, D.R. can be increased by increasing the introducing amount of SiH_2F_2 as much as the increasing amount of the S.R. In accordance with the method explained above, wherein the amount of introducing SiH_2F_2 is controlled so as to obtain D.R. of 0.66 (μm/min), a film is formed on the surface of the wiring, i.e. when a film is formed on the surface of the wiring with an effective deposition rate of 0.66 (μm/min), the film is formed in a condition as shown in FIG. 15. In the above case, the specific dielectric constant ϵ of the formed film is approximately 3.2.

As explained above, if a film is formed with SiH_2F_2 by overlapping the spattering, not only a film having a low specific dielectric constant can be formed, but also the effective film deposition rate can be increased without

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increasing power source of the apparatus and others.

Furthermore, in order to decrease the breaking fraction of wire of the second wiring and improve the production yield, a film structure shown in FIG. 16 may be formed by applying a flattening film, or eliminating extra protrusion of the film by etching back, after forming the film shaped as shown in FIG. 15. In stead of the etching back, mechanical-chemical polishing (CMP) can be used.

(Embodiment 7)

FIG. 17 is a graph indicating a result of the investigation performed by the present inventor. A relationship between dielectric constant ϵ of SiOF film formed under various forming conditions and the half width at half height (HWHH) at a lower wave number side of Si-O peak in infrared spectrum. The result reveals that there is a strong correlation between the ϵ and the HWHH. In order to form a SiOF film having a low dielectric constant, a film having the half width at half height (HWHH) at a lower wave number side of Si-O peak in infrared spectrum of less than 30 cm^{-1} must be formed.

(Embodiment 8)

Breakdown voltage (B.V.) of the SiOF film formed with SiF_4 in embodiment 1 is approximately 5 (MV/cm). Generally, the breakdown voltage (B.V.) of conventional SiOF film is 9 (MV/cm). The breakdown voltage can be improved by forming a film having intermediate composition between the above described SiOF film and the conventional SiO_2 film.

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As a reference example, there is a film forming method using SiH_4, 20 (ml/min), and SiF_4, 20 (ml/min), instead of SiF_4, 40 (ml/min), in embodiment 1. In this case, film deposition rate (D.R.) of the film is 0.19 (μm/min). If composition of the formed film is in a range between the SiOF film and the conventional SiO_2 film, the specific dielectric constant ∈ of the film is a value approximately 3.75. However, ∈ of the SiOF film formed with SiF_4 is approximately 3.9. That means, fluorine doping hardly be achieved even if SiF_4 is used as doping gas of fluorine, F. Because bond energy of Si-F bond in SiF_4 is significantly larger than the bond energy of Si-H bond in SiH_4, and the energy introduced into plasma is hardly used for dissociation of SiF_4, but used for dissociation of SiH_4.

On the other hand, there is a film forming method wherein SiH_4, 20 (ml/min), and SiH_2F_2, 20 (ml/min), are used instead of SiF_4, 40 (ml/min), in embodiment 1 of the present invention. In this case, film deposition rate (D.R.) of the film is 0.38 (μm/min). The specific dielectric constant of the formed film was approximately 3.75. That means, the composition of the formed film is in an intermediate of the SiOF film and the conventional SiO_2 film. Because, bond energy of Si-H bond in SiH_2F_2 is almost similar with the Si-F bond in SiF_4, and the energy introduced into plasma is used evenly for dissociation of both SiH_2F_2 and SiH_4. The specific dielectric constant ∈ in a range of 3.2 -4.0 varies as a primary function of flow rate ratio (SiH_2F_2 /SiH_4).

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Therefore, the specific dielectric constant can be controlled readily.

As explained above, SiH_2F_2 is further preferable for doping of fluorine.

(Embodiment 9)

FIG. 21 illustrates schematically a cross sectional view of a SRAM using an insulator film manufactured by the present invention. The SRAM is manufactured by the following process.

After forming a field oxide film 2 on a p-type silicon substrate 1 by a selective oxide method (LOCOS), a first transistor having a gate 7 and n-type diffused layer 4, 5, and a second transistor adjacent to the first transistor holding the field oxide film 2 between are formed at predetermined locations. Subsequently, a titanium silicide ($TiSi_2$) film 24 which composes local wiring is formed on the diffused layer 4, 5. Unnecessary portion of the titanium silicide film 24 is eliminated by photolithography and etching. Then, an insulator film such as silicon oxide film (BSPG) containing phosphorus and boron is formed on whole surface of the substrate. A step difference of the insulator film is made gentle by re-flow at 750 ℃. Subsequently, a SiO_2 film is formed at 450 ℃ by a plasma CVD method. A planarized passivation insulator film 9 is composed of a BPSG film on the silicon substrate and a SiO_2 film on the BPSG film. The insulator film 9 formed with chemical mechanical polishing (CMP) process. Further,

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contact holes are formed on the titanium silicide ($TiSi_2$) film 24 by photolithography and etching. Bit lines made of tungsten and connecting plugs of wiring layer are formed in the contact holes. Next, a pad for connecting lead wire and a first layer of the wiring layer 11 are formed.

After forming the wiring layer 11, a SiOF film (specific dielectric constant is 3.3) is formed on the whole surface of the substrate by a plasma CVD method using SiH_2F_2. The first layer of the planarized insulator film 12 is formed by treating the SiOF film with a chemical mechanical polishing (CMP) process. The contact holes are formed on the planarized insulator film 12, and plugs 16, 17 made of tungsten are formed in the contact holes. Subsequently, after forming a second layer of the wiring layer 14 is formed, an insulator film 15 composed of the SiOF film is formed using SiH_2F_2. Through holes and the plugs 16, 17 made of tungsten are formed on the insulator film 15.

Consecutively, by the same process as the above, a third layer of the wiring layer 20, a third layer of the planarized insulator film 19, plugs 21, a fourth layer of the wiring layer 22, and a fourth layer of the planarized insulator film 23 are formed, respectively.

In accordance with an investigation by the present inventor, a signal delay time of the above SRAM is 22 ps. On the contrary, the signal delay time of the insulator film composed of the SiO_2 film which is formed with SiH_4 is 28 ps, and the signal delay time of the insulator film

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composed of the SiOF film which is formed with SiF_4 is 25 ps. In an accelerated test equivalent to 100,000 hours, the signal delay time of conventional SRAM fluctuates significantly in a range of 22-36 ps, but the signal delay time of the SRAM of the present invention scarcely change. Accordingly, signal delay of the SRAM can be decreased and reliability of the SRAM can be improved by using the SiOF film formed with SiH_2F_2 as the insulator film among wiring. The above advantage becomes more significant when integration of the SRAM increases and a distance between wires becomes finer.

FIG. 22 illustrates schematically a cross sectional view of a DRAM using an insulator film manufactured by the present invention. FIG. 23 is a plan view of a memory cell of the DRAM. In these figures, BL and WL indicate respectively a bit line and a word line. Furthermore, SN cont., and BL cont. indicate respectively a connecting portion to a storage node and a connecting portion to the bit line. SA indicates the memory cell and its shadow area, and X and Y indicate sizes of the memory cell. In a case of 256 Mbit DRAM, x and y are respectively 0.85 μm and 0.65 μm. The DRAM is manufactured by the following process.

