

**Method of forming a high dielectric constant film and
method of forming a semiconductor device**

5 Technical Field

The present invention relates to a method of forming a high dielectric constant film by atomic layer deposition and to a method of forming a semiconductor device.

Background Art

10 Increasingly thin gate dielectric films are required as large-scale integrated circuits shrink in size. Due to increases in the leakage current, the heretofore used silicon oxide films and silicon nitride films are subject to limits on the extent to which their thickness can be reduced, and the requirement by the sub-0.1 μm CMOS generation of an SiO_2 equivalent film thickness ≤ 1.5 nm has been extremely
15 challenging. As a consequence, it has been proposed that the leakage current be inhibited by using high dielectric constant films (high-k films) in the form of metal oxide films, metal silicate films, or metal aluminate films, which have higher relative permittivities than silicon oxide films or silicon nitride films, and by employing physically thick films.

20 A large number of reports have recently appeared on attempts at using metal silicate films, which have excellent electrical properties, as these high dielectric constant films. Chemical vapor deposition and sputtering are typically used to form metal silicate films.

25 However, in the case of chemical vapor deposition, metal silicate film formation is carried out by a low-temperature film production procedure at around 300°C , and as a result large amounts of impurities ($> 10^{21} \text{ cm}^{-3}$) such as carbon and hydrogen remain in the film, creating the problem of an unacceptable film quality. Moreover,
30 since the film composition is determined by the starting materials used, the

problem arises that the film composition cannot be altered without changing the starting materials used.

In the case of sputtering, on the other hand, damage is produced in the silicon substrate by radical species from, for example, argon, during the initial stage of forming the metal silicate film. This results in the formation of a thick interfacial layer (> about 1 nm) at the metal silicate film/silicon substrate interface, which makes it difficult to reduce the film thickness.

Atomic layer deposition (abbreviated below as ALD), which is capable of forming gate dielectric films on an atomic layer basis, has recently been described. The use of ALD to form gate dielectric films makes it possible to change the film composition without changing the starting materials used. Metal aluminate films have been a widely used ALD-fabricated gate dielectric film. For example, Patent Reference 1 describes the formation of a high dielectric constant film of, for example, Al_2O_3 , by a production method comprising

a first step, in which a silicon substrate is oxidized by an ozone-containing oxidizing gas;

a second step, in which the oxidized surface of the silicon substrate is hydroxylated, followed by the adsorption thereon of a first reactant, such as trimethylaluminum (TMA); and

a third step, in which a second reactant, such as H_2O , is introduced and is reacted with the residues of the first reactant on the oxidized surface.

Patent Reference 2 describes the formation of an amorphous metal aluminate film with the composition $\text{Al}_x\text{M}_{(1-x)}\text{O}_y$ ($0.05 \leq x \leq 0.3$) comprising an amorphous aluminum oxide material and a metal oxide, for example, of zirconium, that is a crystalline dielectric.

Metal aluminate films such as these have been widely used as ALD-fabricated gate dielectric films. This is due to the long-known fact that film formation by ALD using TMA (aluminum source) as a source material is relatively easy.

- 5 There have also been attempts at fabricating metal silicate films, which have excellent electrical characteristics, by ALD. If ALD-fabricated metal silicate films could be used in semiconductor devices, this would enable greater suppression of leakage current generation than for the use of metal aluminate films, thereby improving component reliability. Moreover, since there is no formation of a thick
10 interfacial layer at the metal silicate film/silicon substrate interface, reducing the thickness of metal silicate films will be an easy matter.

In this regard, Patent Reference 3 describes a method for forming metal silicate films by atomic layer deposition. This method uses a metal-containing compound in
15 the form of $\text{Hf}((\text{C}_2\text{H}_5)(\text{CH}_3)\text{N})_4$ and a silicon-containing compound in the form of $\text{O}(\text{Si}(\text{CH}_3)_2\text{H})_2$ or $((\text{CH}_3)_3\text{Si})_2$.

[Patent Reference 1]

Japanese Laid Open (Unexamined or Kokai or A) Patent Application Number
20 2003-188171

[Patent Reference 2]

Japanese Laid Open (Unexamined or Kokai or A) Patent Application Number
2004-214304

[Patent Reference 3]

25 Japanese Laid Open (Unexamined or Kokai or A) Patent Application Number
2004-165668

Disclosure of the Invention

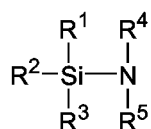
Problems to Be Solved by the Invention

30 With regard to the metal silicate films formed by the prior-art method as cited above, film formation on the substrate has not been adequate and the film

formability requires improvement. Moreover, when these films have been used in semiconductor devices, the component reliability, for example, leakage current generation, has not necessarily been satisfactory.

