Description

The present invention relates to a method of manufacturing a silicon nitride film.

Conventionally, silicon nitride (Si_XN_Y) is a solid and chemically inert dielectric material having a very high hardness, a low thermal conductivity, and high resistance to molecular diffusion. Due to these properties, silicon nitride is used as an oxidation mask, a gate insulating film, a passivation film, or the like in, e.g., the manufacture of a semiconductor device. A method of forming a silicon nitride film on a substrate, e.g., the surface of a semiconductor substrate is disclosed in Published Examined Japanese Patent Application No. 60-10108. According to this method, a substrate is arranged in a reaction tube, a gas mixture of dichlorosilane and ammonia flows in the reaction tube, and the substrate is brought into contact with the gas mixture at a low pressure and a high temperature of 700°C to deposit a silicon nitride film on the substrate by thermal decomposition. The reaction of dichlorosilane and ammonia is given by the following formula:

$$3SiH_2C\ell_2 + 4NH_3 \rightarrow Si_3N_4 + 6HC\ell + 6H_2$$

In order to obtain a high growth rate of a film, uniform deposition, and a high-quality film in an economical process, ammonia must flow in the reaction tube at a gas flow rate five times that of dichlorosilane.

However, since excessive ammonia flows in the reaction tube, non-reacted ammonia remains in the reaction tube. As is apparent from the above reaction formula, hydrochloric acid produced as a reaction product is reacted with the excessive ammonia to produce ammonium chloride. Although ammonium chloride is not solidified at a temperature of 150°C or more, ammonium chloride is deposited in a solid state at a temperature of less than 150°C. For this reason, since portions in the reaction tube or tubes coupled thereto have a temperature of less than 150°C, e.g., portions located on a downstream side from gas supply and exhaust ports in a normal low-pressure CVD (Chemical Vapor Deposition) furnace have a temperature of 150°C or less, ammonium chloride is deposited on these portions. The ammonium chloride deposited as described above is removed from the inner wall of the reaction tube when the pressure in the reaction tube is changed from the atmospheric-pressure state to a low-pressure state or changed from the low-pressure state to the atmospheric-pressure state, and the ammonium chloride is present as particles in the reaction tube. Therefore, the particles are attached on the substrate surface. In addition, when ammonium chloride is attached on a metal portion exposed to the reaction region and having a relatively low temperature of 150°C or less, the metal portion on which the ammonium chloride is attached is corroded by moisture remaining in the reaction tube due to loading or unloading of the substrate. For this reason, the reaction tube must be periodically washed or heated to remove ammonium chloride.

In order to prevent deposition of ammonium chloride, silane (SiH_4) may be used in place of dichlorosilane. In this case, however, since it is difficult to control a deposition speed of silicon nitride, the thickness of a silicon nitride film formed on the surface of the substrate is difficult to uniformize. For example, a thicknesses distribution of a silicon nitride film is not uniform in each wafer, or silicon nitride films having the same thickness cannot be obtained on a plurality of wafers.

The present invention has been made in consideration of the above problem, and has as its object to provide a method of manufacturing a silicon nitride film.

This object is achieved according to independent claim 1. Preferred embodiments are listed in the dependent claims. According to this method, when a silicon nitride film is formed on a substrate surface, ammonium chloride is not produced. For this reason, even when the pressure in a reaction tube is changed, ammonium nitride particles are not attached on the silicon nitride film formed on the substrate surface, and a metal portion such as a reaction vessel is not corroded because no ammonium nitride is attached on the metal portion. In addition, the thickness of the silicon nitride film formed on the substrate surface can be uniformed.

In addition, in deposition of silicon nitride, since a gas decomposing means such as a combination of mixing of ammonia or nitrogen, heating, production of a plasma, or excitation by a radiation beam is also used, the films can be further effectively formed.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a schematic view showing a low-pressure CVD device for performing a method of manufacturing a silicon nitride film according to the first embodiment of the present invention; and

Fig. 2 is a schematic view showing a low-pressure CVD device for performing a method of manufacturing a silicon nitride film according to the second embodiment of the present invention.

