Description

Method for the production of a semiconductor surface coated with fluorine

The present invention relates to a method for the production of a semiconductor surface coated with fluorine. The invention is directed, in particular, to a method for the production of a semiconductor surface coated with fluorine on which subsequently socalled "gate" or "tunnel oxides" can be produced.

In order to retain or increase international competitiveness it is necessary to continue to lower the costs in realising certain electronic functions and thus continually increase productivity. This increase in productivity has been achieved above all by an increased integration of the electronic functions. The increased integration of electronic functions in turn is in the first place achieved by a continuous reduction in the structure of the individual components. It is considered to be fortuitous that the additional demands for faster circuits as well as lower power dissipation can also be fulfilled by the application of increasingly smaller structures.

Correspondingly it is the aim of many developments to provide new methods which allow the production of increasingly smaller structures in a cost-effective manner. The production methods must therein fulfill a number of conditions. Thus it is necessary on the one hand to optimise the parameters of the components in accordance with their desired electronic function. On the other hand it is necessary to ensure a sufficient stability of these parameters during the life span of the components.

Unfortunately there are a number of degradation mechanisms which have a negative effect on the electrical parameters of the individual components.

The degradation mechanism which has been tested most thoroughly is the socalled "HE degradation" (HE = Hot Electron). When operating a MOS transistor, a field strength peak occurs at the drain side of the channel margin which can accelerate the channel electrons up to close to their critical speed. Some of these socalled "hot electrons" can overcome the potential barrier at the gate oxide interfaces and reach the gate oxide. There, these electrons can for instance break up Si-H bonds and thus produce interface states. In a n-channel MOS transistor, the "hot electron effects" manifest themselves above all in degradation of the drain current. In a p- channel, MOS transistors manifest themselves above all in a shortening of the effective channel length.

Besides the degradation of the transistor parameters by "hot electrons", an important role is played by the degradation of the transistor parameters due to the application of a gate voltage at raised temperatures ("bias temperature stress", BTS) over an extended period, in particular for analog or mixed analog/digital circuit functions.

In analog or mixed analog/digital circuit functions some MOS transistors are frequently operated at an operating point which reacts very sensitively to changes in the inception voltage of the transistor. This operating point is characterised by a gate voltage, which is only slightly above the inception voltage of the MOS transistor. Accordingly, even small fluctuations in the inception voltage of the MOS transistor lead to relatively large fluctuations in the current which flows through the MOS transistor at the operating point. Since typical applications in analog circuit functions require a well defined current through the respective MOS transistor, such fluctuations in the

inception voltage of the MOS transistor can as a rule not be tolerated. Unfortunately, it is just the degradation due to "bias temperature stress" (BTS) which leads to a variation of the inception voltage with the above mentioned negative effects on the analog circuit functions.

Further, for erasable programmable read-only memory (EPROM, EEPROM), the long term stability of the electrical parameters also has an important role. In these read-only memories the programmable elements are MOS transistors which have an additional electrically insulated polysilicon gate ("floating gate"). For programming, this polysilicon gate is charged with a tunnel current flowing through a thin oxide (tunnel dielectric). The tunneling charge carriers however produce further boundary surface states, resulting in an increase in the conductivity of the oxide or a decrease of the breakdown voltage respectively. This again can lead to a store cell failing during operation.

To prevent these degradation mechanisms and to increase the long term stability, a number of measures have been suggested. Nowadays, as a rule, as an effective countermeasure against the "HE-degradation" a socalled "LDD doping" (LDD = "Lightly Doped Drain") of the source/drain regions of a MOS transistor is applied. This "LDD-doping" however requires additional process steps which have a negative effect on the production costs.

To solve the problem of the drift caused by the "bias temperature stress" in analog circuits, until now, as a rule, pure circuit-engineering measures were adopted.

These circuit- engineering measures are intended to prevent the application of a voltage at the gate of an MOS Transistor for an extended period. However, the above mentioned circuit engineering measures complicate the design of the circuit and furthermore take up additional chip space which is consequently not available for other electronic circuit functions.

It was further suggested to introduce minor quantities of fluorine or chlorine into the oxide layers to increase their long time stability (P.J. Wright, K.C. Saraswat, "The Effect of Fluorine in Silicon Dioxide Gate Dielectrics", IEEE Transactions on electron Devices, Vo. 36, No. 5, May 1989 or I.C. Chen et al, " Performance and Reliability Enhancement for CVD Tungsten Polycided CMOS Transistors due to Fluorine Incorporation in the Gate Oxide", IEEE Electron Device Letters, Vol. 15, No. 9, September 1994).