5 Means Solving the Problems

The method according to the present invention for forming high dielectric constant films forms a high dielectric constant film comprising metal silicate on a substrate by atomic layer deposition using the gas of a metal-containing compound and the gas of a silicon-containing compound represented by the general formula



wherein

R^1 , R^2 , and R^3 in the preceding general formula are each independently selected from the hydrogen atom, C_{1-3} alkyl, and $\text{N}(\text{R}^6)_2$ (wherein each of the plurality of R^6 groups is independently selected from the hydrogen atom, C_{1-3} alkyl, and $\text{Si}(\text{R}^7)_3$ (wherein each of the plurality of R^7 groups is independently selected from the hydrogen atom and C_{1-3} alkyl));

R^4 and R^5 are each independently selected from the hydrogen atom, C_{1-3} alkyl, and $\text{Si}(\text{R}^8)_3$ (wherein each of the plurality of R^8 groups is independently selected from the hydrogen atom, C_{1-3} alkyl, and $\text{NHSi}(\text{R}^9)_3$ (wherein each of the plurality of R^9 groups is independently selected from the hydrogen atom and C_{1-3} alkyl)); and

the value of (the number of carbon atoms in the preceding general formula)/(number of silicon atoms in the preceding general formula) is no more than 7.

A high dielectric constant film is formed in this film formation method using a silicon-containing compound, as represented by the aforementioned general formula, that contains the Si-N bond. This results in an improved film formability on the substrate and an improved component reliability.

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The inventive method for fabricating a semiconductor device comprises the steps of

forming a high dielectric constant film comprising metal silicate on a silicon substrate;

10 forming a polycrystalline silicon film on the aforesaid high dielectric constant film; and

forming a gate electrode by selectively removing the high dielectric constant film and the polycrystalline silicon film,

wherein the aforesaid step of forming a high dielectric constant film is carried out

15 by the film-forming method described above.

This method for fabricating semiconductor devices, because it employs a silicon-containing compound with the general formula given above to form a high dielectric constant film, provides a reduced concentration of impurities, e.g., carbon, in the high dielectric constant film. This, in turn, can provide a semiconductor device with a lower leakage current. Moreover, the film formability is improved by forming the high dielectric constant film using a silicon-containing compound that contains the Si-N bond. These features make it possible to provide semiconductor devices with an improved reliability.

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Effects of the Invention

The present invention provides a method for forming high dielectric constant films that exhibits an improved film formability and an improved component reliability.

The present invention also provides a method for fabricating a semiconductor device that is provided

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with a high dielectric constant film that provides a reduced leakage current and an improved film formability.

Best Mode for Carrying Out the Invention

5 An embodiment of the present invention is described herebelow with reference to the drawings. A structural element that is the same in all the drawings has been assigned the same reference symbol in all the drawings, and the description thereof has been omitted as appropriate.

10 Figure 1 is a cross-sectional diagram that shows an example of the structure of an MOS transistor as the semiconductor device considered in the instant embodiment. Figures 2 through 4 are cross-sectional process diagrams that show a method for fabricating this semiconductor device. The description that follows takes up the example of a p-channel MOS transistor.

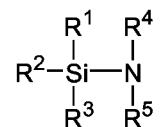
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As shown in the semiconductor device in Figure 1, an n-well region **2** is formed in a p-type silicon substrate **1**, and p-channel MOS transistor-forming regions are partitioned out by an element-isolating trench structure **4** known as shallow trench isolation or STI. The STI **4** is a structure in which a silicon oxide film **6** is embedded
20 in a trench formed in the surface of the silicon substrate **1**. A gate electrode is constructed by stacking an oxide film **16**, a high dielectric constant film **17**, and a polysilicon film **22** in the sequence given on the surface of the silicon substrate **1** in the p-channel MOS transistor-forming region. The high dielectric constant film **17** is formed by stacking a first high dielectric constant film **18** and a second high
25 dielectric constant film **20** in the sequence given. Side walls **26**, with an approximately fan-shaped cross section, are formed on the sides of the gate electrode. In addition, extension regions **24** (regions in which p-type impurity has been introduced at low concentrations) and source · drain regions **28** (regions in which p-type impurity has been introduced at high concentrations) are formed in
30 the silicon substrate **1** in the p-channel MOS transistor-forming region, thereby forming a p-channel MOS transistor. An interlayer dielectric film **30** is formed as a

coating over the p-channel MOS transistor-forming region, and a contact layer **32** is formed in contact holes formed in the interlayer dielectric film **30**. The contact layer **32** is electrically connected to the source · drain regions **28**.

- 5 The following method for forming a high dielectric constant film is used in the method of the instant embodiment for fabricating a semiconductor device.