An embodiment of the present invention will be described below. Fig. 1 is a schematic view showing a low-pressure CVD device for performing the first embodiment of the present invention. Referring to Fig. 1, reference numeral 1 denotes a vertical tubular furnace for constituting a reaction tube. Substrates, a plurality of semiconductor wafers 2 each having a diameter of 6" are arranged in the reaction tube, the pressure of which is decreased to a predetermined pressure. A heater 3 is mounted on the outer wall of the reaction tube to heat the inside of the reaction tube to a desired temperature. An exhaust port 4 coupled to a vacuum pump (not shown) for exhausting air

from the furnace to decrease the pressure thereof is formed in the upper portion of the tubular furnace 1. A first gas supply tube 5 for supplying an organic compound gas containing silicon and an amine group, e.g., $Si(N(CH_3)_2)_4$, to the inside of the tubular furnace 1 and a second gas supply tube 6 for supplying ammonia (NH_3) to the inside of the tubular furnace 1 extend through the outer wall of the tubular furnace 1 such that one end of each of the supply tubes 5 and 6 is open to the inside of the tubular furnace 1. A baking tank 10 for supplying an organic compound gas is coupled to the other end of the first gas supply tube 5. The baking tank 10 is obtained such that a first valve 7 for opening/closing the gas flow path, a first gas flow rate controller for adjusting the gas flow rate, and a gas generator for generating the organic compound gas are coupled to the first gas supply tube 5 toward the upperstream of the supply tube 5. A second valve 11 for opening/closing a gas flow path, a second gas flow rate controller 12 for adjusting the gas flow rate, and a second gas source 13 for supplying ammonia are arranged to the other end of the second gas supply tube 6. Each of the plurality of semiconductor wafers 2 arranged in the tubular furnace 1 is horizontally held in each of a plurality of shelf portions of a quartz boat 14 provided in the furnace 1 so as to have a space for circulating a gas between the semiconductor wafers 2. The heater 3 is uniformly mounted on the outer wall of the tubular furnace 1 to keep the temperature of the outer wall constant and to minimize local differences in temperature in the tubular furnace 1. The intervals between the shelf portions for arranging the semiconductor wafers 2 are not necessarily equal to each other, and the semiconductor wafers 2 are preferably arranged according to the relationship between the concentration, volume, and temperature of a flowing gas. Although not shown or described, the temperature and pressure in the tubular furnace 1 are measured by a general-purpose means, i.e., a thermometer and a vacuum gauge, and a control means having an adjuster for adjusting the measurement value within a predetermined range in the furnace 1, thereby keeping the temperature and pressure in the furnace 1 at desired values.

A process for manufacturing a silicon nitride film on a semiconductor wafer in a method of manufacturing a silicon nitride film according to the present invention using the above arrangement will be described below. The plurality of semiconductor wafers 2 were horizontally set one by one on the shelf portions of the boat 14 arranged in the tubular furnace 1. That is, the wafers were set such that the wafer surfaces were perpendicular to a gas flow. The temperature in the tubular furnace 1 was kept at a temperature of 700°C using the heater 3 arranged on the outer wall of the furnace. The pressure in the furnace was kept at a pressure of 0.5 Torr (1 Torr = 133.3 Pa) by driving the vacuum pump (not shown), and an organic compound gas, i.e., a vapor of $Si(N(CH_3)_2)_4$ was generated from the gas generator 8 of the baking tank 10. The valve 7 was open while the gas flow rate was controlled by the first gas flow rate controller 9, thereby supplying the organic compound gas at a flow rate of 100 SCCM. At the same time, the second valve 11 was open while a gas flow rate was adjusted by the second gas flow rate controller 12 to supply ammonia from the second gas source 13 to the furnace at a flow rate of 1,000 SCCM. The temperature and pressure in the tubular furnace 1 were kept as described above, and the two types of gases were continuously supplied to the inside of the furnace for 60 minutes. The first and second valves were closed. Thereafter, the semiconductor wafers 2 were removed from the furnace. When a deposition state of a silicon nitride film on the surface of each of the removed semiconductor wafers 2 was checked, a silicon nitride film having a thickness of 600 Å was formed. The silicon nitride film was deposited on each wafer to have a uniform thickness, and the uniformity of the nitride films of the wafers at arbitrary positions in the same furnace was held within ±5%.