After forming a field oxide film 2 on a p-type silicon substrate 1 by a selective oxide method (LOCOS), a first transistor having a gate 7 and n-type diffused layer 4, 5, and a second transistor adjacent to the first transistor holding the field oxide film 2 between are formed at

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predetermined locations. Subsequently, an insulator film such as silicon oxide film (BSPG) containing phosphorus and boron is formed on whole surface of the substrate. Then, a SiO_2 film is formed by a plasma CVD method. A planarized passivation insulator film 9 is formed by treating a multilayer body composed of the SiO_2 film and the insulator film with a chemical mechanical polishing (CMP) process. Further, contact holes are formed on the planarized passivation insulator film 9. A connecting plug made of phosphorus doped silicon for being connected to the bit line BL, the storage node SN, and the first layer of the wiring layer is formed in the contact holes. Next, a pad for being connected to the bit line BL and the storage node SN and the wiring layer 11 are formed. Both the pad and the wiring layer have a multilayer structure of TiN/Al/TiN, and are formed simultaneously.

After forming the wiring layer 11, a SiOF film is formed on the whole surface of the substrate by a plasma CVD method using SiH_2F_2. The first layer of the planarized insulator film 12 is formed by treating the SiOF film with a chemical mechanical polishing (CMP) process. The contact holes are formed on the planarized insulator film 12, and plugs 13, 14 made of tungsten are formed in the contact holes.

Subsequently, a capacitor is formed. Size of projected area of the capacitor formed portion is 0.65 μm X 0.65 μm. The capacitor has a cylindrical structure of 0.5 μm high in

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order to increase charge storage capacity. The capacitor is formed by the following process.

A lower electrode of the storage node SN is formed from tungsten film of 0.5 μm thick, which is formed by a CVD method, by manufacturing with photolithography and dry etching. Next, in order to form side electrode of the storage node SN, a SiO_2 film of 0.3 μm thick is deposited. The SiO_2 film is manufactured to a columnar block of 0.4 μm X 0.4 μm by photolithography and dry etching. A tungsten film of 0.2 μm thick is formed on the columnar block by a CVD method. The tungsten film is manufactured to side walls of the storage node SN by etching back. Unnecessary columnar block is eliminated by wet etching. Subsequently, a tantalum pentaoxide (Ta_2O_5) film is formed by a CVD method, and unnecessary portion of the tantalum pentaoxide film is eliminated by photolithography and dry etching. Next, a titanium nitride (TiN) film of 0.2 μm thick is formed on whole surface. A plate electrode PL is formed by etching back after a plate electrode PL lead out portion of the titanium nitride film is coated with resist by photolithography. At this time, a capacitor of 0.5 μm X 0.5 μm is formed on the plug 14. Next, after forming a TiN film, an Al film, and a TiN film orderly, a wiring layer of periphery circuit is formed by manufacturing the multilayer body with photolithography and dry etching.

Subsequently, an insulator film is formed in order to

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protect the capacitor and to insulate the second layer of the wiring layer. The insulator film is composed of an oxide film formed with organic silane. Next, through holes and the plugs 16, 17 made of tungsten are formed. By a method using selective growing of tungsten, it becomes possible to form the plugs 16, 17 having respectively different height as shown in FIG. 22.

Next, the third layer of the wiring layer 18 and the pad 19 are formed. Further, the third layer of the planarized SiOF insulator film 20 is formed by the method previously described. Subsequently, in accordance with the above described steps, the plug 21, the fourth layer of the wiring layer 22, and the fourth planarized insulator layer 23 are formed.

According to an investigation by the present inventor, a fraction defective in 200 hours' pressure cooker test of the above described DRAM relating to the present invention is 3 %. On the contrary, when the insulator film is the SiOF film formed with SiH_4, the fraction defective is approximately 38 %, and when the insulator film is the SiOF film formed with SiF_4, the fraction defective is approximately 62 %. Accordingly, the reliability of the DRAM can be increased by using the SiOF film formed with SiH_2F_2 as the insulator film.

Furthermore, the present inventor examined TFT characteristics of a TFT using the SiOF film formed with SiH_2F_2 as a gate insulator film of a TFT-LCD, and of a TFT

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using the SiO_2 film formed with conventional SiH_4. In accordance with the result, the mobility μ in the case using SiOF film is approximately 0.6 (cm^2/v.s), and the mobility μ in the case using SiO_2 film is approximately 0.4 (cm^2/v.s). The difference in μ as above described is caused by fluorine isolated in plasma when SiH_2F_2 is used, which flattens the surface of the formed film.

The SiOF film is preferable as a passivation film for LSI, power transistor, and TFT, because it is hydrophobic.

(Embodiment 10)

The present inventor investigated the SiOF film manufactured by the same apparatus and method as embodiment 1 under various reaction pressure, input power, and gas flow rate. Results of the investigation are explained hereinafter.

FIG. 18 is a graph indicating a relationship between specific dielectric constant and density of the formed film. The specific dielectric constant depends on the density, and especially, the specific dielectric constant can be expressed approximately by a primary function of the density when the density is in a range of 1.8-2.4 (g/cm^3). That means, the dielectric constant can be decreased by lowering the density.

FIG. 19 is a graph indicating a relationship between breakdown voltage and density of the formed film. The film has a sufficient breakdown voltage as an insulator film between wires in a region where the density is larger than

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1.8 (g/^{c}).

As explained above, the SiOF film having a density in a range of 1.8-2.4 (g/^{c}) is preferable as an insulator film of low dielectric constant.

(Embodiment 11)

A result of investigation by the present inventor on desorption amount of the SiOF film in embodiment 10 is explained hereinafter.

FIG. 20 indicates a relationship between the specific dielectric constant of the formed film and the desorption amount of the film when the film is heated at 600 ℃. The value of the desorption amount is normalized with the specific dielectric constant of the film formed with SiH_2F_2 in embodiment 1. As FIG. 20 indicates, when the specific dielectric constant is in a range of 2.8-3.2, the desorption amount is a constant. However, when the specific dielectric constant is less than 2.8 or larger than 3.2, the desorption amount increases. When the specific dielectric constant is less than 2.8, coarse portions of the film material is generated in the formed film because of low density, and moisture in air is taken into the coarse portions. Consequently, the desorption amount increases. When the specific dielectric constant is larger than 3.2, moisture in air or hydroxide group in moisture is readily taken into the film because of existing O-F bond Si-Si bond. Consequently, the desorption amount increases.

As explained above, in order to decrease moisture

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content of the film, use of the film having the specific dielectric constant in a range of 2.8-3.2 is preferable. By using such a film as described above, reliability of semiconductor devices such as LSI and the like can be improved.

SiNF film can be formed by using nitration gas such as N_2, or NH_3 instead of oxidation gas. When a SiN film formed with SiH_2F_2 and nitration gas such as N_2, or NH_3 is used as a TFT gate film, more preferable characteristics can be obtained than a TFT using a SiN film formed with SiH_4 as a gate film. As explained above, SiH_2F_2 is preferable for forming a gate insulator film of semiconductor.

In accordance with the present invention, a dielectric film having a low dielectric constant and high reliability can be formed, and consequently, a semiconductor device of less wiring delay of signal and a semiconductor device having preferable characteristics can be manufactured. Because the dielectric film having a low dielectric constant and high reliability can be formed effectively, such an advantage as reducing manufacturing cost of the semiconductor devices can be realized.

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A DIELECTRIC, A MANUFACTURING METHOD THEREOF, AND SEMICONDUCTOR DEVICE

Abstract of the Disclosure

A silicon oxide fluoride film having Si-F bonds and Si-O bonds is used for insulator wiring of a semiconductor device, and a dielectric film is formed using SiF_2X_2 gas (X = H, Cl, Br, OCH_3, OC_2H_5, and OC_3H_5) as a reactant.