The method for forming the high dielectric constant film in the instant embodiment forms a high dielectric constant film comprising metal silicate on the substrate by
 10 atomic layer deposition using the gas of a metal-containing compound and the gas of a silicon-containing compound represented by the general formula



wherein

- R^1 , R^2 , and R^3 in the preceding general formula are each independently
 15 selected from the hydrogen atom, C_{1-3} alkyl, and $\text{N}(\text{R}^6)_2$ (wherein each of the plurality of R^6 groups is independently selected from the hydrogen atom, C_{1-3} alkyl, and $\text{Si}(\text{R}^7)_3$ (wherein each of the plurality of R^7 groups is independently selected from the hydrogen atom and C_{1-3} alkyl));
- R^4 and R^5 are each independently selected from the hydrogen atom, C_{1-3}
 20 alkyl, and $\text{Si}(\text{R}^8)_3$ (wherein each of the plurality of R^8 groups is independently selected from the hydrogen atom, C_{1-3} alkyl, and $\text{NHSi}(\text{R}^9)_3$ (wherein each of the plurality of R^9 groups is independently selected from the hydrogen atom and C_{1-3} alkyl)); and
- the value of (the number of carbon atoms in the preceding general
 25 formula)/(number of silicon atoms in the preceding general formula) is no more than 7.

This film-forming method provides an improved film formability and an improved component reliability due to its use of the Si–N bond-containing silicon compound with the general formula given above to form the high dielectric constant film.

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The method of the instant embodiment for fabricating a semiconductor device using this method for producing a high dielectric constant film is described herebelow with reference to Figures 2 to 4.

10 The method of the instant embodiment for fabricating a semiconductor device can be carried out by the following steps:

- (1) a step in which a high dielectric constant film **17** comprising metal silicate is formed on the silicon substrate **1** using the film-forming method described in the preceding (Figures 2(b) to 3(c));
- 15 (2) a step in which a polycrystalline silicon film **14** is formed on the high dielectric constant film **17** (Figure 3(d)); and
- (3) a step in which a gate electrode is formed by selectively removing the high dielectric constant film **17** and the polycrystalline silicon film **14** (Figures 4(e) to (h)).

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A step in which a silicon oxide film is formed on the surface of the silicon substrate (Figures 2(a) to (b)) can also be carried out prior to the step in which the high dielectric constant film **17** is formed.

25 First, as shown in Figure 2(a), an n-well region **2** is formed in the p-type silicon substrate **1** and shallow trenches are also formed in the element-isolating regions of the p-type silicon substrate **1**. A silicon oxide film **6** is then embedded within the trenches to form the STI **4**. This silicon oxide film **6** can be embedded, for example, by the following procedure: a silicon oxide film **6** is formed on the surface of the
30 silicon substrate **1** in such a manner that it fills into the trench and the silicon oxide film **6** is then etched back, for example, by chemical mechanical polishing (CMP),

to expose the surface of the silicon substrate **1** while leaving the silicon oxide film **6** within the trench.

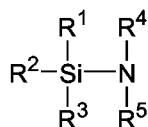
5 The surface of the silicon substrate **1** is then cleaned and treated with dilute hydrofluoric acid (DHF), after which an approximately 0.5 nm-thick silicon oxide film **8** is formed on the surface of the silicon substrate **1**. A first high dielectric constant film **10** is then formed on the surface of the silicon oxide film **8** (Figure 2(b)). The formation of the silicon oxide film **8** makes it possible to prevent the diffusion of the metal element in the first high dielectric constant film **10** into the
10 silicon substrate **1**.

This first high dielectric constant film **10** is provided by forming a high dielectric constant film comprising metal silicate on the silicon substrate **1** by atomic layer deposition. More specifically, operating within an ALD device, metal oxide is
15 deposited on the silicon substrate **1** by feeding a gas of a metal-containing compound onto the silicon substrate **1** and thereafter feeding an oxidizing gas onto the silicon substrate **1** (first step). Silicon oxide is then deposited on the silicon substrate **1** by feeding a gas of a silicon-containing compound onto the silicon substrate and thereafter feeding an oxidizing gas onto the silicon substrate (second
20 step). Repetition of these first and second steps results in the formation on the surface of the silicon substrate **1** of the first high dielectric constant film **10** comprising metal silicate composed of metal, oxygen, and silicon. That is, the first high dielectric constant film **10** is formed by the sequential deposition of metal oxide and silicon oxide. The thickness of the first high dielectric constant film **10**
25 can be from 0.5 nm to 3 nm. The oxidizing gas can be, for example, ozone or an oxygen-containing gas.