Upon completion of the film formation step, when deposits in the furnace and the tubes of the exhausting system was checked, no corrosive deposits could be detected.

The conditions of the above embodiment were changed, i.e., the temperature in the furnace was controlled within a range of 300°C to 1,000°C, and the pressure in the furnace was controlled within a range of 1 mTorr to 10 Torr. When silicon nitride films were formed under these conditions, uniform films could be obtained within the above ranges.

When $SiH(N(CH_3)_2)_3$, $SiH_2(N(CH_3)_2)_2$, or $SiH_3(N(CH_3)_2)$ which do not contain chlorine as a constituant element were used as the organic compound gas in place of $Si(N(CH_3)_2)4$, a uniform film could be obtained as described above. In addition, when a silicon nitride film was formed using nitrogen in place of ammonia in the above embodiment by setting a time required for supplying the gas to the furnace to be longer than that of the above embodiment to prolong a time for keeping the gas in contact with the semiconductor wafer 2, films could be uniformly formed. When only the organic compound gas was used, although film formation required a long time, films could be uniformly formed.

Fig. 2 is a schematic view showing a low-pressure CVD device for performing the second embodiment of the present invention. The same reference numerals as in Fig. 1 denote the same parts in Fig. 2, and a detailed description thereof will be omitted. A pair of electrodes 15 are arranged on the inner wall of a tubular furnace 1 and are coupled to an AC power source (not shown).

With the above arrangement, a gas flowed in a furnace 1 while the pressure in the tubular furnace 1

was decreased, and a predetermined voltage was applied to the pair of electrodes 15. In this case, a plasma was produced from any one of $Si(N(CH_3)_2)_4$, $SiH(N(CH_3)_2)_3$, $SiH_2(N(CH_3)_2)_2$, and $SiH_3(N(CH_3)_2)$ gases to be decomposed inside the tubular furnace. Uniform silicon nitride films could be effectively formed on the surfaces of the semiconductor wafers 2. Note that, since the plasma was produced from the gas, the reaction temperature was decreased to 300°C. Although the plasma was produced from the gas as a means for decomposing the gas, when an ultraviolet beam was radiated on the gas to excite and decompose the gas, same result as described above could be obtained. Other radiation beams may be used in place of the ultraviolet beam. The plasma may be produced from the gas or the gas may be excited by a radiation beam while a heating operation is performed.

As is apparent from the above description, according to the present invention, when a silicon nitride film is formed on a substrate surface, an organic compound gas which contains silicon and nitrogen but not containing chlorine as constituting elements is used, and the substrate and the gas are reacted at a low pressure. In this case, the following effects can be obtained. A silicon nitride film formed on each substrate surface can be uniformly distributed on the substrate to have a predetermined thickness. Differences in thicknesses of silicon nitride films on a plurality of substrate can be decreased. Since an unnecessary solid product is not produced and therefore is not attached on the silicon nitride film, an exposed metal portion such as a reaction vessel is not corroded.

Claims

1. A method of manufacturing a silicon nitride film on semiconductor substrates using a low-pressure CVD apparatus, comprising the steps of:
setting a plurality of semiconductor wafers (2) in a boat (14) in a reaction furnace (1);
increasing the temperature in said reaction tube (1) to a predetermined temperature and decreasing the pressure in said reaction tube (1) to a predetermined pressure; and
supplying an organic compound gas containing silicon, nitrogen, hydrogen and carbon which organic compound gas contains an amine group, but no chlorine, from a first gas source (8) to said reaction tube and supplying NH_3 or N_2 gas from a second gas source (13) to said reaction tube (1).

2. The method according to claim 1, characterized in that the temperature and pressure in said reaction tube (1) are 700°C and 0.5 Torr, and flow rates of said organic compound gas and NH_3 or N_2 gas are 100 SCCM and 1,000 SCCM, respectively.