A semiconductor device having a small wiring delay and high reliability can be manufactured, because the silicon oxide fluoride film having Si-F bonds and Si-O bonds has a smaller dielectric constant than a silicon oxide fluoride film having Si-Si bonds and O-F bonds.

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Title of the Invention

A DIELECTRIC, A MANUFACTURING METHOD THEREOF, AND SEMICONDUCTOR DEVICE

Background of the Invention

The present invention relates to a dielectric, a manufacturing method thereof, and a semiconductor device, especially to a dielectric having a low dielectric constant suitable for moderating the wiring delay of signals and improving the durability of semiconductor integrated circuits and the like.

In accordance with the conventional manufacturing process for semiconductor devices, a trial for moderating wiring delay of signals has been performed, and is as follows. The signals are transmitted through wiring and an organic film with a low dielectric constant is used to insulate the wiring. However, the insulation of the wiring using an organic film is hardly used in practice because of a problem with the durability of the organic film.

Currently, to improve the durability, methods of forming a dielectric film composed of silicon, oxygen, and fluorine (called SiOF film hereinafter) have been developed. For instance, a method using silicon tetrafluoride (SiF_4) and oxygen as reacting gases is disclosed in "Preparation of SiOF Films with Low Dielectric Constant by ECR Plasma Chemical Vapor Deposition" p158, Extended Abstract of the 1993 Conference on Solid State Devices and Materials (1993). Further, another method in which gases from the fluorine group are added to the gases necessary for forming a silicon oxide film is disclosed in

"Formation Mechanism of F-added SiO_2 Films using Plasma CVD" p.133, The 16th Proceedings of Symposium on Dry Process (1994).

In connection with conventional SiOF films, fluctuation in the dielectric constant of the films is so large that it is not possible to form a film with a low dielectric constant. The humidity resistance of the film also is low.

The present invention has been developed in consideration of the above problems.

Summary of the Invention

The dielectricrelating to the present invention comprises silicon oxide fluoride compounds, having covalent bonds of fluorine atoms and silicon atoms.

Further, in accordance with a method for manufacturing a dielectric relating to the present invention, a SiOF film is formed by supplying an amount of energy, which does not dissociate the covalent bonds of fluorine atoms and the silicon atoms of SiF_2X_2, to a gas which contains the SiF_2X_2.

Furthermore, in accordance with the semiconductor device relating to the present invention, dielectric bodies comprising silicon oxide fluoride compounds, having covalent bonds of fluorine atoms and silicon atoms, are provided between a plurality of wirings which are located on the substrate of the semiconductor device.

The dielectric constant of a substance is the sum of components based on orientation polarization, ionic polarization, and electronic polarization. The main component of a dielectric constant of a non-orientated

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substance, such as SiO_2 or SiOF film, is almost the same as the dielectric constant based on electronic polarization. The dielectric constant based on electronic polarization can be obtained from atomic refraction of constituent atoms, or electronic group refraction of bonds between the atoms.

FIG. 1 illustrates a molecular structure of a SiOF film relating to the present invention, and FIGs. 2-8 illustrate molecular structures of conventionally known films of SiO, SiO_2, or SiOX (X = OF, H, OH, Cl). In FIGs. 2-8, specific dielectric constants ϵ are shown, which have been respectively calculated by the present inventor from their atomic refraction. The atomic fraction of F is calculated by subtracting the atomic refraction of C from the molecular refraction of CF_4. The atomic fraction of Si is calculated by subtracting the atomic refraction of F from the molecular refraction of SiF_4. The specific dielectric constant of the SiOF film is smaller than that of SiO and SiO_2 films, as shown in FIGs. 2-8 and the specific dielectric constants ϵ. Furthermore, in accordance with investigation by the present inventor, the dielectric constant ϵ of a molecular structure of a SiOF film having a covalent bond of Si and F is smaller than that of a molecular structure of a SiOF film having a covalent bond of Si and O.

FIG. 9 indicates dissociation energies of various bonds. The O-F bond is weaker than the Si-F bond by approximately 1/3. Therefore, a SiOF film having a Si-F bond has a smaller dielectric constant ϵ and is chemically more stable than the SiOF film having a O-F bond.

In order to form a SiOF film with a molecular

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structure having a Si-F bond, SiF_2X_2 molecules are used. These molecules have at least two Si-F bonds and another two Si-X bonds, where X is an atom or an atomic group. The Si-F bonds have a smaller bond energy than the Si-F bond energy. As shown in FIG. 9, bond energies of the Si-H, Si-Cl, Si-O bonds are smaller than the bond energy of the Si-F bond. Accordingly, molecules of Si-X, wherein X is any of H, Cl, OCH_3, OC_2H_5, OC_3H_7, and the like, are preferable.

When using a molecule wherein the bond energy of the Si-X bond is smaller than the bond energy of the Si-F bond, a condition of the SiF_2X_2 molecules can be generated, wherein the Si-F bond keeps bonding, but the Si-X bond dissociates.

In practice, the reaction temperature of a thermal CVD apparatus or the input power of a plasma treating apparatus are controlled so as to add 541 kJ per one mole of SiF_2X_2 molecule, which does not dissociate the Si-F bond. In the above case, oxygen is combined with the Si atom which has two Si-F bonds and dissociates the X atoms. Furthermore, the residual uncombined oxygen valence forms a bond with a similar Si in another SiF_2X_2 molecule. Accordingly, the SiOF film having a molecular structure, wherein F is combined with Si, as shown in FIG. 1, can be formed.

As shown in FIG. 9, the bond energy of the Si-H bond is smaller than the bond energies of the Si-Cl and Si-O bonds. Therefore, using a molecule of Si-X, wherein X is H, the margins of the operating conditions can be broadened.

Brief Description of the Drawings

FIG. 1 illustrates schematically a molecular structure

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of a SiOF film of the present invention;

FIG. 2 illustrates schematically a molecular structure of a conventional SiO (OF) film;

FIG. 3 illustrates schematically a molecular structure of a conventional SiO_2 film;

FIG. 4 illustrates schematically a molecular structure of a conventional SiOCl film;

FIG. 5 illustrates schematically a molecular structure of a conventional SiO film;

FIG. 6 illustrates schematically a molecular structure of a conventional SiOH film;

FIG. 7 illustrates schematically a molecular structure of a conventional SiOF film;

FIG. 8 illustrates schematically a molecular structure of a conventional SiO(OH) film,

FIG. 9 is a table which indicates dissociation energies of various bonds,

FIG. 10 is a schematic cross section of an ECR-CVD apparatus in accordance with the present invention for forming a SiOF film,

FIG. 11 is an infrared absorption spectrum of the SiOF film in accordance with the present invention,

FIG. 12 is a schematic cross section of a parallel plate type RF-CVD apparatus in accordance with the present invention for forming a SiOF film,

FIG. 13 is a schematic cross section of an ICP-CVD apparatus in accordance with the present invention for forming a SiOF film,

FIG. 14 schematically indicates a condition in accordance with the present invention, wherein wires on a semiconductor substrate are covered with the SiOF film,

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FIG. 15 schematically indicates a condition in accordance with the present invention, wherein wires on a semiconductor substrate are covered with the SiOF films, which are formed by overlapped spattering,

FIG. 16 schematically indicates a condition in accordance with the present invention, wherein wires on a semiconductor substrate are covered with the planarized SiOF film,

FIG. 17 is a graph indicating a relationship between the dielectric constant and HWHH (A Half Width at Half Height) of the SiOF film in accordance with the present invention,

FIG. 18 is a graph indicating a relationship between the specific dielectric constant and the density of the SiOF film in accordance with the present invention;

FIG. 19 is a graph indicating a relationship between the density and dielectric breakdown electric field of the SiOF film in accordance with the present invention;

FIG. 20 is a graph indicating a relationship between the specific dielectric constant and the desorption amount in accordance with the present invention;

FIG. 21 is a schematic cross section of a SRAM in accordance with the present invention; wherein the SiOF film is used,

FIG. 22 is a schematic cross section of a DRAM in accordance with the present invention; wherein the SiOF film is used, and

FIG. 23 is a plan view of a memory cell of the DRAM shown in FIG. 22.