The metal element in the metal-containing compound used to form the first high dielectric constant film **10** can be exemplified by hafnium (Hf), zirconium (Zr),
30 tantalum (Ta), scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium

(Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), ytterbium (Yb), and lutetium (Lu), and one or more selections from the preceding can be used. Hafnium (Hf) or zirconium (Zr) is preferably used in the instant embodiment as the metal element in the metal-containing compound. The metal-containing compound itself can be specifically exemplified by tetramethylethylamidohafnium ($\text{Hf}(\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5))_4$), tetradimethylamidohafnium ($\text{Hf}(\text{N}(\text{CH}_3)_2)_4$), and tetraethylnamidohafnium ($\text{Hf}(\text{N}(\text{C}_2\text{H}_5)_2)_4$).

The silicon-containing compound is represented by the general formula



wherein

R^1 , R^2 , and R^3 in the preceding general formula are each independently selected from the hydrogen atom, C_{1-3} alkyl, and $\text{N}(\text{R}^6)_2$ (wherein each of the plurality of R^6 groups is independently selected from the hydrogen atom, C_{1-3} alkyl, and $\text{Si}(\text{R}^7)_3$ (wherein each of the plurality of R^7 groups is independently selected from the hydrogen atom and C_{1-3} alkyl));

R^4 and R^5 are each independently selected from the hydrogen atom, C_{1-3} alkyl, and $\text{Si}(\text{R}^8)_3$ (wherein each of the plurality of R^8 groups is independently selected from the hydrogen atom, C_{1-3} alkyl, and $\text{NHSi}(\text{R}^9)_3$ (wherein each of the plurality of R^9 groups is independently selected from the hydrogen atom and C_{1-3} alkyl)); and

the value of (the number of carbon atoms in the preceding general formula)/(number of silicon atoms in the preceding general formula) is no more than 7.

Among silicon-containing compounds defined by the preceding general formula, the use is preferred of silicon-containing compounds in which R^1 , R^2 , and R^3 are each independently selected from the hydrogen atom, methyl, $N(CH_3)_2$, and $NHSi(CH_3)_3$ and R^4 and R^5 are each independently selected from the hydrogen atom, methyl, SiH_3 , $Si(CH_3)_3$, and $NHSi(CH_3)_3$.

The concentration of impurities, such as carbon, in the high dielectric constant film 17 can be reduced because the value of (number of carbon atoms)/(number of Si atoms) is set at no greater than 7 for silicon-containing compounds with the preceding general formula. Furthermore, the film formability of the high dielectric constant film 17 is improved because the silicon-containing compound has a structure that contains the Si-N bond. As a consequence, the generation of leakage current is inhibited in the semiconductor device provided with the high dielectric constant film 17 and the device reliability is improved.

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The silicon-containing compound can be specifically exemplified by $(SiH_3)_3N$ (trisilylamine or TSA, melting point = $-106^\circ C$, boiling point = $52^\circ C$), $SiH_2(N(CH_3)_2)_2$ (bisdimethylaminosilane or BDMAS, melting point = $-104^\circ C$, boiling point = $93^\circ C$), $SiH(N(CH_3)_2)_3$ (tridimethylaminosilane or TDMAS, melting point = $-90^\circ C$, boiling point = $145^\circ C$), and $SiH_2(NHSi(CH_3)_3)_2$ (bis(trimethylsilyl)aminosilane or BITS, melting point = $28^\circ C$, boiling point = $40^\circ C$), and one or more selections from the preceding can be used. The use of these silicon-containing compounds provides even better outcomes and can efficiently inhibit leakage current generation and can yield additional improvements in reliability. $(SiH_3)_3N$, $SiH_2(N(CH_3)_2)_2$, and $SiH(N(CH_3)_2)_3$ are more preferred as the silicon-containing compound, and $(SiH_3)_3N$ is particularly preferred for the silicon-containing compound. Since $(SiH_3)_3N$ lacks carbon, it provides a particularly good reduction in the concentration of impurities such as carbon in the high dielectric

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constant film, resulting in a particularly strong inhibition of leakage current generation. Furthermore, because it has a structure that includes the Si-N bond, it also provides an excellent film formability with respect to substrate. $(\text{SiH}_3)_3\text{N}$ (trisilylamine or TSA) thus provides excellent balance between leakage current
5 inhibition and better film formability.

Formation of the first high dielectric constant film **10** as described above may be followed by a densification treatment of the first high dielectric constant film **10**. The densification treatment procedure can use, for example, nitrogen gas or a gas
10 afforded by the addition of a very small amount of oxygen gas to nitrogen gas, and can be carried out as a rapid heat treatment by ramp annealing at heat treatment times from 1 to 60 seconds and heat treatment temperatures from 700°C to 1050°C. The densification treatment procedure may also be carried out as a rapid heat treatment by flash ramp annealing at heat treatment times from 0.3
15 millisecond to 100 milliseconds.