3. The method according to claim 1, characterized in that the organic compound gas is selected from the group consisting of $Si(N(CH_3)_2)4$, $SiH(N(CH_3)_2)3$, $SiH_2(N(CH_3)_2)2$, and $SiH_3(N(CH_3)_2)$ gases and in that a plasma is produced from said gas supplied to said reaction tube (1).

Patentansprüche

1. Verfahren zum Herstellen eines Siliziumnitridfilms auf Halbleitersubstraten unter Benutzung einer Niedrigdruck-CVD-Vorrichtung mit den Schritten:
Anordnen einer Vielzahl von Halbleiterwafern (2) in einem Boot (14) in einer Reaktionsröhre (1);
Erhöhen der Temperatur in der Reaktionsröhre (1) auf eine vorbestimmte Temperatur und Absenken des Drucks in der Reaktionsröhre (1) auf einen vorbestimmten Druck; und
Zuführen eines organischen Verbundgases mit Silizium, Stickstoff, Wasserstoff und Kohlenstoff, wobei das organische Verbundgas eine Amingruppe enthält, aber kein Chlor, von einer ersten Gasquelle (8) an die Reaktionsröhre und Zuführen von NH_3 oder N_2 von einer zweiten Gasquelle (13) an die Reaktionsröhre (1).

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Temperatur und der Druck in der Reaktionsröhre (1) 700°C und 0,5 Torr sind, und die Flußraten des organischen Verbundgases und NH_3 oder N_2-Gas jeweils 100 und 1000 SCCM sind.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das organische Verbundgas ausgewählt ist aus der Gruppe bestehend aus den Gasen $Si(N(CH_3)_2)_4$, $SiH(N(CH_3)_2)_3$, $SiH_2(N(CH_3)_2)_2$, und $SiH_3(N(CH_3)_2)$ und daß ein Plasma erzeugt wird aus dem an die Reaktionsröhre (1) zugeführtem Gas.

Revendications

1. Procédé de fabrication d'une couche de nitrure de silicium sur des substrats semiconducteurs utilisant un appareil CVD à basse pression, comprenant les étapes consistant :
à déposer de nombreuses tranches semiconductrices (2) dans une nacelle (14) dans un four de réaction (1) ;
à augmenter la température dans ledit tube de réaction (1) jusqu'à une température pré-

was decreased, and a predetermined voltage was applied to the pair of electrodes 15. In this case, a plasma was produced from any one of $Si(N(CH_3)_2)_4$, $SiH(N(CH_3)_2)_3$, $SiH_2(N(CH_3)_2)_2$, and $SiH_3(N(CH_3)_2)$ gases to be decomposed inside the tubular furnace. Uniform silicon nitride films could be effectively formed on the surfaces of the semiconductor wafers 2. Note that, since the plasma was produced from the gas, the reaction temperature was decreased to 300°C. Although the plasma was produced from the gas as a means for decomposing the gas, when an ultraviolet beam was radiated on the gas to excite and decompose the gas, same result as described above could be obtained. Other radiation beams may be used in place of the ultraviolet beam. The plasma may be produced from the gas or the gas may be excited by a radiation beam while a heating operation is performed.

As is apparent from the above description, according to the present invention, when a silicon nitride film is formed on a substrate surface, an organic compound gas which contains silicon and nitrogen but not containing chlorine as constituting elements is used, and the substrate and the gas are reacted at a low pressure. In this case, the following effects can be obtained. A silicon nitride film formed on each substrate surface can be uniformly distributed on the substrate to have a predetermined thickness. Differences in thicknesses of silicon nitride films on a plurality of substrate can be decreased. Since an unnecessary solid product is not produced and therefore is not attached on the silicon nitride film, an exposed metal portion such as a reaction vessel is not corroded.

Claims

1. A method of manufacturing a silicon nitride film on semiconductor substrates using a low-pressure CVD apparatus, comprising the steps of:
   setting a plurality of semiconductor wafers (2) in a boat (14) in a reaction furnace (1);
   increasing the temperature in said reaction tube (1) to a predetermined temperature and decreasing the pressure in said reaction tube (1) to a predetermined pressure; and
   supplying an organic compound gas containing silicon, nitrogen, hydrogen and carbon which organic compound gas contains an amine group, but no chlorine, from a first gas source (8) to said reaction tube and supplying NH_3 or N_2 gas from a second gas source (13) to said reaction tube (1).