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Description of the Preferred Embodiments

The present invention will be explained in detail while referring to the figures hereinafter.

(Embodiment 1)

FIG. 10 is a schematic cross section of an Electron Cyclotron Resonance (ECR)-CVD apparatus, which is one type of CVD apparatus used for forming a SiOF film. The apparatus comprises a plasma generating chamber 2 having a microwave introducing window 1, a reaction chamber 3, a magnetic field generating coil 4, reaction gas inlets 5 and 6, a holder 8 for holding a substrate 7, and a high frequency power source for supplying high frequency waves to the substrate 7.

First, a process for forming a SiOF film using silicon tetrafluoride (SiF_4) and oxygen (O_2) gas in accordance with the present invention will be explained. From the reaction gas inlets 5 and 6, O_2 at 200 (ml/min) and SiF_4 at 40 (ml/min) are introduced respectively into the reaction chamber 3. The pressure in the reaction chamber 3 is adjusted to 0.2 (Pa) by controlling the amount of exhaust gas. An exhaust gas system is not shown in FIG. 10. A magnetic field of 0.0875 (T) is generated in the plasma generating chamber 2 by the magnetic field generating coil 4, and ECR plasma is generated by introducing microwaves of 2.45 (GHz) so that a SiOF film is formed on the surface of the substrate because of reaction between O_2 and SiF_4. In this case, a p-type Si substrate 126 mm in diameter is used as the substrate. The introduced microwave power ($P\mu$) is 600 (W).

The film depositing rate (D.R.) increases in proportion to the introduced microwave power ($P\mu$), for

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instance, the depositing rate D.R. is 0.2 (μm/min) at 600 (W) of Pμ. The specific dielectric constant ϵ of the formed film is approximately 3.5. The bonding condition of the formed film is such that a Si-Si bond is 10 % of the O-Si-O bond, and the Si-O-F bond is 30 % of the Si-F bond. The specific dielectric constant ϵ can be measured by the formation of an aluminum electrode on the formed film. The bonding condition of the formed film can be measured by fluorescent X ray (XPS) analysis or nuclear magnetic resonance (NMR) analysis.

Next, a method of forming SiOF film by introducing silane difluoride (SiH_2F_2), as an embodiment of the present invention, will be explained. Conditions for forming a SiOF film are the same as those of above process which uses SiF_4. The film deposition rate does not depend on the introduced microwave power, but increases in proportion to the amount of introduced SiH_2F_2 gas. When the SiH_2F_2 gas is introduced at a rate of 40 (ml/min), the film deposition rate (D.R.) is equal to 0.38 (μm/min), approximately twice the rate when SiF_4 is used. The reason why the film deposition rate increases when using SiH_2F_2 gas is because the dissociation energy of SiH_2F_2 is lower than that of SiF_4.

FIG. 11 indicates the infrared absorption spectra of SiOF films formed by SiH_2F_2 and SiF_4, respectively. In the case of SiF_4 (hereinafter case: B), the center of the Si-O vibration is 1065 (cm^{-1}), and said half width at the half height (HWHH) at a lower wave number side is 33 (cm^{-1}), although slight moisture (O-H) can be observed.

On the other hand, in a case of SiH_2F_2 (case:A), the center of the Si-O vibration is 1080 (cm^{-1}), and said half width at the half height (HWHH) at a lower wave number side

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is 24 (cm^{-1}). A larger wave number indicates a stronger bond of Si-O, and a smaller WHWW indicates a simpler network with a fewer kind of bonds.

When the bonding condition is measured by fluorescent X ray (XPS) analysis and nuclear magnetic resonance (NMR) analysis, no Si-Si bond and Si-O-F bond can be observed. Accordingly, the structure of the film is mostly composed of the Si-O bond and the Si-F bond, of the formed film reason why the O-H bond is not observed in the infrared spectrum is because the structure does not contain a weak bond of Si-O-F.

The specific dielectric constant ϵ of is approximately 3.2. The specific dielectric constant ϵ is a value obtained by multiplying an estimated dielectric constant ϵ (= 1.88) of the SiOF film shown in FIG. 1 by a coas shown in FIG. 1. The the SiO_2 film (= 2.27), estimated from the atomic refraction and the dielectric constant ϵ of the observed glassy SiO_2 (= 4.0).

As explained above, when the SiOF film is formed by introducing silane difluoride (SiH_2F_2), the deposition rate of the film increases, and a dielectric film having a preferable chemical stability, such as a moisture-resistance and a low dielectric constant, can be formed because the formed SiOF film is mostly composed of Si-O bonds and Si-F bonds.

(Embodiment 2)

When a film is formed under the same conditions as the above embodiment 1, except for introducing silicon dichloride difluoride (SiF_2Cl_2) instead of SiH_2F_2, a SiOF film can be formed, wherein no Cl is observed. The

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deposition rate of the film is almost the same as the rate when SiH_2F_2 is used, and is D.R. = 0.36 (μm/min). The dielectric constant ϵ is approximately 3.3, slightly higher than that of the case using SiH_2F_2. That means, when SiF_2Cl_2 is used, an insulator film having a lower dielectric constant than that of the insulator film obtained by using SiH_2F_2 can be formed.

Furthermore, when a film is formed under the same conditions as used in embodiment 1, except for introducing silicon dibromide difluoride (SiF_2Br_2) instead of SiH_2F_2, a SiOF film, wherein no Br is observed, can be formed. The deposition rate of the film is almost the same as the rate in the case of using SiH_2Cl_2, and the deposition rate D.R. = 0.36 (μm/min). Therefore, a dielectric film having a low dielectric constant ϵ, such as approximately 3.3, can be formed.

(Embodiment 3)

When a film is formed under the same conditions as embodiment 1, except for introducing dimethoxy silicon difluoride ($SiF_2(OCH_3)_2$) instead of SiH_2F_2, a SiOF film, wherein no C is observed, can be formed. The deposition rate of the film is approximately the same as the rate in the case of using SiH_2F_2, and the deposition rate D.R. = 0.36 (μm/min). The dielectric constant ϵ is slightly higher than in the case of using SiH_2F_2 and is approximately 3.3.

When a film is formed under the same conditions as in embodiment 1, except for introducing diethoxy silicon difluoride ($SiF_2(OC_2H_5)_2$) instead of SiH_2F_2, a SiOF film, wherein C is hardly observed, can be formed. The deposition rate D.R. of the film is 0.36 (μm/min), and is slower than that in the case using SiH_2F_2. The reason of the slower

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deposition rate is because $SiF_2(OC_2H_5)_2$ has a lower vapor pressure at room temperature than SiH_2F_2. Therefore, if the temperature of the source vessel and the temperature of the piping are elevated so as to make it possible to introduce a necessary amount of $SiF_2(OC_2H_5)_2$, 40 (ml/min), the deposition rate D.R. increases to 0.36 (μm/min). The ϵ dielectric constant is approximately 3.3.