A second high dielectric constant film **12** is then formed on the surface of the first high dielectric constant film **10** (Figure 3(c)). More specifically, a second high dielectric constant film **12**, comprising metal silicate composed of metal, oxygen,
20 and silicon, is formed by atomic layer deposition. The metal element in the second high dielectric constant film **12** is the same as that constituting the first high dielectric constant film **10**, and the use of hafnium (Hf) or zirconium (Zr) is particularly preferred. The second high dielectric constant film **12** is formed in such a manner that the (metal element)/(metal element + Si) ratio is no greater than 0.6.
25 It is believed that reaction between the second high dielectric constant film **12** and the polycrystalline silicon film **14**, vide infra, can be inhibited by this measure and the generation of leakage current can thereby be inhibited. The second high dielectric constant film **12** can be formed in a thickness of about 0.5 nm.

30 The second high dielectric constant film **12** may also be a metal silicate composed of metal, oxygen, silicon, and nitrogen. In this case, the nitrogen peak

concentration in the second high dielectric constant film **12** can be from 10 to 30 atomic%. When the nitrogen peak value is less than this value, densification of the second high dielectric constant film **12** will be inadequate and the diffusion into the first high dielectric constant film **10** of impurities, such as phosphorus or boron, that have been introduced into the polysilicon during gate electrode formation cannot be adequately prevented during the activating heat treatment. After the second high dielectric constant film **12** has been formed, it is subjected to a densification treatment just as for the first high dielectric constant film **10**.

The formation of the second high dielectric constant film **12** is followed by the formation of a polycrystalline silicon film **14** on the surface of the second high dielectric constant film **12** and by ion implantation into the polycrystalline silicon film **14** (Figure 3(d)). Boron (B) is ion-implanted in the example under consideration due to the formation of the n-well region **2**. Phosphorus (P) is ion-implanted when a p-well region is formed.

A photoresist mask is then formed by forming a photoresist film (not shown) on the surface of the polycrystalline silicon film **14**, exposing the gate electrode pattern, and development. Etching using the photoresist mask as the mask then gives a gate electrode in which the silicon oxide film **16**, first high dielectric constant film **18**, second high dielectric constant film **20**, and polysilicon film **22** are stacked in the sequence given (Figure 4(e)). This etch is followed by removal of the photoresist mask. Then, using the gate electrode as the mask, low-concentration ion implantation is carried out on the surface of the silicon substrate **1** to form self-aligned extension regions **24**. Boron (B) is ion-implanted in the n-well region **2** in the embodiment under consideration. Arsenic (As) is ion-implanted in the case of a p-well region.

A silicon nitride film is then formed in a desired thickness so as to cover the surface of the silicon substrate **1**, and this silicon nitride film is etched back by anisotropic

etching. As a result, the silicon nitride film remains only at the side surfaces of the gate electrode, forming the side wall **26** (Figure 4(f)).

Ion implantation is then carried out using the gate electrode and side walls **26** as the mask, thereby forming self-aligned source · drain regions **28** in the surface of the silicon substrate **1**. In the embodiment under consideration, boron (B) is ion-implanted in the n-well region **2**. Arsenic (As) is ion-implanted in the case of a p-well region (Figure 4(g)).

After formation of the source · drain regions **28**, the silicon substrate **1** is submitted to a fast heat treatment using ramp annealing. This ramp anneal activates the polysilicon film **22**, extension region **24**, and source · drain region **28**. The temperature in this activating heat treatment is at least 10°C lower than the temperature of the densification treatment that follows formation of the first high dielectric constant film **10** and second high dielectric constant film **12**. A p-channel MOS transistor is formed by the preceding steps. An interlayer dielectric film **30** is then formed covering the silicon substrate **1** and electrically conductive material is embedded in contact holes opened in the interlayer dielectric film **30** to form a contact layer **32** for electrical connection to the source region and drain region, thereby producing a semiconductor device that has the MOS transistor structure shown in Figure 1.

The advantageous effects of this embodiment are described below.

Improvement in the film formability on the substrate has been desired of the metal silicate films afforded by prior-art ALD, for example, the metal silicate film formed by the silicon-containing compound described in Patent Reference 3. Problems with film formability on the substrate surface have existed even with SiH₄ (monosilane).

The inventors carried out focused investigations in view of these circumstances in order to improve the film formability by metal silicate films on the substrate surface and discovered as a result that film formability on the substrate could be efficiently improved by using a silicon-containing compound (silicon source) that has a specific structure. More specifically, the inventors discovered that the use of a silicon-containing compound containing the Si-N bond can provide a semiconductor device that exhibits an excellent film formability on the substrate and an improved reliability. This improvement in film formability on the substrate and in addition the above-described inhibition of leakage current generation are manifested through the use of $(\text{SiH}_3)_3\text{N}$, $\text{SiH}_2(\text{N}(\text{CH}_3)_2)_2$, or $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$, while a good balance is manifested in particular by the use of $(\text{SiH}_3)_3\text{N}$.