In the methods of introducing fluorine into the oxide layers which have been used up to now, the fluorine diffuses through the oxide layer to the semiconductor interface. However the structure of the oxide layer is damaged by the fluorine diffusion in such a manner, that a further diffusion of doping substances through the oxide layer can no longer be sufficiently prevented. As a consequence, the decrease for instance of the HE degradation is, as a rule, not enough to warrant the extra expenditure which an introduction of fluorine or chlorine entails. Furthermore, in the diffusion of fluorine through the oxide layer, the amount of fluorine which finally is available at the semiconductor surface can only be determined very inaccurately. Accordingly this method is usually not employed in mass productions.

It is therefore the object of the present invention to provide a method, which avoids or diminishes the above mentioned disadvantages of the state of the art. The object of the present invention is, in particular, to provide a method for the production of a surface coated with fluorine on which subsequently oxide layers of high quality can be produced so that the problem of the degradation of oxide layers can be solved or essentially reduced by a technological approach.

This task is solved by the method according to Claim 1. Further advantageous realisations, embodiments and aspects of the present invention are described in the subclaims and the enclosed drawings.

In accordance with the invention, a method for the production of a surface coated with fluorine is provided. The method in accordance with the invention includes the following steps:

a) a semiconductor substrate in a reaction chamber is provided;

b) the substrate surface is wetted with water and/or alcohol;

c) a fluorine-containing compound is supplied to the substrate surface so that a cleaned semiconductor surface coated with fluorine is produced.

d) the fluorine-containing compound is removed from the reaction chamber; and

e) the cleaned semiconductor surface coated with fluorine is wetted with a mixture which contains at least 10 vol %

water and at least 10 vol % alcohol, so that a cleaned semiconductor surface coated with a predetermined amount of fluorine is produced.

By employing the method in accordance with the invention, on the one hand, a semiconductor surface cleaned of oxide residue is obtained. Such oxide residues can for instance be caused by natural oxidation of the semiconductor surfaces or by oxide residue from preceding process steps. By way of the cleaning effect of the method according to the invention, a semiconductor surface is obtained, on which now further layers of high quality may be applied.

By employing the method in accordance with the invention, on the other hand, a quantity of fluorine which can be freely selected from a wide range can be applied to the semiconductor surface. In a subsequent production of the oxide layer, preferably by way of oxidation by thermal activation, the effect is being utilised of introducing the fluorine into the oxide as well as into the semiconductor interface. Thus at the end of the method in accordance with the invention, the fluorine has the optimum concentration in each respective application exactly at the location where it is required to achieve the stabilising effect without having the negative attendant phenomena hitherto known. By having the option of freely selecting the fluorine concentration depending on the component class to be produced, it is avoided that insufficient fluorine is introduced to saturate the unsaturated bonds or that too much fluorine is introduced so that the structure of the oxide is damaged.

However, the method in accordance with the present invention is not restricted to the production of oxide layers. For instance, a semiconductor epitaxial layer can be applied to the surface coated with fluorine. The surface which has been cleaned

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and conditioned with fluorine therein ensures a homogenous growth of the epitaxial layer.

Preferably, the alcohol used is methanol or ethanol. It is furthermore preferred that the fluorine-containing compound is HF gas.

In accordance with a preferred embodiment, the wetting of the substrate surface is performed in that the water and the alcohol are introduced supplied to the substrate surface in the form of water or alcohol vapour.

Preferably, as per step b) the pressure in the reaction chamber is reduced, so that only a thin wetting layer, about one to two mono-layers, remains on the substrate surface. In this way, it is possible to set well defined conditions for the subsequent cleaning reaction.

It is further preferred that the fluorine-containing compound be removed from the reaction chamber by a reduction of pressure, whereby preferably also the water and/or the alcohol as well as the reaction products resulting during the cleaning of the substrate surface can be removed from the substrate surface.

In the event that high or very high fluorine concentrations are required on the cleaned semiconductor surface, it is preferable if subsequently HF gas as well as ozone and/or oxygen are supplied to the cleaned semiconductor surface coated with fluorine.

The invention is explained in greater detail below by reference to the drawing. Figure 1 shows a diagrammatic view of a so called "cluster tool" to implement the method in accordance with the invention.

The cluster tool 10 shown in Figure 1 includes four processing chambers 11 to 14, where a silicon wafer can be subjected to different processing steps. For feeding and ejecting the silicon wafer, the cluster tool 10 further has socalled load locks 15 and 16. Within the cluster tool, the silicon wafer is transported by a robot arm 17 to the individual processing chambers 11 to 14 under defined conditions.

In the present case, the processing chamber 11 is destined for implementing the method in accordance with the invention. For this purpose, the processing chamber 11 is held at a temperature of approx. 40°C. This can be achieved for instance by an integrated, temperature-controlled water cycle (not shown). Any crystal windows present in the processing chamber 11 can be held at the temperature by an appropriate air flow.

A silicon wafer is introduced into the processing chamber 11 by means of a robot arm 17 and deposited in the processing chamber 11. There the silicon wafer is also heated to approx. 40°C by means of an IR lamp.