When a film is formed under the same conditions as in embodiment 1, except for introducing dipropoxy silicon difluoride ($SiF_2(OC_3H_7)_2$) instead of SiH_2F_2, a SiOF film can also be formed. However, the temperature of the source vessel and the piping must be elevated so as to make it possible to introduce a necessary amount of $SiF_2(OC_3H_7)_2$, 40 (ml/min). In this case, the deposition rate D.R. is 0.36 (μm/min), and the dielectric constant ϵ is approximately 3.3.

In accordance with a study by the present inventors, the coating condition of the substrate surface when an SiOF film is formed on a substrate having an uneven surface becomes more preferable, depending on the source materials being used, in the order of $SiF_2(OC_3H_7)_2$, $SiF_2(OC_2H_5)_2$, ($SiF_2(OCH_3)_2$), and SiH_2F_2.

(Embodiment 4)

FIG. 12 illustrates schematically a cross section of a parallel plate type RF (RF: radio frequency)-CVD apparatus for forming a SiOF film. The apparatus comprises a reaction chamber 11, reaction gas inlets 5 and 6, a holder 12 for holding and heating a substrate 7, and a frequency power source 13 for supplying high frequency waves for plasma generation.

First, a process for forming a SiOF film from SiH_2F_2

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and nitrogen monoxide (N_2O) gas using the present apparatus will be explained hereinafter.

The film is formed by introducing N_2O gas at 800 (ml/min) and SiH_2F_2 at 200 (ml/min) through the reaction gas inlets 5 and 6, respectively. The pressure in the reaction chamber 3 is adjusted to 200 (Pa) by controlling the amount of the exhaust gas (the exhaust gas system is not shown in the figure). The SiOF film is formed on a substrate by generating plasma by supplying high frequency waves 400 (W) of 13.6 (MHz) to the upper electrode 14, and reacting N_2O with SiH_2F_2. The temperature of the substrate is kept at 350 .

When SiF_4 is used, the film is scarcely formed. However, when SiH_2F_2 is used, the film can be formed with a deposition rate D.R. of 0.20 (μm/min). When O_2 is used instead of N_2O with SiH_2F_2, a SiOF film can be formed, but the deposition rate D.R. is less than 0.1 (μm/min). The film is scarcely formed when SiF_4 is used, because the bond energy of Si-F is large. However, the SiOF film can be formed by RF plasma using SiH_2F_2, because SiH_2F_2 has a Si-H bond with a weak bond energy.

As explained above, the deposition rate increases by using N_2O instead of O_2, because N_2O has a lower generation energy of active oxygen than that of O_2. The dielectric constant ϵ of the formed SiOF film is approximately 3.2.

As described above, the SiOF film having a low dielectric constant can be formed with a RF plasma when SiH_2F_2 is used.

(Embodiment 5)

FIG. 13 illustrates schematically a cross section of an ICP (ICP: Inductively Coupled Plasma)-CVD apparatus for

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forming a SiOF film. The apparatus comprises a reaction chamber 15 made of quartz, reaction gas inlets 5 and 6, a holder 16 for holding a substrate 7, and a coil 17 for supplying high frequency waves for plasma generation.

First, in order to provide a comparison with the present invention, a process for forming SiOF film using SiF_4 and oxygen gas will be explained hereinafter. From the reaction gas inlets 5 and 6, O_2 at 200 (ml/min) and SiF_4 atby 40 (ml/min) are respectively introduced into the reaction chamber 15. The pressure in the reaction chamber 15 is adjusted to 0.2 (Pa) by controlling the amount of exhaust gas (the exhaust gas system is not shown in the figure). Plasma is generated by supplying 1 (kW) high frequency waves at 13.6 (MHz) to the coil 17 so that the SiOF film is formed on the surface of the substrate by reacting of O_2 and SiF_4. The film depositing rate (D.R.) is 0.2 (μm/min), and the specific dielectric constant ϵ of the formed film is approximately 3.5. The bonding condition of the formed film is such that Si-Si bond is 10 % of the O-Si-O bond, and the Si-O-F bond is 30 % of the Si-F bond.

Next, a method for forming SiOF film by introducing silane difluoride (SiH_2F_2), according to an embodiment of the present invention, will be explained hereinafter. Other conditions for forming the film, except for the introducing gas, are the same as the above explained process which uses SiF_4. The film deposition rate D.R. is 0.38 (μm/min), and is approximately twice that of the case using SiF_4. The reason for the increase of the film deposition rate is that the dissociation energy of SiH_2F_2 is lower than that of SiF_4.

Regarding the infrared absorption spectra of SiOF films formed by SiH_2F_2 and SiF_4, in a case of SiF_4 similar to

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the ECR plasma, the center of the Si-O vibration is 1065 (cm^{-1}), and the half width at half height (HWHH) at a lower wave number side is 33 (cm^{-1}). Although only slightly, some moisture (O-H) can be observed. On the other hand, in a case of using SiH_2F_2 (case:A), the center of the Si-O vibration is 1080 (cm^{-1}), and the half width at half height (HWHH) at a lower wave number side is 24 (cm^{-1}).

Furthermore, no Si-Si bond or Si-O-F bond can be observed in the film formed by SiH_2F_2. Accordingly, the structure of the film is mostly composed of a Si-O bond and a Si-F bond. The reason why the O-H bond is not observed in the infrared spectrum is because the structure does not contain a weak bond of Si-O-F. Further, the dielectric constant ϵ is approximately 3.2 the same as in embodiment 4, and so a film having a low dielectric constant can be formed. Furthermore, the film formed in the present embodiment has a preferable chemical stability.

As explained above, a SiOF film having a low dielectric constant can be formed by ICP plasma if silane difluoride (SiH_2F_2) is used.

(Embodiment 6)

In the above described embodiments, when wiring 18 provided on the surface of the semiconductor substrate of the semiconductor device is coated with a SiOF film 19, as shown in FIG. 14, the width of the concave portion on the surface of the formed film becomes narrower than the width of the interval between the wiring. Therefore, when a second wiring is formed on the film for multilayer wiring, the breaking fraction of the wire of the second wiring increases and accordingly, the production yield of the semiconductor device decreases. In order to prevent such a

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decrease of the production yield, the spattering must be overlapped in forming the SiOF film using SiH_4 and O_2.

As a reference example for forming a film by overlapping the spattering, a case of a SiO_2 film with SiH_4 instead of SiF_4 using the apparatus shown in FIG. 10 will be explained hereinafter. In this case, high frequency waves 400 (kHz) of 400 (W) are supplied to the substrate from a high frequency power source 9, the other conditions are set to be the same as the embodiment 1.

The film deposition rate (D.R.) is 0.38 (μm/min) when the spattering is not overlapped, and the film deposition rate when the spattering is overlapped is 0.27 (μm/min), resulting in a 30 % reduction. The reduced amount of the film deposition is a spattering rate (S.R.), and, in the above case, spattering rate S.R. is 0.11 (μm/min). The film forming condition in the above case is shown in FIG. 15. The film forming condition is determined by the ratio the deposition rate D.R. and the spattering rate S.R. The deposition rate D.R. can be increased by increasing the amount of SiH_4 being introduced, but the spattering rate S.R. can not be increased even if the amount of O_2 is increased. The specific dielectric constant ϵ of the formed film is approximately 4.0.