A semiconductor device is fabricated in the instant embodiment by forming a high dielectric constant film on a silicon substrate using a silicon-containing compound with the general formula given above. A semiconductor device is therefore provided that exhibits reduced levels of impurities, such as carbon, in the high dielectric constant film and thus a reduced leakage current and an improved reliability.

The $\text{Si}(\text{OC}_2\text{H}_5)_4$ (tetraethoxysilane or TEOS) heretofore generally used as the silicon-containing compound has a value for (number of carbon atoms)/(number of silicon atoms) of 8. This results in a high concentration of impurity (carbon) in the high dielectric constant film and hence in the generation of leakage current.

In contrast to this, the silicon-containing compounds used in the instant embodiment have a value for (number of carbon atoms)/(number of silicon atoms) of no greater than 7. This can efficiently lower the impurity (carbon) concentration in the high dielectric constant film and as a consequence can inhibit the generation of leakage current. Among the silicon-containing compounds specified above,

these effects are manifested in particular by the use of the carbon-free $(\text{SiH}_3)_3\text{N}$ (trisilylamine (TSA)).

While the preceding embodiment of the present invention has been described with
5 reference to the drawings, this is an example of the present invention and various structures other than this structure can also be employed.

For example, the high dielectric constant film **17** is described in the instant
embodiment in terms of a two-layer structure, but it need merely be formed of one
10 or more layers and thus may be a stacked structure of three or more layers.

In addition, the high dielectric constant film **17** can be formed by one layer as long
as the (metal element)/(metal element + Si) ratio of the high dielectric constant film
is no greater than 0.6.

15 Moreover, the preceding example concerns the formation of a high dielectric constant film **17** on the surface of the silicon substrate **1** with a silicon oxide film **16** therebetween, but the high dielectric constant film **17** may also be formed directly on the surface of the silicon substrate **1**.

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Examples

The following silicon-containing compounds were used in the examples provided below.

25 Silicon-containing compounds

- $(\text{SiH}_3)_3\text{N}$ (trisilylamine or TSA, melting point = -106°C , boiling point = 52°C)
- $\text{SiH}_2(\text{N}(\text{CH}_3)_2)_2$ (bisdimethylaminosilane or BDMAS, melting point = -104°C , boiling point = 93°C)
- $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$ (tridimethylaminosilane or TDMAS, melting point = -90°C ,
30 boiling point = 145°C)

Vapor pressure curves for these silicon-containing compounds are reported in Figure 5. $\text{Si}(\text{OC}_2\text{H}_5)_4$ (tetraethoxysilane or TEOS), which is in wide use as a silicon-containing compound, is also reported for reference. Figure 5 shows that TSA, BDMAS, and TDMAS have higher vapor pressures than TEOS and thus are easy to handle. TSA in particular offers a number of advantages, i.e., it has a very high vapor pressure and gas feed from an ordinary cylinder is possible and it is also free of carbon.

10 Test Example 1

The relationship between SiO_2 film thickness and number of cycles was verified using TDMAS, BDMAS, and TSA as the silicon-containing compounds. The results are reported in Figure 6. Specifically, a silicon oxide film was formed by depositing SiO_2 on the surface of a silicon substrate **1** by admitting the silicon-containing compound into the chamber and feeding it onto the silicon substrate **1** and by thereafter introducing ozone gas into the chamber. This was carried out at a substrate temperature of 275°C . The process of forming silicon oxide film with a thickness of about 0.08 nm was set up as one cycle.

When TDMAS was used as the silicon source, the interior chamber pressure was held at 5.0 torr in order to secure a film formation rate of about 0.08 nm/cycle. It is thought that this was due to a greater difficulty in adsorption to the silicon substrate due to the lower vapor pressure as compared to the other silicon sources. When, on the other hand, BDMAS was used as the silicon source, the interior chamber pressure was held at 2.0 torr to obtain a film formation rate that was about the same as for TDMAS. The interior chamber pressure was held at 0.5 torr with TSA to obtain about the same film formation rate. Thus, pressure control for the individual silicon sources is necessary in order to bring the film formation rate to 0.08 nm/cycle.

These results confirmed that the use of TDMAS, BDMAS, and TSA as the silicon-containing compound provided an excellent film formability on the surface of silicon substrate.

5 Test Example 2

High dielectric constant films (Hf silicate film) were formed according to the method of the hereinabove described embodiment, using tetramethylethylamidohafnium ($\text{Hf}(\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5))_4$) as the metal compound and using TDMAS, BDMAS, or TSA as the silicon-containing compound. Figure 7 reports the Hf composition ratio ($\text{Hf}/(\text{Hf} + \text{Si})$) in the Hf silicate film as a function of $\text{Hf}/(\text{Hf} + \text{Si})$ in the starting material. The interior chamber pressure was changed as a function of the starting material used, and was 0.5 torr for TSA, 2.0 torr for BDMAS, and 5.0 torr for TDMAS. A substrate temperature of 275°C was used.