In the present example, the method in accordance with the invention is employed to prepare the production of the gate oxide. Usually, the isolations, for instance LOCOS isolations or STI isolations (STI = shallow trench isolation) are already present on or in the silicon substrate. As a rule, there are still oxide residues on the silicon surface from these preceding process steps, which would inhibit the subsequent production of a thin gate oxide.

Therefore, for cleaning and conditioning the silicon surface, 2slm of a mixture of methanol vapour and water vapour in nitrogen are supplied at a pressure of 500 mBar for 60 seconds

to the silicon surface. The methanol vapour or water vapour is introduced into the processing chamber 11 through two socalled "nitrogen bubblers", each of which is held at approx. 30°C. Thereby a thin fluid film is formed on the wafer surface wetting it.

Following this, the pressure in the chamber is reduced to about 100 mBar and subsequently 100 sccm of HF gas are supplied into the processing chamber 11 via a gas line heated to 40°C, whilst the pressure is being held constant at 100 mBar. After 30 to 60 seconds any remaining oxide residue or natural oxide are almost completely removed by way of this etching. The following reaction results:

$$SiO_2\ (a) + 4\ HF\ (g) \rightarrow SiF_4\ \ (g) + 2H_2O,$$

which is catalysed by the presence of the OH groups of the alcohol and the water.

After the etching, the pressure in the processing chamber is reduced to a value less than 0.5 mBar, so that the HF gas is removed from the processing chamber. Subsequently, 2slm of a mixture of water vapour and alcohol vapour in nitrogen supplied at a pressure of 500 mBar for 60 seconds to the cleaned silicon surface. The following rule applies: the higher the water portion (maximum 90 %) selected, the lower the remaining fluorine concentration at the silicon surface. In this way an almost completely cleaned silicon surface is achieved, the uppermost layer of which is coated with fluorine up to <1% to 30 % with fluorine.
Subsequently the pressure in the processing chamber is again reduced to a value smaller than 0.5 mBar, so that the water and the alcohol are removed from the silicon surface by evaporation.

Thus, at the end of the method in accordance with the invention, the fluorine is in the optimum concentration for each application at exactly the location, where it is required to achieve the stabilising effect. By having the option of freely selecting the fluorine concentration depending on the component class to be produced it is avoided that insufficient fluorine is introduced to saturate the unsaturated bonds or that too much fluorine is introduced so that the structure of the oxide is damaged.

In the event particularly high concentrations of fluorine are required at the silicon surface for specific applications, this can be adjusted by a subsequent treatment step with a fluorine containing compound.

For this purpose, preferably a mixture of ozone and oxygen (portion of ozone in this mixture between 0.5 % and 15 %) as well as HF gas at a temperature of approx. 40°C to 700 °C and a pressure of approx. 1000 mBar are supplied into the processing chamber 11. In this way a very thin oxide layer with a high fluorine concentration is produced.

As alternatives, oxygen and HF gas at a raised temperature of above 700°C are supplied into the processing chamber 11. In this way a very thin oxide layer with a high fluorine concentration is produced.

When the cleaning and conditioning of the silicon surface has been completed, the silicon wafer is removed from the processing chamber by the robot arm 17 and can for

instance be taken to the processing chamber 12, where by way of thermal oxidation or by a CVD precipitation a thin gate oxide layer is produced.

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Patent Claims

1. Method for the production of a surface coated with fluorine including the steps:

a) a semiconductor substrate in a reaction chamber is provided;

b) the substrate surface is wetted with water and/or alcohol;

c) a fluorine-containing compound is supplied to the substrate surface so that a cleaned semiconductor surface coated with fluorine is produced;

d) the fluorine containing compound is removed from the reaction chamber; and

e) the cleaned semiconductor surface coated with fluorine is wetted with a mixture, which contains at least 10 vol % water and at least 10 vol % alcohol, so that a cleaned semiconductor surface coated with a predetermined amount of fluorine is produced.

2. Method according to claim 1, characterised in that the alcohol used is methanol or ethanol.

3. Method according to claim 1 or 2, characterised in that he fluorine-containing compound is HF gas.

4. Method according to one of the preceding claims, characterised in that the water and the alcohol are supplied to the substrate surface in the form of water vapour or alcohol vapour.

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5. Method according to one of the preceding claims, characterised in that after step b) the pressure in the reaction chamber is decreased so that only a thin wetting layer remains on the substrate surface.

6. Method according to one of the preceding claims, characterised in that the fluorine-containing compound is removed by a decrease in pressure from the reaction chamber, wherein preferably also the water and/or the alcohol as well as the reaction products which result during the cleaning of the substrate surface are removed from the substrate surface.

7. Method according to one of the Claims 1 to 6, characterised in that subsequently HF gas as well as ozone and/or oxygen are supplied to the cleaned semiconductor surface coated with fluorine.