On the other hand, when SiOF film is formed with SiH_2F_2 and O_2 according to, an embodiment of the present invention, the film deposition rate (D.R.) when the spattering is not overlapped is 0.38 (μm/min), and the deposition rate D.R. when the spattering is overlapped is 0.19 (μm/min), resulting in a 50 % reduction. The reduced amount 0.19 (μm/min) is the spattering rate S.R., and is larger than the spattering rate S.R. in the case when SiH_4 is used. The

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remarkable increase in the spattering rate (S.R.) when the spattering is overlapped is caused by etching of the film by the F of SiH_2F_2. Therefore, the deposition rate D.R. can be increased by increasing the amount of SiH_2F_2 being introduced as much as the amount the S.R. is increased. In accordance with the spattering rate method explained above, wherein the amount of SiH_2F_2 being introduced is controlled so as to obtain a deposition rate D.R. of 0.66 (μm/min), a film is formed on the surface of the wiring, i.e. when a film is formed on the surface of the wiring with an effective deposition rate of 0.66 (μm/min), the film is formed in a condition as shown in FIG. 15. In the above case, the specific dielectric constant ϵ of the formed film is approximately 3.2.

As explained above, if a film is formed with SiH_2F_2 by overlapping the spattering, not only can a film having a low specific dielectric constant be formed, but also the effective film deposition rate can be increased without increasing the power supply of the apparatus and other factors.

Furthermore, in order to decrease the breaking fraction of wire of the second wiring and improve the production yield, a film structure as shown in FIG. 16 may be formed by applying a flattening film, or by eliminating an extra protrusion of the film by etching back, after forming the film shaped as shown in FIG. 15. Instead of the etching back, mechanical-chemical polishing (CMP) also can be used.

(Embodiment 7)

FIG. 17 is a graph indicating a result of an investigation performed by the present inventor. A

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relationship between the dielectric constant ϵ of a SiOF film formed under various forming conditions and the half width at half height (HWHH) at a lower wave number side of the Si-O peak in the infrared spectrum reveals that there is a strong correlation between the dielectric constant ϵ and the half width at half height HWHH. In order to form a SiOF film having a low dielectric constant, a film having the half width at half height (HWHH) at a lower wave number side of the Si-O peak in the infrared spectrum of less than 30 cm^{-1} must be formed.

(Embodiment 8)

The breakdown voltage (B.V.) of the SiOF film formed with SiF_4 in embodiment 1 is approximately 5 (MV/cm). Generally, the breakdown voltage (B.V.) of a conventional SiOF film is 9 (MV/cm). The breakdown voltage can be improved by forming a film having an intermediate composition between the above described SiOF film and the conventional SiO_2 film.

As a reference example, there is a film forming method using SiH_4, 20 (ml/min), and SiF_4, 20 (ml/min), instead of SiF_4, 40 (ml/min), in embodiment 1. In this case, the film deposition rate (D.R.) of the film is 0.19 (μm/min). If the composition of the formed film is in a range between the SiOF film and the conventional SiO_2 film, the specific dielectric constant ϵ of the film has a value of approximately 3.75. However, the dielectric constant ϵ of the SiOF film formed with SiF_4 is approximately 3.9. That means, fluorine doping hardly can be achieved even if SiF_4 is used as the doping gas of fluorine F. Because the bond energy of the Si-F bond in SiF_4 is significantly larger than the bond energy of the Si-H bond in SiH_4, the energy

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introduced into the plasma is hardly used for dissociation of SiF_4, but is used for dissociation of SiH_4.

On the other hand, there is a film forming method wherein SiH_4, 20 (ml/min), and SiH_2F_2, 20 (ml/min), are used instead of SiF_4, 40 (ml/min), in embodiment 1 of the present invention. In this case, the film deposition rate (D.R.) of the film is 0.38 (μm/min). The specific dielectric constant of the formed film was approximately 3.75. That means, the composition of the formed film is in intermediate the SiOF film and the conventional SiO_2 film. Because the bond energy of Si-H bond in SiH_2F_2 is almost similar with the Si-F bond in SiF_4, the energy introduced into the plasma is used evenly for dissociation of both SiH_2F_2 and SiH_4. The specific dielectric constant ϵ in a range of 3.2 -4.0 varies as a primary function of the flow rate ratio (SiH_2F_2 /SiH_4). Therefore, the specific dielectric constant can be controlled readily.

As explained above, SiH_2F_2 is preferable for the doping of fluorine.

(Embodiment 9)

FIG. 21 illustrates schematically a cross sectional view of a SRAM using an insulator film manufactured according to the present invention. The SRAM is manufactured by the following process.

After forming a field oxide film 2 on a p-type silicon substrate 1 using a selective oxide method (LOCOS), a first transistor having a gate 7 and n-type diffused layer 4, 5, and a second transistor adjacent to the first transistor, holding the field oxide film 2 therebetween are formed at predetermined locations. Subsequently, a titanium silicide ($TiSi_2$) film 24, which composes local wiring, is formed on

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the diffused layer 4, 5. Unnecessary portions of the titanium silicide film 24 are eliminated by photolithography and etching. Then, an insulator film, such as silicon oxide film (BSPG) containing phosphorus and boron, is formed on the whole surface of the substrate. A step difference of the insulator film is made gentle by re-flow at 750 . Subsequently, a SiO_2 film is formed at 450 by a plasma CVD method. A planarized passivation insulator film 9 is composed of a BPSG film on the silicon substrate and a SiO_2 film on the BPSG film. The insulator film 9 is formed using a chemical mechanical polishing (CMP) process. Further, contact holes are formed on the titanium silicide ($TiSi_2$) film 24 by photolithography and etching. Bit lines made of tungsten and connecting plugs of a wiring layer are formed in the contact holes. Next, a pad for connecting the lead wire and a first layer of the wiring layer 11 are formed.

After forming the wiring layer 11, a SiOF film (specific dielectric constant is 3.3) is formed on the whole surface of the substrate by a plasma CVD method using SiH_2F_2. The first layer of the planarized insulator film 12 is formed by treating the SiOF film using a chemical mechanical polishing (CMP) process. The contact holes are formed on the planarized insulator film 12, and plugs 16, 17 made of tungsten are formed in the contact holes. Subsequently, after a second layer of the wiring layer 14 is formed, an insulator film 15 composed of the SiOF film is formed using SiH_2F_2. Through holes and the plugs 16, 17 made of tungsten are formed on the insulator film 15.

Consecutively, using the same process as described above, a third layer of the wiring layer 20, a third layer

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of the planarized insulator film 19, plugs 21, a fourth layer of the wiring layer 22, and a fourth layer of the planarized insulator film 23 are formed, respectively.

In accordance with an investigation by the present inventor, the signal delay time of the above SRAM was found to be 22 ps. On the contrary, the signal delay time of the insulator film composed of the SiO_2 film which is formed with SiH_4 is 28 ps, and the signal delay time of the insulator film composed of the SiOF film which is formed with SiF_4 is 25 ps. In an accelerated test equivalent to 100,000 hours, the signal delay time of a conventional SRAM fluctuates significantly in a range of 22-36 ps, but the signal delay time of the SRAM of the present invention scarcely changes. Accordingly, the signal delay of the SRAM can be decreased and the reliability of the SRAM can be improved by using an SiOF film formed with SiH_2F_2 as the insulator film for the wiring.

The above advantage becomes more significant when integration of the SRAM increases and the distance between wires becomes finer.

FIG. 22 illustrates schematically a cross sectional view of a DRAM using an insulator film manufactured according to the present invention. FIG. 23 is a plan view of a memory cell of the DRAM. In these figures, BL and WL indicate respectively a bit line and a word line. Furthermore, SN cont., and BL cont. indicate respectively a connecting portion to a storage node and a connecting portion to the bit line. SA indicates the memory cell and its shadow area, and X and Y indicate the sizes of the memory cell. In a case of a 256 Mbit DRAM, x and y are respectively 0.85 μm and 0.65 μm. The DRAM is manufactured

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by the following process.