Figure 7 shows that the composition of the Hf silicate film could be very well controlled through the $\text{Hf}/(\text{Hf} + \text{Si})$ ratio of the starting material, and it was also confirmed that the $\text{Hf}/(\text{Hf} + \text{Si})$ composition ratio of the Hf silicate film could be controlled over a broad range from 0 to 100%. In addition, it was confirmed that the $\text{Hf}/(\text{Hf} + \text{Si})$ ratio for the individual silicon sources and the $\text{Hf}/(\text{Hf} + \text{Si})$ composition ratio were controlled at the same level due to having made the SiO_2 film formation rate about the same for the individual silicon sources.

Example 1

A semiconductor device was fabricated according to the method of the hereinabove described embodiment using tetramethylethylamidohafnium as the metal compound and TDMAS as the silicon-containing compound. The first high dielectric constant film **10** was about 2 nm thick and the second high dielectric constant film **12** was about 0.5 nm thick. The carbon (C) and hydrogen (H) concentrations in the high dielectric constant film (Hf silicate film) **17** were measured by secondary ion-microprobe spectrometric (SIMS) analysis. Figure 8(a) reports the concentration profile into the silicon substrate **1** from the surface of the

Hf silicate film. Figure 8(a) shows that the carbon concentration in the Hf silicate film was about $3 \times 10^{20} \text{ cm}^{-3}$ for the use of TDMAS as the silicon source.

Example 2

- 5 A semiconductor device was fabricated as described in Example 1, except that in this case BDMAS was used as the silicon-containing compound. Figure 8(b) reports the concentration profile into the silicon substrate 1 from the surface of the Hf silicate film. Figure 8(b) shows that the carbon concentration in the Hf silicate film was about $1 \times 10^{20} \text{ cm}^{-3}$ for the use of BDMAS.

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Example 3

- A semiconductor device was fabricated as described in Example 1, except that in this case TSA was used as the silicon-containing compound. Figure 8(c) reports the concentration profile into the silicon substrate 1 from the surface of the Hf silicate film. Figure 8(c) shows that the carbon concentration in the Hf silicate film was about $3 \times 10^{19} \text{ cm}^{-3}$ for the use of TSA.

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- These results demonstrated that the use of TDMAS, BDMAS, or TSA as the silicon-containing compound provides a significant reduction in the impurity (e.g., carbon) concentration in a high dielectric constant film (Hf silicate film) from that for TEOS. The use of these silicon-containing compounds to form high dielectric constant films on a silicon substrate therefore enables a reduction in leakage current in the semiconductor device. In addition, it was shown that the carbon concentration in high dielectric constant films can be controlled by the selection of these silicon-containing compounds.

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Brief Description of the Drawings

Figure 1 is a schematic cross-sectional diagram of a semiconductor device fabricated by the method of fabrication in the herein described embodiment.

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Figure 2 is a process diagram in cross section that illustrates the method of fabricating a semiconductor device in the herein described embodiment.

Figure 3 is a process diagram in cross section that illustrates the method of fabricating a semiconductor device in the herein described embodiment.

Figure 4 is a process diagram in cross section that illustrates the method of fabricating a semiconductor device in the herein described embodiment.

Figure 5 is a graph that shows the vapor pressure curves of the silicon-containing compounds used in the examples.

Figure 6 is a graph that shows the relationship between film thickness and number of cycles for the case in which the process of forming a silicon oxide film with a film thickness of about 0.08 nm was set up as one cycle.

Figure 7 is a graph showing the relationship between the Hf/(Hf + Si) ratio of the starting material and the Hf/(Hf + Si) composition ratio of the Hf silicate film.

Figure 8 is a graph that shows the carbon (C) and hydrogen (H) concentration profiles in Hf silicate film.

Reference symbols

	1		silicon substrate
25	2		n-well region
	4		STI
	6		silicon oxide film
	8		silicon oxide film
	10		first high dielectric constant film
30	12		second high dielectric constant film
	14		polycrystalline silicon film

	16		silicon oxide film
	17		high dielectric constant film
	18		first high dielectric constant film
	20		second high dielectric constant film
5	22		polysilicon film
	24		extension region
	26		side wall
	28		source · drain region
	30		interlayer dielectric film
10	32		contact layer

CLAIMS

Claim 1.