2. The method according to claim 1, characterized in that the temperature and pressure in said reaction tube (1) are 700°C and 0.5 Torr, and flow rates of said organic compound gas and NH_3 or N_2 gas are 100 SCCM and 1,000 SCCM, respectively.

3. The method according to claim 1, characterized in that the organic compound gas is selected from the group consisting of $Si(N(CH_3)_2)4$, $SiH(N(CH_3)_2)3$, $SiH_2(N(CH_3)_2)2$, and $SiH_3(N(CH_3)_2)$ gases and in that a plasma is produced from said gas supplied to said reaction tube (1).

Patentansprüche

1. Verfahren zum Herstellen eines Siliziumnitridfilms auf Halbleitersubstraten unter Benutzung einer Niedrigdruck-CVD-Vorrichtung mit den Schritten:
   Anordnen einer Vielzahl von Halbleiterwafern (2) in einem Boot (14) in einer Reaktionsröhre (1);
   Erhöhen der Temperatur in der Reaktionsröhre (1) auf eine vorbestimmte Temperatur und Absenken des Drucks in der Reaktionsröhre (1) auf einen vorbestimmten Druck; und
   Zuführen eines organischen Verbundgases mit Silizium, Stickstoff, Wasserstoff und Kohlenstoff, wobei das organische Verbundgas eine Amingruppe enthält, aber kein Chlor, von einer ersten Gasquelle (8) an die Reaktionsröhre und Zuführen von NH_3 oder N_2 von einer zweiten Gasquelle (13) an die Reaktionsröhre (1).

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Temperatur und der Druck in der Reaktionsröhre (1) 700°C und 0,5 Torr sind, und die Flußraten des organischen Verbundgases und NH_3 oder N_2-Gas jeweils 100 und 1000 SCCM sind.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das organische Verbundgas ausgewählt ist aus der Gruppe bestehend aus den Gasen $Si(N(CH_3)_2)_4$, $SiH(N(CH_3)_2)_3$, $SiH_2(N(CH_3)_2)_2$, und $SiH_3(N(CH_3)_2)$ und daß ein Plasma erzeugt wird aus dem an die Reaktionsröhre (1) zugeführtem Gas.

Revendications

1. Procédé de fabrication d'une couche de nitrure de silicium sur des substrats semiconducteurs utilisant un appareil CVD à basse pression, comprenant les étapes consistant :
   à déposer de nombreuses tranches semiconductrices (2) dans une nacelle (14) dans un four de réaction (1) ;
   à augmenter la température dans ledit tube de réaction (1) jusqu'à une température pré-

* C L M S *

déterminée et à réduire la pression dans ledit tube de réaction (1) jusqu'à une pression prédéterminée ; et

à introduire un gaz de composé organique contenant du silicium, de l'azote, de l'hydrogène et du carbone, lequel gaz de composé organique contient un groupe amine, mais pas de chlore, à partir d'une première source de gaz (8) dans ledit tube de réaction et à introduire du gaz de NH_3 ou de N_2 à partir d'une seconde source de gaz (13) dans ledit tube de réaction.

2. Procédé selon la revendication 1, caractérisé en ce que la température et la pression dans ledit tube de réaction (1) sont de 700°C et de 0,5 Torr et les débits dudit gaz de composé organique et du gaz de NH_3 ou de N_2 sont respectivement de 100 Ncm³/min et de 1 000 Ncm³/min.

3. Procédé selon la revendication 1, caractérisé en ce qu'on choisit le gaz de composé organique parmi les gaz de $Si(N(CH_3)_2)_4$, $SiH(N(CH_3)_2)_3$, $SiH_2(N(CH_3)_2)_2$ et $SiH_3(N(CH_3)_2)$ et en ce qu'on produit un plasma à partir dudit gaz introduit dans ledit tube de réaction (1).