After forming a field oxide film 2 on a p-type silicon substrate 1 using a selective oxide method (LOCOS), a first transistor having a gate 7 and n-type diffused layer 4, 5, and a second transistor adjacent to the first transistor, holding the field oxide film 2 therebetween are formed at predetermined locations. Subsequently, an insulator film, such as a silicon oxide film (BSPG) containing phosphorus and boron, is formed on the whole surface of the substrate. Then, a SiO_2 film is formed by a plasma CVD method. A planarized passivation insulator film 9 is formed by treating a multilayer body composed of the SiO_2 film and the insulator film with a chemical mechanical polishing (CMP) process. Further, contact holes are formed on the planarized passivation insulator film 9. A connecting plug made of phosphorus doped silicon, to be connected to the bit line BL, the storage node SN, and the first layer of the wiring layer, is formed in the contact holes. Next, a pad to be connected to the bit line BL and the storage node SN and the wiring layer 11 are formed. Both the pad and the wiring layer have a multilayer structure of TiN/Al/TiN, and are formed simultaneously.

After forming the wiring layer 11, a SiOF film is formed on the whole surface of the substrate by a plasma CVD method using SiH_2F_2. The first layer of the planarized insulator film 12 is formed by treating the SiOF film with a chemical mechanical polishing (CMP) process. The contact holes are formed on the planarized insulator film 12, and plugs 13, 14 made of tungsten are formed in the contact holes.

Subsequently, a capacitor is formed. The size of the

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projected area of the capacitor formed portion is 0.65 μm X 0.65 μm. The capacitor has a cylindrical structure which is 0.5 μm high in order to increase the charge storage capacity. The capacitor is formed by the following process.

A lower electrode of the storage node SN is formed from a tungsten film, which is 0.5 μm thick, and is formed by a CVD method, by manufacturing with photolithography and dry etching. Next, in order to form a side electrode of the storage node SN, a SiO_2 film 0.3 μm thick is deposited. The SiO_2 film is manufactured to a columnar block of 0.4 μm X 0.4 μm by photolithography and dry etching. A tungsten film 0.2 μm thick is formed on the columnar block by a CVD method. The tungsten film is manufactured to side walls of the storage node SN by etching back. Any unnecessary columnar block is eliminated by wet etching. Subsequently, a tantalum pentaoxide (Ta_2O_5) film is formed by a CVD method, and any unnecessary portion of the tantalum pentaoxide film is eliminated by photolithography and dry etching. Next, a titanium nitride (TiN) film 0.2 μm thick is formed on the whole surface. A plate electrode PL is formed by etching back after a plate electrode PL lead out portion of the titanium nitride film is coated with resist by photolithography. At this time, a capacitor of 0.5 μm X 0.5 μm is formed on the plug 14. Next, after forming a TiN film, an Al film, and a TiN film in order, a wiring layer of the periphery circuit is formed by manufacturing the multilayer body using photolithography and dry etching.

Subsequently, an insulator film is formed in order to protect the capacitor and to insulate the second layer of the wiring layer. The insulator film is composed of an oxide film formed with organic silane. Next, through holes

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and the plugs 16, 17 made of tungsten are formed. By a method using selective growing of tungsten, it becomes possible to form the plugs 16, 17 having respectively different heights, as shown in FIG. 22.

Next, the third layer of the wiring layer 18 and the pad 19 are formed. Further, the third layer of the planarized SiOF insulator film 20 is formed by the method previously described. Subsequently, in accordance with the above described steps, the plug 21, the fourth layer of the wiring layer 22, and the fourth planarized insulator layer 23 are formed.

According to an investigation by the present inventor, a fraction defective a 200 hours' pressure cooker test of the above described DRAM relating to the present invention was found to be 3 %. On the contrary, when the insulator film is a SiOF film formed with SiH_4, the fraction defective is approximately 38 %, and when the insulator film is a SiOF film formed with SiF_4, the fraction defective is approximately 62 %. Accordingly, the reliability of the DRAM can be increased by using a SiOF film formed with SiH_2F_2 as the insulator film.

Furthermore, the present inventor examined the TFT characteristics of a TFT using a SiOF film formed with SiH_2F_2 as a gate insulator film of a TFT-LCD, and the TFT characteristics of a TFT using a SiO_2 film formed with conventional SiH_4. In accordance with the result, the mobility μ in the case using a SiOF film is approximately 0.6 ($cm^2/v.s$), and the mobility μ in the case using a SiO_2 film is approximately 0.4 ($cm^2/v.s$). The difference in μ as above described is caused by fluorine isolated in the plasma when SiH_2F_2 is used, which flattens the surface of

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the formed film.

The SiOF film is preferable as a passivation film for a LSI, a power transistor, and a TFT, because it is hydrophobic.

(Embodiment 10)

The present inventor investigated the SiOF film manufactured by the same apparatus and method as embodiment 1 under various values of reaction pressure, input power, and gas flow rate. The results of the investigation will be explained hereinafter.

FIG. 18 is a graph indicating a relationship between the specific dielectric constant and the density of the formed film. The specific dielectric constant depends on the density, and especially, the specific dielectric constant can be expressed approximately by a primary function of the density when the density is in a range of 1.8-2.4 (g/cm^3). That means, the dielectric constant can be decreased by lowering the density.

FIG. 19 is a graph indicating a relationship between the breakdown voltage and the density of the formed film. The film has a sufficient breakdown voltage as an insulator film between wires in a region where the density is larger than 1.8 ($g/^c$).

As explained above, the SiOF film having a density in a range of 1.8-2.4 ($g/^c$) is preferable as an insulator film of low dielectric constant.

(Embodiment 11)

A result of investigation by the present inventor concerning the desorption amount of the SiOF film in embodiment 10 will be explained hereinafter.

FIG. 20 indicates a relationship between the specific

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dielectric constant of the formed film and the desorption amount of the film when the film is heated at 600 . The value of the desorption amount is normalized with the specific dielectric constant of the film formed with SiH_2F_2 in embodiment 1. As FIG. 20 indicates, when the specific dielectric constant is in a range of 2.8-3.2, the desorption amount is a constant. However, when the specific dielectric constant is less than 2.8 or larger than 3.2, the desorption amount increases. When the specific dielectric constant is less than 2.8, coarse portions of the film material are generated in the formed film because of the low density, and moisture in the air is taken into the coarse portions. Consequently, the desorption amount increases. When the specific dielectric constant is larger than 3.2, moisture in the air or a hydroxide group in the moisture is readily taken into the film because of the existing O-F bond Si-Si bond. Consequently, the desorption amount increases.

As explained above, in order to reduce the moisture content of the film, use of a film having a specific dielectric constant in a range of 2.8-3.2 is preferable. By using such a film as described above, the reliability of semiconductor devices, such as an LSI and the like, can be improved.

SiNF film can be formed by using a nitration gas such as N_2 or NH_3 instead of an oxidation gas. When a SiN film formed with SiH_2F_2 and a nitration gas such as N_2 or NH_3 is used as a TFT gate film, more preferable characteristics can be obtained than provided by a TFT using a SiN film formed with SiH_4 as a gate film. As explained above, SiH_2F_2 is preferable for forming a gate insulator film of a

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semiconductor.

In accordance with the present invention, a dielectric film having a low dielectric constant and high reliability can be formed, and consequently, a semiconductor device of having less signal wiring delay and a semiconductor device having preferable characteristics can be manufactured. Because a dielectric film having a low dielectric constant and high reliability can be formed effectively, such an advantage as reducing manufacturing cost of the semiconductor devices can be realized.