- 5 A method of forming a high dielectric constant film, wherein a high dielectric constant film comprising metal silicate is formed on a substrate by atomic layer deposition using the gas of a metal-containing compound and the gas of a silicon-containing compound represented by the general formula



wherein

- 15 R^1 , R^2 , and R^3 in the preceding general formula are each independently selected from the hydrogen atom, C_{1-3} alkyl, and $\text{N}(\text{R}^6)_2$ (wherein each of the plurality of R^6 groups is independently selected from the hydrogen atom, C_{1-3} alkyl, and $\text{Si}(\text{R}^7)_3$ (wherein each of the plurality of R^7 groups is independently selected from the hydrogen atom and C_{1-3} alkyl));
- 20 R^4 and R^5 are each independently selected from the hydrogen atom, C_{1-3} alkyl, and $\text{Si}(\text{R}^8)_3$ (wherein each of the plurality of R^8 groups is independently selected from the hydrogen atom, C_{1-3} alkyl, and $\text{NHSi}(\text{R}^9)_3$ (wherein each of the plurality of R^9 groups is independently selected from the hydrogen atom and C_{1-3} alkyl)); and
- 25 the value of (the number of carbon atoms in the preceding general formula)/(number of silicon atoms in the preceding general formula) is no more than 7.

Claim 2.

A method of fabricating a semiconductor device, comprising the steps of

forming a high dielectric constant film comprising metal silicate on a silicon substrate;

5 forming a polycrystalline silicon film on the aforesaid high dielectric constant film; and

forming a gate electrode by selectively removing the high dielectric constant film and the polycrystalline silicon film,

wherein the aforesaid step of forming a high dielectric constant film is carried out
10 by the film-forming method according to claim 1.

Claim 3.

The method according to claim 2 of fabricating a semiconductor device, wherein R^1 , R^2 , and R^3 in the preceding general formula are each independently selected

15 from the hydrogen atom, methyl, $N(CH_3)_2$, and $NHSi(CH_3)_3$, and R^4 and R^5 are each independently selected from the hydrogen atom, methyl, SiH_3 , $Si(CH_3)_3$, and $NHSi(CH_3)_3$.

Claim 4.

20 The method according to claim 2 or 3 of fabricating a semiconductor device, wherein the compound with the aforementioned general formula is at least one selection from the group consisting of $(SiH_3)_3N$, $SiH_2(N(CH_3)_2)_2$, $SiH(N(CH_3)_2)_3$, and $SiH_2(NHSi(CH_3)_3)_2$.

25 Claim 5.

The method according to claim 2 or 3 of fabricating a semiconductor device, wherein the compound with the aforementioned general formula is $(SiH_3)_3N$.

Claim 6.

The method according to claim 2 or 3 of fabricating a semiconductor device, wherein the compound with the aforementioned general formula is $\text{SiH}_2(\text{N}(\text{CH}_3)_2)_2$.

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Claim 7.

The method according to claim 2 or 3 of fabricating a semiconductor device, wherein the compound with the aforementioned general formula is $\text{SiH}(\text{N}(\text{CH}_3)_2)_3$.

10 Claim 8.

The method according to any of claims 2-7 of fabricating a semiconductor device, wherein the metal/(metal + Si) composition ratio of the high dielectric constant film is no greater than 0.6 in at least the upper region of the high dielectric constant film.

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Claim 9.

The method according to any of claims 2 to 8 of fabricating a semiconductor device, wherein the aforementioned step of forming the high dielectric constant film comprises

20 a step of forming, by atomic layer deposition, a first high dielectric constant film comprising metal silicate on the aforementioned silicon substrate; and

a step of layering, on the surface of the first high dielectric constant film, a second high dielectric constant film that has a metal/(metal + Si) composition ratio no greater than 0.6.

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Claim 10.

The method according to any of claims 2 to 9 of fabricating a semiconductor device, wherein the metal comprises Hf or Zr.

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Claim 11.

The method according to any of claims 2 to 10 of fabricating a semiconductor device, wherein

a step of forming a silicon oxide film on the surface of the silicon substrate is carried out before the aforementioned step of forming the high dielectric constant film, and

the step of forming the high dielectric constant film is a step of forming, by atomic layer deposition, a high dielectric constant film comprising metal silicate on the aforesaid silicon oxide film on the surface of the silicon substrate.

Claim 12.

The method according to any of claims 2 to 10 of fabricating a semiconductor device, wherein the step of forming the high dielectric constant film by atomic layer deposition is a step of forming a high dielectric constant film comprising metal silicate on the silicon substrate by repetitively carrying out the steps of

depositing a metal oxide on the silicon substrate by feeding a gas of a metal-containing compound onto the silicon substrate and subsequently feeding an oxidizing gas onto the silicon substrate; and

depositing silicon oxide on the silicon substrate by feeding a gas of a silicon-containing compound onto the silicon substrate and subsequently feeding an oxidizing gas onto the silicon substrate.