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* C L M S *

What is claimed is;

1. A dielectric comprising a silicon oxide fluoride compound having a covalent bond between a fluorine atom and a silicon atom.

2. A dielectric as claimed in claim 1, wherein said silicon oxide fluoride compound has an additional covalent bond between a silicon atom and an oxygen atom.

3. A dielectric comprising a silicon oxide fluoride compound, which has a half width at half height of equal to or less than 30 cm^{-1} at a region in the infrared spectrum with low frequency waves.

4. A dielectric comprising a silicon oxide fluoride compound, which has a density in a range of 1.8-2.4 g/c.

5. A dielectric comprising a silicon oxide fluoride compound, which has a specific dielectric constant in a range of 2.8-3.2.

6. A method of manufacturing a dielectric comprising the steps of :

introducing a gas containing SiF_2X_2 gas onto a substrate, and

supplying an energy which does not dissociate the covalent bond between a fluorine atom and a silicon atom in said SiF_2X_2 gas to said gas containing SiF_2X_2 gas.

7. A method of manufacturing a dielectric as claimed in

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* C L M S *

claim 6, wherein

said X is any one selected from a group consisting of H, Cl, Br, OCH_3, OC_2H_5, and OC_3H_5.

8. A method of manufacturing a dielectric as claimed in claim 6, wherein

said energy is less than 541 kJ per 1 mol of SiF_2X_2.

9. A method of manufacturing a dielectric as claimed in claim 6, wherein

said energy is supplied by a CVD apparatus.

10. A method of manufacturing a dielectric as claimed in claim 6, wherein

said energy is supplied by a plasma treating apparatus.

11. A method of manufacturing a dielectric as claimed in claim 9, wherein

spattering processes are overlapped.

12. A method of manufacturing a dielectric as claimed in claim 10, wherein

said plasma is generated by radio waves.

13. A semiconductor device comprising :

a plurality of wiring located on the surface of a semiconductor substrate, and

a dielectric comprising a silicon oxide fluoride compound having a covalent bond between a fluorine atom and a silicon atom located at intervals between said plurality

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* C L M S *

of wiring.

14. A semiconductor device comprising :

a plurality of wiring located on the surface of a semiconductor substrate, and

a dielectric comprising a silicon oxide fluoride compound, which has a half width at half height of equal to or less than 30 cm^{-1} at a region in the infrared spectrum with low frequency waves.

15. A semiconductor device comprising :

a plurality of wiring located on the surface of a semiconductor substrate, and

a dielectric comprising a silicon oxide fluoride compound, which has a density in a range of 1.8-2.4 g/^{c}.

16. A semiconductor device comprising :

a plurality of wiring located on the surface of a semiconductor substrate, and

a dielectric comprising a silicon oxide fluoride compound, which has a specific dielectric constant in a range of 2.8-3.2.

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* C L M S *

17. A semiconductor memory device comprising :

a plurarity of memory cells disposed over the main surface of a semiconductor body;

a plurarity of wiring layers disposed over said memory cells;

an insulator film including a silicon oxide fluorine compond having a covalent bond between a fluorine atom and a silicon atom, formed on said wiring layers; and

a plurarity of upper wiring layers formed on said insulator film.

18. A semiconductor memory device as claimed in claim 17, wherein eace of said memory cells consists of an insulated gate field effect transistor and a capacitor.

19. A semiconductor memory device as claimed in claim 18, wherein said capacitor has a cylindrical structure.

20. A semiconductor memory device as claimed in claim 17, wherein the surface of said insulator film is planarized by treating a chemical mechanical polishing process.

21. A semiconductor memory device as claimed in claim 17, wherein the insulator film has a specific dielectric constant in a renge of 2.8 - 3.2.

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Abstract of the Disclosure

A DIELECTRIC, A MANUFACTURING METHOD THEREOF, AND SEMICONDUCTOR DEVICE

A silicon oxide fluoride film having Si-F bonds and Si-O bonds is used for insulator wiring of a semiconductor device, and a dielectric film is formed using SiF_2X_2 gas (X = H, Cl, Br, OCH_3, OC_2H_5, and OC_3H_5) as a reactant.

A semiconductor device having a small wiring delay and high reliability can be manufactured, because the silicon oxide fluoride film having Si-F bonds and Si-O bonds has a smaller dielectric constant than a silicon oxide fluoride film having Si-Si bonds and O-F bonds.

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☑ Claim(s) : paged 27 to paged 29
☐ Drawing(s) : paged ..... to paged .....
☐ Abstract : paged ..... to paged .....
DATE OF RECEIPT 27 AUG 1998

What is claimed is;

1. A dielectric comprising a silicon oxide fluoride compound having a covalent bond between a fluorine atom and a silicon atom, wherein the dielectric hardly has carbon and a specific dielectric constant of the dielectric is 3.3 or less.

2. A dielectric as claimed in claim 1, wherein said silicon oxide fluoride compound has an additional covalent bond between a silicon atom and an oxygen atom.

3. A dielectric comprising a silicon oxide fluoride compound, which has a half width at half height of equal to or less than $30cm^{-1}$ at a region in the infrared spectrum with low frequency waves.

4. A dielectric as claimed in Claim 1, wherein said silicon oxide fluoride compound has a density in a range of 1.8 - 2.4 g/c.

5. A dielectric comprising a silicon oxide fluoride compound, which has a specific dielectric constant in a range of 2.8-3.2.

6. A method of manufacturing a dielectric by plasma chemical vapor deposition comprising the steps of :

introducing a gas containing SiF_2X_2 gas onto a substrate, and

supplying an energy which does not dissociate the covalent bond between a fluorine atom and a silicon atom in said SiF_2X_2 gas to said gas containing SiF_2X_2 gas.

7. A method of manufacturing a dielectric as claimed in

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claim 6, wherein

said X is any one selected from a group consisting of H, Cl, Br, OCH_3, OC_2H_5, and OC_3H_5.

8. A method of manufacturing a dielectric as claimed in claim 6, wherein

said energy is less than 541 kJ per 1 mol of SiF_2X_2.

9. A method of manufacturing a dielectric as claimed in claim 6, wherein

said energy is supplied by an electron cyclotron resonance-CVD apparatus.

10. A method of manufacturing a dielectric as claimed in claim 6, wherein

said energy is supplied by a plasma treating apparatus.

11. A method of manufacturing a dielectric as claimed in claim 9, wherein

spattering processes are overlapped.

12. A method of manufacturing a dielectric as claimed in claim 10, wherein

said plasma is generated by radio waves.

13. A semiconductor device comprising :

a plurality of wiring located on the surface of a semiconductor substrate, and

a dielectric comprising a silicon oxide fluoride compound having a covalent bond between a fluorine atom and a silicon atom located at intervals between said plurality of wiring, wherein the dielectric hardly has carbon and a specific dielectric constant of the dielectric is 3.3 or less.

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14. A semiconductor device comprising :

a plurality of wiring located on the surface of a semiconductor substrate, and

a dielectric comprising a silicon oxide fluoride compound, which has a half width at half height of equal to or less than 30 cm^{-1} at a region in the infrared spectrum with low frequency waves.

15. A semiconductor device comprising :

a plurality of wiring located on the surface of a semiconductor substrate, and

a dielectric comprising a silicon oxide fluoride compound, which has a density in a range of 1.8 - 2.4 g/c and hardly has carbon and a specific dielectric constant of the dielectric is 3.3 or less.

16. A semiconductor device comprising :

a plurality of wiring located on the surface of a semiconductor substrate, and

a dielectric comprising a silicon oxide fluoride compound, which has a specific dielectric constant in a range of 2.8-3.2.

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